New eco-friendly random copolyesters based on poly(propylene cyclohexanedicarboxylate): Structure-properties relationships

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Received 15 April 2015; accepted in revised form 13 June 2015

Abstract. A series of novel random copolymers of poly(propylene 1,4-cyclohexanedicarboxylate) (PPCE) containing neopentyl glycol sub-unit (P(CEXNCEy)) were synthesized and characterized in terms of molecular and solid-state properties. In addition, biodegradability studies in compost have been conducted.

The copolymers displayed a high and similar thermal stability with respect to PPCE. At room temperature, all the copolymers appeared as semicrystalline materials: the main effect of copolymerization was a lowering of crystallinity degree (χ_c) and a decrease of the melting temperature compared to the parent homopolymer. In particular, Wide Angle X-Ray diffraction (WAXD) measurements indicated that P(CEXNCEy) copolymers are characterized by cocrystallization, PNCE co-units cocrystallizing in PPCE crystalline phase. Final properties and biodegradation rate of the materials under study were strictly dependent on copolymer composition and χ_c . As a matter of fact, the elastic modulus and the elongation at break decreased and increased, respectively, as neopentyl glycol cyclohexanedicarboxylate (NCE) unit content was increased. The presence of a rigid-amorphous phase was evidenced by means of Dynamic Mechanical Thermal Analysis (DMTA) analysis in all the samples under investigation. Lastly, the biodegradation rate of P(CEXNCEy) copolymers was found to slightly increase with the increasing of NCE molar content.

Keywords: biodegradable polymers, poly(propylene 1,4-cyclohexanedicarboxylate), neopentyl glycol, random copolymers, solid-state properties

1. Introduction

Over the last 60 years, plastics have brought economic, environmental and social advantages; synthetic polymeric materials have found wide applications in many aspects of life and industries. This success is mainly due to their low cost, their reproducibility, and their resistance to physical aging and biological attacks [1].

In 2012, around 288 Mt of plastics have been produced worldwide, but within a short period of time almost half of them are disposed to the environ-

ment. Only in Europe, over 25 Mt of plastics ended up in the waste stream during 2012 [2].

In this scenario, the resistance of synthetic polymers to biodegradability is becoming highly disadvantageous particularly in those domains where they are used for a limited period of time before becoming wastes. It is the case in surgery, in pharmacology, in agriculture, and in packaging as well. In these fields, time-resistant polymeric wastes are no longer acceptable.

The use of polymeric materials satisfying, among all, the conditions of biodegradability and biocompati-

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bility is therefore clear and urgent. On the other hand, the depletion of natural resources as well as high oil and gas prices have a significant impact on increasing use of renewable raw materials in world production of polymers. The application of natural raw materials of plant origin in organic synthesis is compatible with sustainable development being a rational model of technological development including environmental aspects. In this view, in recent years both academic and industrial researchers focused their attention on the use of biodegradable materials, possibly starting from renewable sources.

Taking all these considerations into due account, aliphatic polyesters are therefore expected to be one of the most economically competitive biodegradable polymers [3]. It is also worth remembering that some of the commonly used monomers for the production of aliphatic polyesters, such as succinic acid, adipic acid, 1,3-propanediol, 1,4-butanediol, lactic acid and γ -butyrolactone can be either obtained from fossil fuels and from renewable resources [4].

Within the polyester class, poly(alkylene 1,4-cyclohexanedicarboxylate)s offer various advantages: the introduction of cycloaliphatic units to the main chain of the polymer can be a way to increase the rigidity of the macromolecular chains. Moreover, conformational transitions of cyclohexylene rings in the backbone originate secondary relaxations in dynamical mechanical spectrum, which contribute to improve the performances of the materials [5].

The synthesis and properties of polyesters and copolyesters containing these cycloaliphatic units were studied at the beginning of the eighties by Eastman Chemical Company, interested to develop materials with excellent tensile strength, stiffness and impact properties as well as materials to be used as improved hot melt adhesives.

Although 1,4-cyclohexane dicarboxylic acid is now obtained from petroleum resources, however, it can be prepared from bio-based terephthalic acid, starting from limonene and other terpenes [6]. Therefore, polymers derived, for example, from 1,4-cyclohexane dicarboxylic acid and a diol obtainable from biomass (as 1,3-propanediol, obtainable by renewable feedstocks, such as corn) can be considered as fully sustainable materials.

Moreover, the presence of the 1,4-cyclohexylene units along a macromolecule does not hinder the attack of microorganisms in some homopolymers and copolymers [7–9]. Therefore, the polyesters con-

taining the 1,4-cyclohexylene units can be considered biodegradable materials and are very promising, environmentally friendly polyesters.

Unfortunately, homopolymers usually do not possess optimal physic-mechanical properties. As a result, many attempts are necessary to solve these issues through appropriate modification of their structure. In this view, copolymerization probably represents the most interesting tool for tailoring materials which display the right combination of properties for the desired application. Moreover, copolymerization permits to prepare novel materials possessing unique properties in that they combine the inherent nature of the parent homopolymers, improving their non-suitable characteristics without compromising those already satisfying. Finally, through this strategy, it is possible to synthesize a new class of polymers with a broad range of properties just varying the mutual amount of the comonomeric units.

The research work described in the present paper is strictly connected to these urgent necessities and is focused mainly in finding new biopolymers, in particular biopolyesters, which are obtainable from biomass and characterized by a wide range of properties, in order to potentially substitute polyolefins and aromatic polyesters. In particular, it is focused on the synthesis and characterization of new fully aliphatic Poly(propylene/neopentyl glycol cyclohexanedicarboxylate) (P(PCExNCEy)) random copolymers, with the aim of establishing structure-property relationships which are very useful to design a material for a specific application.

2. Experimental

2.1. Materials

1,4-dimethylcyclohexanedicarboxylate (DMCE), containing 99% of *trans* isomer (TCI Europe, Zwijndrecht, Belgium), 1,3-propanediol (1,3-PD), neopentyl glycol (NPG), and titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) (Sigma Aldrich, Milan, Italy) were reagent grade products; all reagents were used as supplied, with the exception of $\text{Ti}(\text{OBu})_4$ which was distilled before use.

2.2. Synthesis of poly(propylene cyclohexanedicarboxylate) and poly(propylene/neopentyl glycol cyclohexanedicarboxylate) copolymers

Poly(propylene cyclohexanedicarboxylate) (PPCE) and poly(propylene/neopentyl glycol cyclohexanedi-

carboxylate) random copolymers (P(PCE_xNCE_y)) were synthesized in bulk starting from DMCE and 1,3-PD in the case of homopolymer and different ratios PD/NPG in the case of copolymers, using 40% mol in excess of glycol with respect to dimethyl-ester. Ti(OBu)₄ was employed as catalyst (about 150 ppm of Ti/g of polymer). All the syntheses were carried out in a 250 mL stirred glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were prepared according to the usual two-stage polymerization procedure. In the first stage, under pure nitrogen flow, the temperature was raised to 180°C and kept constant until more than 90% of the theoretical amount of methanol was distilled off (about 120 min). In the second stage, the pressure was reduced to about 0.1 mbar to facilitate the removal of the glycol in excess, and the temperature was risen to 240°C; the polymerization was carried out until a constant torque value was measured (about 180 min).

The copolymers under investigation in this work will be indicated as P(PCE_xNCE_y): where *x* and *y* are the mol% of propylene cyclohexanedicarboxylate (PCE) and neopentyl glycol cyclohexanedicarboxylate (NCE) co-units, respectively. The chemical structure of the copolyesters is the following:

2.3. Film preparation and thickness determination

Films of P(PCE_xNCE_y) were obtained by hot pressing the polymers between Teflon sheets in an hydraulic press (Carver Inc., Wabash, Indiana USA) for 2 minutes at a temperature *T* equal to *T_m* + 40°C. The films were cooled in press to room temperature by running water. Before analyses the films were stored at room temperature for at least two weeks in order to attain equilibrium crystallinity.

The film thickness was determined using the Sample Thickness Tester DM-G (Brugger, Munich, Germany) consisting of a digital indicator (Digital Dial Indicator), connected to a computer. Once planted the tool on the film, the reading is made twice per sec-

ond (the tool automatically performs three readings, minimum value that cannot be changed), measuring a minimum, maximum and average value of a series of measures. The reported results are an average of three experimental tests run at 10 different points on the polymer film surface, at room temperature. Measurements were performed at least in triplicate and the mean value thickness is presented.

2.4. Molecular characterization

The polymers structure and the actual copolymer composition were determined by means of ¹H-NMR spectroscopy. The samples were dissolved (15 mg/mL) in chloroform-*d* solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. ¹H-NMR spectra were recorded at room temperature for solutions with a polymer concentration of 0.5 wt% (a relaxation delay of 0 s, an acquisition time of 1 s and up to 100 repetitions) using a Varian INOVA 400 spectrometer (Varian Inc., Palo Alto USA).

Molecular weight data were obtained by gel-permeation chromatography at 30°C using a 1100 Hewlett Packard system (Palo Alto, USA) equipped with PL gel 5 μ MiniMIX-C column (250/4.6 length/i.d., in mm) and a refractive index detector. Chloroform was used as eluent at a 0.3 mL/min flow and sample concentrations were adjusted to about 2 mg/mL. A molecular weight calibration curve was obtained by means of several polystyrene standards in the molecular weight range of 2000–100 000.

2.5. Thermal characterization

Thermogravimetric analysis was performed under nitrogen atmosphere using a Perkin Elmer TGA 4000 apparatus (Waltham, USA) at 10°C/min heating rate up to 850°C (gas flow: 30 mL/min).

Calorimetric measurements were carried out by means of a Perkin Elmer DSC7 instrument (Waltham, USA) equipped with a liquid sub ambient accessory and calibrated with high purity standards (indium and cyclohexane). With the aim of measuring the glass transition and the melting temperatures of the polymers under investigation, the external block temperature control was set at –120°C and weighed samples of c.a. 10 mg were encapsulated in aluminum pans and heated to about 40°C above fusion temperature at a rate of 20°C/min (first scan), held there for 3 min, and then rapidly quenched (about 100°C/min) to –80°C. Finally, they were reheated from –80°C to a temperature well above the melting

point of the sample at a heating rate of 20°C/min (second scan). The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment ΔC_p associated with the glass-to-rubber transition. The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak value of the endothermal and the exothermal phenomena in the DSC curve, respectively. When multiple endotherms were observed, the highest peak temperature was taken as T_m . The specific heat increment ΔC_p , associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass transition temperature. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) of the crystal phase were calculated from the total areas of the DSC endotherm and exotherm, respectively. In order to determine the crystallization rate under non-isothermal conditions, the samples were heated at 20°C/min to about 40°C above fusion temperature, kept there for 3 min and then cooled at 5°C/min. The temperature corresponding to the maximum of the exothermic peak in the DSC cooling-curve (T_{cc}) can be correlated to the crystallization rate. At least five replicates were run for each sample. Repeated measurements showed excellent reproducibility.

2.6. Structural characterization

X-ray diffraction (XRD) patterns of polymeric films were carried out in the wide angle region by using a PANalytical X'PertPro diffractometer (Almelo, Netherlands) equipped with a fast solid state X'Celerator detector and a copper target ($\lambda = 0.15418$ nm). Data were acquired in the 5–60° 2 θ intervals, by collecting 100 sec at each 0.10° step. The indices of crystallinity (X_c) were evaluated from the XRD profiles by the ratio between the crystalline diffraction area (A_c) and the total area of the diffraction profile (A_t), $\chi_c = A_c/A_t$. The crystalline diffraction area has been obtained from the total area of the diffraction profile by subtracting the amorphous halo. The amorphous was modelled as bell shaped peak baseline. The non-coherent scattering was taken into consideration.

2.7. Stress-strain measurements

Stress-strain measurements were performed using an Instron 4465 tensile testing machine (Pianezza, (TO) Italy) equipped with a 100 N load cell, on rectangular films (40 mm high, 5 mm wide and 0.2 mm

thick). The gauge length was 20 mm and the cross-head speed was 5.0 mm/min. Load-displacement curves were obtained and converted to stress strain curves. Tensile elastic modulus was determined from the initial linear slope of the stress-strain curve. At least six replicate specimens were run for each sample and the results were provided as the average value $\pm$ standard deviation.

2.8. Dynamic mechanical measurements

Suitable specimens for dynamic mechanical measurements were obtained by injection moulding in a Mini Max Molder (Custom Scientific Instruments, Easton USA), supplied with a rectangular mould (30×8×1.6 mm). Immediately after moulding, samples were quenched in liquid nitrogen and then stored in a desiccator under vacuum for 1 month prior analysis.

Dynamic mechanical measurements were performed with a dynamic mechanical thermal analyser (Rheometric Scientific, DMTA IV, New Castle USA), operated in the dual cantilever bending mode, at a frequency of 3 Hz and a heating rate of 3°C/min, over a temperature range from –150 to T_{final} , which changes according to the polyester analysed.

2.9. Composting experiments

Degradation tests were performed at 40°C. Each polyester film (diameter of 16 mm, 0.2 mm thick) was placed in a darkened vessel and sandwiched between two layers of compost (20 g each). Finally, 10 mL of deionized water were added.

Home-made compost was prepared by means of an automatic composter (NatureMill, San Francisco, USA): organic waste fraction was collected, cultured in the composter for three weeks, and then transferred in the cure chamber for at least four weeks prior to use.

Film weight loss analyses

Prior to degradation experiments, each specimen was immersed in a 70% ethanol solution for 10 min, washed repeatedly with deionized water and placed over P₂O₅ under vacuum at room temperature to constant weight (at least 24 h). Lastly, each sample was weighed to obtain the initial mass. At different time intervals, duplicate sacrificial specimens of each sample were recovered from the compost and washed according to the following procedure to remove microbial cells adhered on the film:

- immersion in a 2% sodium dodecyl sulphate (SDS) solution at 50°C for 2 h;
- repeated washing with 70% ethanol (3×);
- immersion in 70% ethanol and stirring at 120 rpm, then storing at RT for 10 min;
- repeated washing with deionized water (3×);
- drying over P₂O₅ under vacuum for 2 days to constant weight.

The mass loss was then gravimetrically determined by comparing the residual dry weight with the initial value.

Scanning electron microscopy (SEM)

SEM images were acquired on a desktop Phenom microscope (Shanghai, China) on metal sputtered film samples glued with carbon tape on aluminium stubs.

3. Results and discussion

3.1. Synthesis, molecular and thermal characterization

At room temperature the as-synthesized polyesters are opaque light yellow coloured solids. Their solubility was checked in various solvents: all the samples showed a good solubility at room temperature in the most common organic solvents, i.e. chloroform, tetrachloroethane, methylene chloride, etc. The

polymers are listed in Table 1, which also collects the data of molecular characterization: as it can be seen, the polymers were characterized by relatively high and comparable molecular weights, indicating that appropriate synthesis conditions and a good polymerization control were achieved. In order to have an understanding into their chemical structure, the ¹H-NMR investigation was performed. The analysis confirmed the awaited structures (see as an example the ¹H-NMR spectrum of P(BCE70TECE30) shown in Figure 1).

The copolymer composition was calculated from the relative areas of the ¹H-NMR resonance peak of the 3 aliphatic proton of the propylene diol subunit located at 4.15 ppm and of the 5 protons of the methylene groups of the neopentyl diol subunit at

Table 1. Molecular characterization data of PPCE and P(PCE_xNCE_y) random copolymers

Polymer	M _n ^a	D ^b	NCE ^c [mol%]	Thickness [μm]
PPCE	36 398	2.2	0	246±22
P(PCE95NCE5)	29 549	2.9	5	292±31
P(PCE90NCE10)	31 124	2.2	10	268±18
P(PCE85NCE15)	27 522	2.6	15	238±33
P(PCE80NCE20)	25 386	2.4	20	308±10

^anumber average molecular weight calculated by GPC analysis

^bpolydispersity index calculated by GPC analysis

^creal copolymer composition calculated by ¹H-NMR

Figure 1. ¹H-NMR spectra of P(PCE80NCE20) with resonance assignments

3.87 ppm. From the data of Table 1, it can be seen that in all cases the actual molar composition is close to the feed one.

Previous studies [10, 22] reported that the 1,4-cyclohexylene ring present in DMCE can isomerize during polymer synthesis, due to the high temperatures employed for long times, moving toward the thermodynamically stable *cis/trans* ratio of 34–66%. Therefore, $^1\text{H-NMR}$ analysis has been also used to calculate the *trans* percentage in the polymers under study: in particular, the ratio of the areas of the signals centred at 2.28 ppm (*trans* isomer) and 2.44 ppm (*cis* isomer) has been considered (Figure 1). From the data obtained it can be evicted that no significant isomerization from the *trans* form to the *cis* one occurred during polymerization, the *cis* content being in all cases less than 5%.

Subsequently, the polymers were subjected to thermogravimetric analysis and the temperature corresponding to 5% weight loss ($T_{5\% \text{ w.loss}}$) has been determined and collected in Table 2. As evidenced in Figure 2, where the thermogravimetric curves of the parent homopolymer and of the synthesized copolyesters are reported, the weight loss takes place in all cases in one-step.

All the copolyesters showed a high thermal stability, comparable with that of PPCE. This is due to the presence of bulky and thermally stable cyclohexylene groups, which render the polymer even more thermally stable than the corresponding aromatic polyester, i.e. Polybutylene terephthalate (PBT) and to neopentyl glycol sub-unit [10–11]. The result demonstrated that the introduction of NCE co-units along the PPCE macromolecular chain did not have any detrimental effect on thermal stability, which, as well known is crucial during polymer processing. In order to provide the same heat treatments to all the investigated samples, prior to thermal analysis each film was kept at room temperature for two weeks.

Figure 2. Thermogravimetric curves of PPCE and P(PCE_xNCE_y) copolymers under nitrogen atmosphere (heating rate: 10°C/min)

DSC traces of so-treated samples are reported in Figure 3 and the data obtained in Table 2.

As evidenced in Figure 3, all P(PCE_xNCE_y) copolymers presented a glass transition and a melting endotherm. The glass transition phenomenon is always not so evident, due to the high amount of crystalline phase present in these samples.

As to the melting process, the samples showed a pre-melting peak at low temperature (around 50°C), whose heat of fusion regularly increased as the NCE unit content is increased, which can be ascribed to the fusion of crystals with a poor degree of perfection. At much higher temperature, the main melting peak can be observed. The calorimetric results indicate that an increase in the amount of the comonomer NCE leads to a reduction in the samples both of the melting temperature and the heat of fusion, as usually found in random copolymers with the comonomeric units present in minor amount completely rejected from the crystalline phase or partially incorporated in it (see Table 2) [12, 13]. Furthermore, in the copolymers, the endotherm region is broader, suggesting the presence of a larger distribution of crystallites with different degree of perfection.

Table 2. Thermal and diffractometric characterization data for PPCE and P(PCE_xNCE_y) copolymers

Polymer			1 st scan		2 nd scan							
	$T_{5\% \text{ w.loss}}$ [°C]	T_{max} [°C]	T_m [°C]	ΔH_m [J/g]	T_g [°C]	ΔC_p [J/(°C·g)]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	T_{cc} [°C]	X_c^a [°C]
PPCE	381	413	148	58	9	0.132	148	31	63	17	91	29 (4)
P(PCE95NCE5)	385	416	142	49	11	0.183	143	26	90	26	75	26 (3)
P(PCE90NCE10)	386	420	135	43	12	0.189	135	13	97	13	—	25 (2)
P(PCE85NCE15)	387	423	125	42	13	0.262	—	—	—	—	—	25 (2)
P(PCE80NCE20)	388	425	119	39	13	0.236	—	—	—	—	—	24 (2)

^aEstimated standard deviation (e.s.d.) in parentheses

Figure 3. Calorimetric curves of PPCE and P(PCE_xNCE_y) copolymers, (a) 1st scan; (b) 2nd scan after melt quenching

To better understand the nature of the crystalline phase present in the polymers under investigation, the structural characterization of P(PCE_xNCE_y) copolymers was carried out by X-ray diffraction (XRD). The patterns are reported in Figure 4, together with that of PPCE added for sake of comparison. The PPCE sample shows the main reflections at 2θ values of 16.7, 17.5, 19.5, 23.3°.

As far as the copolymers are concerned, the corresponding WAXD patterns appear to be characterized by relatively intense diffraction peaks over the whole composition range.

The copolymer samples are characterized by the same XRD pattern of PPCE, indicating that the crys-

tal structure which develops in these copolymers has the characteristics of PPCE lattice.

Nevertheless, the presence of NCE units causes the collapse of the two reflections at 16.7 and 17.5° and the reflections seems to be shifted towards lower angles (higher distances, see Figure 4b panel), the shifting being higher as the content of NCE units increases. Such increases of the interplanar distances could be caused by the insertion of bigger NCE units into the PPCE crystal cell. Cocrystallization is supported by the modest decrease of crystallinity degree with copolymer composition (see Table 2), which is lower than the value expected on the basis of the complete rejection of the ‘foreign’ units from the

Figure 4. X-ray diffraction profiles of PPCE and P(PCE_xNCE_y) copolymers (a). An enlarged view (b); vertical line are reference for the reader.

crystalline phase present in the sample. In conclusion, it can be plausible that at least a certain amount of comonomeric units enter into the crystal lattice.

It is well known that a partially crystalline material usually exhibits a different glass transition behavior than the completely amorphous analogs. In fact, although some conflicting results are reported in the literature, [14] crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on the segmental motion of amorphous polymer chains. Therefore, in order to study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the total absence of crystallinity. In this view, all the samples under investigation were subjected to rapid cooling (quenching) from the melt. The DSC curves after melt quenching are shown in Figure 3: the calorimetric traces of PPCE and P(PCE_xNCE_y) copolymers containing up to 10 mol% of NCE units showed a glass transition followed by an exothermal ‘cold crystallization’ peak and a melting endotherm at higher temperature. In particular, as concern PPCE, the enthalpy associated with the crystallization phenomenon is lower than that of the fusion endotherm, indicating that this sample cannot be frozen into a completely amorphous state by quenching. Nevertheless, a portion of amorphous material, once T_g is exceeded, acquires enough mobility to rearrange and crystallize. The DSC curves of such sample is therefore typical of partially crystalline polymers. In the case of P(PCE₉₅NCE₅) and P(PCE₉₀NCE₁₀) copolymers, the enthalpy of crystallization very well compares with the corresponding heat of fusion, indicating that these polymers are completely amorphous. As regards the calorimetric curves of copolymers containing from 15 to 20 mol% of NCE units, only an intense endothermal baseline deviation associated with the glass transition is observed. Therefore, the DSC scans indicate that the phase behaviour of PPCE changed even for small amount of neopentyl glycol sub-units (5 mol%). On the other hand, no effect of copolymer composition on material phase behaviour was observed.

As can be seen from the data collected in Table 2, the glass transition temperature is slightly influenced by the presence of NCE units in the chain, the T_g copolymer values being higher than that of PPCE and increasing with the molar content of NCE units. As is well known, the second-order transition temperature is affected by several factors, such as

chain flexibility, steric effects, molar mass, branching and crosslinking. For high molecular weight polymers, the flexibility of the chain is undoubtedly the most important factor influencing T_g . This latter is a measure of the ability of a chain to rotate, and therefore the more flexible chains are, the lower the T_g . The increase in the glass transition temperature on introducing the two methyl side groups into the polymeric chain of PPCE can be explained as due to the steric effect of these two groups which hinder the rotation, imposing restrictions.

To evaluate the tendency of PPCE to crystallize in the copolymers under study, non-isothermal experiments were carried out, subjecting the samples to a controlled cooling rate from the melt. The temperatures of the maximum of the exothermal crystallization peak (T_{cc}) of the samples under investigation, which can be correlated to the isothermal melt crystallization rate, are collected in Table 2. As it can be observed, the crystallization rate of P(PCE₉₅NCE₅) is significantly lower than that of parent homopolymer. Moreover, amounts of NCE co-units ≥ 10 mol% completely undone the PPCE ability of crystallizing, indicating that the co-units act as obstacles in the regular packing of polymer chains. This result is in agreement with those obtained previously by some of us in investigating other copolymeric systems containing neopentyl glycol sub-unit [10, 15].

3.2. Dynamic mechanical characterization

The dynamical mechanical spectra of the samples under investigation are shown in Figure 5.

The upper curve of each polymer refers to the sample stored at room temperature: in the temperature range $-150/100^\circ\text{C}$, all the polymers exhibits three relaxations regions denoted as γ , β and α in order of increasing temperature. In all cases, the γ relaxation was detected in the range $-150/-100^\circ\text{C}$ at 3 Hz, has small intensity and is rather broad. The β relaxation is approximately located at about -75°C and has a small intensity too. On the other hand, the α relaxation, detected around 40°C , has higher intensity and a certain asymmetry, being steeper on the low-temperature side and broader on the high-temperature one. Looking into more detail to the high-temperature side of α relaxation, one can see a shoulder, denoted as α' . As regards the storage modulus E' , at low temperature it exhibits values typical of the glassy state (*ca.* 10^{10} Pa) and decreases slightly with increasing temperature due to thermal expansion. In

Figure 5. Dynamical mechanical curves at 3 Hz: for each sample, top row room stored sample; bottom row after cooling from high temperature under dry nitrogen flow

correspondence with α relaxation the modulus shows a steep decrease of about two orders of magnitude. As regards the assignment of these relaxations, α relaxation is confidently assigned to the glass-to-rubber transition, its temperature location being in good agreement with the calorimetric T_g . The small intensity of the peak and the high value of the modulus above the relaxation evidence the partially crystalline character of the polymer, in agreement with the calorimetric results. The location of the main relaxation shifts toward higher temperature values as the NCE unit content is increased (see Table 3), in agreement with calorimetric results. This can be explained on the basis of the progressive decrease in chain flexibility as the amount of

Table 3. Dynamical mechanical data

Polymer	1 st scan			2 nd scan ^{a)}		
	T_α [°C]	T_β [°C]	T_γ [°C]	T_α [°C]	T_β [°C]	T_γ [°C]
PPCE	40	-74	-130	23	-73	-125
P(PCE95NCE5)	40	-76	-133	27	-75	-123
P(PCE90NCE10)	42	-78	-132	29	-76	-125
P(PCE85NCE15)	43	-78	-133	32	-77	-123
P(PCE80NCE20)	46	-79	-131	40	-75	-123

^{a)} 2nd scan after cooling from high temperature under nitrogen flow

NCE units increases. The α' process can be related to a rigid confined amorphous phase, analogously to another similar copolymeric systems previously investigated by some of us [16].

Concerning the identification of the molecular origin of the γ relaxation, it can be traditionally associated with restricted motions of the chain in polymers with aliphatic sequences: in particular, the relaxation is generally attributed to rotations of the methylene units of glycol sub-unit which is the flexible part of the repeating unit [5].

As regards the attribution of the β relaxation to a molecular motion, as reported in the literature [5], this relaxation originates from the chair-boat-chair conformational transition of the cyclohexylene ring. Indeed, the cyclohexylene rings in chair conformations can transform from chair to chair via an intermediate twist boat conformation [17].

In the second scan after cooling from high temperature under dry nitrogen gas, the shoulder α' disappeared, the α peak keeping anyway a certain asymmetry. Moreover, α intensity decreases indicating that during the cooling crystallization occurs in the samples under investigation. Surprisingly, however, the α relaxation moves to lower temperature: taking into account that α' shoulder disappears, such result can be explained as due to a significant improving of crystal phase perfection that reduces significantly the rigid-amorphous phase fraction.

The copolymer with the highest content of NCE co-unit, P(PCE80NCE20), is characterized by a different behaviour: as a matter of fact, the α' relaxation does not disappear in 2nd scan after cooling from high temperature under dry nitrogen flow and the intensity of α relaxation doesn't decrease in magnitude. This last result clearly indicates that no significant crystallization occurred on cooling, due to slow crystallization kinetic of this copolymer. As it is well known, the amount of rigid amorphous phase depend upon the area of the crystalline-amorphous boundary, the degree of irregularity of the crystalline phase and the molecular mobility [11]. In the case of P(PCE80NCE20), the non-crystallizable comonomer hinders significantly the crystallization process, leading to small and imperfect crystallites. The crystalline phase turns out to be highly dispersed, and the increase in crystal surface results into extensive constraints on the amorphous phase. As to elastic modulus E' in second scan, also the steepness and intensity of the modulus drop in the α transition region show a great reduction as the crystallinity increases, reflecting the typical behaviour of partially crystalline polymers [18].

3.3. Mechanical characterization

In an application perspective, the analysis of the mechanical properties of the polymers under study is of primary importance. Therefore, P(PCE x NCE y) copolymers were subjected to stress-strain measurements. In Table 4 their elastic modulus (E), stress at break (σ_b), and deformation at break (ϵ_b) are shown, together with the data of PPCE and Polypropylene terephthalate (PPT) added for sake of comparison.

As it can be seen, the elastic modulus regularly decreased as NCE unit content was increased; on the contrary, the elongation at break, increased with the increasing of the molar amount of NCE co-unit. Since all the investigated polymers display a soft amorphous phase (T_g values are in all cases below room temperature), the observed trend can be ascribed to crystallinity degree (Table 2).

It is in fact well known [19, 20] that crystallinity degree has a considerable effect on the mechanical properties of a polymer: in particular high X_c results in harder, stiffer and less ductile behaviour. As therefore expected, the higher the PCE content, the higher the elastic modulus and the lower the elongation ability of the investigated polymers. Moreover, it is worth emphasizing that the copolymer containing the 20 mol% of NCE is characterized by an elastomeric behaviour.

In conclusion, a new class of aliphatic polyesters with tunable mechanical properties has been here presented. Indeed, by just varying the molar composition of the copolymers, even for modest changes of crystallinity degree, it is possible to synthesize a new material which can be used for rigid plastic containers or soft wrapping films.

Last but not least, substituting the aromatic ring with the aliphatic one, the modulus changes dramatically (see Table 4): it is lower in aliphatic sample. In particular, PPT, due to the presence of the aromatic ring has a very high modulus and a brittle behavior.

Table 4. Mechanical characterization data of PPT, PPCE and P(PCE x NCE y) copolymers

Polymer	E [MPa]	σ_b [MPa]	ϵ_b [%]
PPCE	435 $\pm$ 26	15 $\pm$ 2	11 $\pm$ 1
P(PCE95NCE5)	381 $\pm$ 29	20 $\pm$ 1	150 $\pm$ 14
P(PCE90NCE10)	338 $\pm$ 20	12 $\pm$ 1	190 $\pm$ 32
P(PCE85NCE15)	248 $\pm$ 12	12 $\pm$ 2	332 $\pm$ 32
P(PCE80NCE20)	232 $\pm$ 20	20 $\pm$ 1	559 $\pm$ 18
PPT	942 $\pm$ 85	42 $\pm$ 5	5 $\pm$ 1

3.4. Composting studies

The biodegradability of P(PCE_xNCE_y) copolymers was monitored by subjecting them to composting, which is a particularly useful technique to biodegrade a polymeric material which has been contaminated by organic matter. Biodegradation rate was investigated by weight loss measurements.

After 140 days of incubation the highest weight loss value was of 11%, measured for P(PCE80NCE20). Degradation rate was found dependent on composition: the higher the NCE content, the higher the weight loss. As a matter of fact, weight losses were equal to 3, 4, 6 and 8% for PPCE, P(PCE95NCE5), P(PCE90NCE10) and P(PCE85NCE15), respectively.

As expected, the higher the crystallinity degree of the polymers under study, the lower the biodegradation rate in compost; in fact they are well known factors influencing the biodegradation rate of a polymer [21–23].

The morphology of the polymer films was analysed by SEM. As an example, micrographs of PPCE and P(PCE_xNCE_y) films after 140 days of incubation in compost are reported in Figure 6.

All the samples under investigation showed a smooth and homogenous surface before incubation. After incubation, SEM analyses highlighted results in agreement with weight loss measurements: PPCE film presented only a surface roughening after 140 days of incubation in compost, while in the copolymer large damaged areas appeared, with

numerous cracks and channels, whose intensity depended on the degree of degradation.

4. Conclusions

The introduction of neopentyl glycol along the PPCE macromolecular chain has been carried out by the polycondensation reaction of 1,4-dimethylcyclohexanedicarboxylate with 1,3-propanediol and neopentyl glycol. This easy synthesis strategy allowed the preparation of a new class of aliphatic polyesters with improved properties with respect to the parent homopolymer. Moreover, the final material properties can be effectively tailored simply varying the copolymer composition.

As expected, the introduction of neopentyl glycol sub-unit in the PPCE resulted in a decrease of the crystallinity degree and melting point, due to a decrement of chain symmetry and regularity. The higher the mol% of NCE co-units, the greater the effect on these properties. As a consequence, the mechanical properties and the biodegradation rate turned out to be influenced. As a matter of fact it has been observed a decrease in the elastic modulus and an increase in the elongation to break till to an elastomeric behaviour.

The biodegradation rate in compost resulted in all cases higher than that of PPCE, and once again dependent on the copolymer composition: the higher the NCE mol%, the higher the weight losses of the copolymers under study.

It is notable all the new materials are potentially bio-based and biodegradable, and can be candidates

Figure 6. SEM micrographs of PPCE and P(PCE_xNCE_y) before composting (top) and after 140 days of incubation (bottom)

for substituting some traditional petroleum-based polymers in specific applications.

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