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Elastomeric/antibacterial properties in novel random *Ricinus communis* based-copolyesters

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Abstract

Poly(ricinoleic acid) (PRA), coming from the self-polycondensation of ricinoleic acid (RA), which derives from castor oil, is a very interesting polymer because of its intrinsic antimicrobial activity. However, its mechanical properties are insufficient for whatever application, thus copolymerization is required. In this work, two polyesters based on 1,3 propanediol (PD), such as poly(propylene terephthalate) (PPT) and poly(propylene isophthalate) (PPI), were chosen to prepare random copolyesters containing ricinoleate units. Different content of RA have been tested, such as 10 and 25 mol% respect to the comonomer (terephthalic or isophthalic dimethylester), to evaluate the lowest composition able to confer antibacterial activity. The materials were tested against *Staphylococcus aureus* and *Escherichia coli*, and 25 mol% of RA unit resulted to impart antimicrobial activity. Furthermore, thermal properties (DSC and TGA) as well as the elastomeric response of films were investigated. The copolymer PPI/PRA containing 10 mol% of RA presents very high elongation at break, around 1300%. Therefore, by tuning the RA amount it is possible to obtain outstanding elastomeric or antibacterial materials, suitable for textiles and/or film engineering applications.

Keywords: Ricinoleic acid; poly(propylene terephthalate); poly(propylene isophthalate); antibacterial properties; elastomeric properties.

1. Introduction

Infections by pathogenic microorganisms are of great concern in many fields, such as in designing medical devices and water purification systems, in textile industry, in food packaging, etc. Thanks to their non-toxicity, polymers, are materials suitable for preventing or counteracting microbial infections. In particular, polymers exhibiting intrinsic antimicrobial activity are of particular interest. They have the advantage of a long-term antimicrobial ability, with respect to the systems containing low molecular weight biocides, which could be released from the polymeric matrix [1]. In this sense, a very interesting polymer is the poly(ricinoleic acid) (PRA), coming from the self-polycondensation of ricinoleic acid (RA) (12-hydroxy-9-cis-octadecenoic acid), the main constituent of castor oil,

which derives from the beans of the castor plant, *Ricinus communis*, of the *Euphorbiaceae* family. RA contains a hydroxyl and carboxyl group, as well as a Δ^9 unsaturation and an aliphatic side chain, which is probably responsible of its biocidal activity, because it is able to interact with the bacteria membranes causing their damage and/or disruption [2-7].

The mechanical properties of PRA are insufficient for whatever application, thus copolymerization is often required. Literature reports many examples of RA-based copolymers, with potential application in biomedical field, such as drug delivery systems, implants or tissue engineering materials. Recent studies report about the melt polycondensation of RA, sebacic acid and methoxy poly(ethylene glycol), as carrier for hydrophobic drug delivery, in cancer therapy [8]. Alternating poly(ester-anhydride)s based on sebacic acid, with RA at regular intervals, are reported by Haim-Zada et al. [9]: they show enhanced hydrolytic stability as carriers for controlled drug release. Copolymers of RA and ϵ -caprolactone, via both enzymatic and chemical polymerisation, are also reported to produce biomedical materials [10-11]. Random copolymers of RA with 1,4 butanediol and dimethyl succinate, as well as blends of PRA/poly(butylene succinate) were also prepared, with the aim of obtaining antibacterial electrospun membranes, useful for water filtration and air disinfection [2-3]. Other potential applications include adhesives, sealants and coatings. For example, Laurentino et al. report the epoxidation of the double bonds of RA, followed by the ring opening reaction in the presence of acrylic acid to form the acrylated ricinoleic acid (ARA). Free radical copolymerizations of ARA and methyl methacrylate, carried out in miniemulsion, result in latexes stable over a long storage time [12]. Epoxidized RA has been also used to react with the isocyanate groups of toluene-2,4-diisocyanate, in order to prepare renewable resource-based dual cross-linked materials [13].

Additional applications include lubricants [14-15] and plasticizers for polymers [16].

In this work, some polyesters based on 1,3 propanediol (PD), such as poly(propylene terephthalate) (PPT) and poly(propylene isophthalate) (PPI), were chosen to prepare RA-based copolymers by random copolymerization. PPT is a semicrystalline aromatic polyester, synthesized from terephthalic acid and PD, both potentially derivable from renewable resources [17-18]. It is an engineering thermoplastic because many of its properties, such as elastic recovery, chemical resistance and resilience, are included between those of poly(ethylene terephthalate) (PET) and those of poly(butylene terephthalate) (PBT). PPT can be used in different applications such as films, mechanical parts, and mainly fibers, which combine the advantageous properties of polyesters and polyamides. They stand out for their high elasticity, excellent recovery rate, strain resistance, high UV stability, low water absorption, and low electrostatic charging. In addition, PPT films show good barrier properties [19]. However, some applications are restricted because of a relatively low glass

transition temperature (around 50 °C) and a fast crystallization rate; therefore, the incorporation of a comonomer could overcome some difficulties in the manufacturing processes [20]. PPT has been used with polyethylene terephthalate to obtain elastomultiester filaments [21]; with 2-methyl-ethylene terephthalate, to decrease the thermal characteristics [20]; with poly(ethylene oxide terephthalate), as soft segments for a new type of poly(ether-ester) [22]; with 1,4-cyclohexylene dimethylene terephthalate, to impart rigidity to PPT [23]; with PPI, to modify the crystallization behavior [24].

On the other hand, a limited number of works were published about PPI [25-26]. Unlike PPT, PPI is an amorphous polyester, useful in soft packaging.

In order to prepare safe materials, non-cytotoxic, with potent and broad antimicrobial activity, long-last response and even reusable, in this work a series of random copolymers based on PRA, PPT or PPI were synthesized starting from the corresponding monomers. Different content of ricinoleic acid were tested, such as 10 and 25 mol% respect to the comonomer (terephthalic or isophthalic dimethyl ester), to evaluate the lowest composition able to confer antibacterial activity. In addition to a thermal and mechanical characterization, which includes also cyclic stress-strain tests, the antibacterial properties against *Staphylococcus aureus* and *Escherichia coli* were studied.

2. Experimental

2.1 Materials

1,3-propanediol (PD), dimethyl isophthalate (DMI), dimethyl terephthalate (DMT) and titanium tetrabutoxide (TBT) were purchased from Aldrich Chemical. Ricinoleic acid (RA, purity >80%) was purchased from Zentec. All materials have high purity and were used as received.

For the study of antibacterial activity *S. aureus* ATCC 6538 and *E. coli* ATCC 8739 were used as target strains. Nutrient Broth (NB) (Merck, Darmstadt, Germany) was used for revitalizing the microorganisms, saline solution (0.9% w/v NaCl) was used for serial dilution and Plate Count Agar (PCA) (Biolife, Milano, Italt) for plating the dilutions and counting the cells.

2.2 Methods

2.2.1 Melt polycondensation for the synthesis of ricinoleic acid-derived polyesters

All syntheses were carried out in a round bottom wide-neck glass reactor (250 mL capacity), charged with reagents and catalyst. The reactor was closed with a three-necked flat flange lid equipped with a heating band, a mechanical stirrer and a torque-meter. The system was connected to a water-cooled condenser and immersed in a thermostatic oil-bath at 200 °C and stirred. The heating band was set at

different temperatures according to the monomers used. At the end of the first stage, all the condensation products (water or methanol) distilled off. The distillate was collected and analyzed by Fourier Transformed Infrared Spectroscopy. The temperature was then increased, the lid was maintained at the same temperature set during the first stage with the heating band and the reactor was connected to a liquid nitrogen-cooled condenser. Dynamic vacuum was then applied and these conditions were maintained until the polymer was discharged from the reactor.

All the molecular structures were confirmed by ^1H NMR. Reaction steps are summarized in Schemes 1-5. Specific details and amounts of each polycondensation synthesis are reported below.

2.2.2 Synthesis of poly(ricinoleic acid) (PRA)

The reactor was charged with RA (50 g, 0.168 mol) and TBT (0.0585 g, 1.72×10^{-4} mol) and the mechanical stirrer was set up to 170 rpm. The first stage was maintained for more than 2 h. After almost 2 h of vacuum-temperature ramp, the second stage was maintained approximately 4 h; the final temperature was 230 °C with a pressure of 0.200 mbar. The product discharged from the reactor was a dark brown liquid with low viscosity (42 g).

^1H NMR (400 MHz, CDCl_3 , δ): 0.80-0.88 (t, 3H; $\text{C}^{\text{m}}\text{H}_3$), 1.20-1.38 (m, 16H; $\text{C}^{\text{c}}\text{H}_2$ and $\text{C}^{\text{l}}\text{H}_2$), 1.42-1.56 and 1.56-1.70 (m, 2H; $\text{C}^{\text{i}}\text{H}_2$ and $\text{C}^{\text{b}}\text{H}_2$), 1.95-2.10 (m, 2H; $\text{C}^{\text{d}}\text{H}_2$), 2.23-2.40 (m, 4H; $\text{C}^{\text{a}}\text{H}_2$ and $\text{C}^{\text{s}}\text{H}_2$), 4.82-4.92 (m, 1H; $\text{C}^{\text{h}}\text{H}$), 5.28-5.36 and 5.40-5.50 (2m, 2H; $\text{C}^{\text{f}}\text{H}$ and $\text{C}^{\text{e}}\text{H}$). The carbon labels are referred to the chemical structure reported in Fig. S1, ESI.

2.2.3 Synthesis of poly(propylene isophthalate) (PPI)

The reactor was charged with DMI (35 g, 0.180 mol), PD (27 g, 0.360 mol) and TBT (0.0395 g, 1.16×10^{-4} mol). The reactor was kept at 170 rpm and 190 °C for 30 min, then the temperature was raised up to 200 °C. The first stage was maintained for more than 2 h. After almost 2 h of vacuum-temperature ramp, the second stage was maintained approximately 3 h; the final temperature was 240 °C with a pressure of 0.400 mbar. When the torque-meter was around 10, 32 g of transparent polymer were discharged from the reactor.

^1H NMR (400 MHz, CDCl_3 , δ): 2.22-2.34 (m, 2H; $\text{C}^{\text{b}}\text{H}_2$), 4.47-4.56 (t, 4H; $\text{C}^{\text{a}}\text{H}_2$), 7.43-7.49 (t, 1H; $\text{C}^{\text{e}}\text{H}$), 8.15-8.20 (d, 2H; $\text{C}^{\text{d}}\text{H}$), 8.62-8.66 (t, 1H; $\text{C}^{\text{c}}\text{H}$). The carbon labels are referred to the chemical structure reported in Fig. S2, ESI.

2.2.4 Synthesis of poly(propylene terephthalate) (PPT)

The reactor was charged with DMT (30 g, 0.154 mol), PD (20 g, 0.263 mol) and TBT (0.0395 g, 1.16×10^{-4} mol) and the mechanical stirrer was set up to 170 rpm. The first stage was maintained for more

than 2 h. After 2 h of vacuum-temperature ramp, the second stage was maintained approximately 2 h; the final temperature was 240 °C with a pressure of 0.300 mbar. When the torque-meter was around 7, 27 g of white polymer were discharged from the reactor.

¹H NMR (400 MHz, CDCl₃/TFA, δ): 2.24-2.52 (m, 2H; C^aH₂), 4.45-4.66 (m, 4H; C^bH₂), 7.98-8.26 (s, 4H; C^cH₂). The carbon labels are referred to the chemical structure reported in Fig. S3, ESI.

2.2.5 Synthesis of poly(propylene isophthalate-co-ricinoleic acid) (P(PI-co-RA))

Random copolymers were synthesized starting from PD, DMI and RA. The copolymers are named P(PI-co-RA)-X/Y, where X and Y indicate the molar feed ratio of DMI-to-RA. As an example, the synthesis of P(PI-co-RA)-90/10 is reported: PD (23 g, 0.306 mol), DMI (30 g, 0.153 mol), RA (5.0 g, 0.017 mol) and TBT (0.045 g, 1.33 × 10⁻⁴ mol) as catalyst, were put into the glass reactor. The reactor was kept at 136 rpm and 190 °C for 30 min, then the temperature was raised up to 200 °C. The first stage was conducted for more than 2 h while the second stage, after almost 2 h 45 min of vacuum-temperature ramp, lasted more than 3 h; the final temperature was 240 °C with a pressure of 0.37 mbar. When the torque-meter was around 5, a rubbery caramel product was discharged from the reactor (36 g).

In order to rule out potential crosslinking reactions, solubilization tests were carried out.

¹H NMR (400 MHz, CDCl₃/TFA, δ): 0.80-0.95 (t, 3H; CⁱH₃), 1.20-1.48 (m, 16H; C^qH₂ and C^hH₂), 1.55-1.65 and 1.65-1.75 (m, 2H; C^pH₂ and C^gH₂), 1.80-2.10 (m, 2H; CⁱH₂), 2.10-2.20 (m, 2H; CⁿH₂), 2.23-2.40 (m, 2H; C^bH₂), 2.40-2.50 (m, 2H; C^fH₂), 4.15-4.30 (m, 2H; C^{a'}H₂), 4.35-4.45 (m, 2H; C^aH₂), 4.45-4.55 (m, 4H; C^aH₂), 5.10-5.20 (m, 1H; C^oH), 5.35-5.45 and 5.45-5.50 (2m, 2H; C^mH and C^lH), 7.42-7.55 (m, 1H; C^eH), 8.15-8.25 (d, 2H; C^dH), 8.60-8.72 (s, 1H; C^cH). The carbon labels are referred to the chemical structure reported in Fig. S4, ESI.

2.2.6 Synthesis of poly(propylene terephthalate-co-ricinoleic acid) (P(PT-co-RA))

Random copolymers were synthesized starting from PD, DMT and RA. The copolymers are named P(PT-co-RA)-X/Y, where X and Y indicate the molar feed ratio of DMT-to-RA. As an example, the synthesis of P(PT-co-RA)-90/10 is reported: PD (20 g, 0.260 mol), DMT (25 g, 0.131 mol), RA (5.0 g, 0.017 mol) and TBT (0.039 g, 1.16 × 10⁻⁴ mol) as catalyst, were put into the glass reactor and stirred at 170 rpm. The first stage was conducted for more than 2 h while the second stage, after almost 2 h of vacuum-temperature ramp, lasted approximately 2 h; the final temperature was 240 °C with a pressure of 0.22 mbar. When the torque-meter was around 9, a viscous brown product was discharged from the system (29 g).

¹H NMR (400 MHz, CDCl₃/TFA, δ): 0.86 (t, 3H; C^pH₃), 1.20-1.50 (m, 16H; C^fH₂ and C^oH₂), 1.54-1.69 (m, 2H; CⁿH₂), 1.68-1.82 (m, 2H; C^eH₂), 1.94-2.10 (m, 2H; C^sH₂), 2.14-2.26 (m, 4H; C^lH₂), 2.26-2.45 (m, 2H; C^aH₂), 2.45-2.56 (m, 4H; C^dH₂), 4.30-4.40 (m, 2H; C^{b''}H₂), 4.45-4.52 (m, 2H; C^{b'}H₂), 4.53-4.75 (m, 4H; C^bH₂), 5.09-5.25 (m, 1H; C^mH), 5.25-5.44 and 5.45-5.60 (2m, 2H; CⁱH and C^hH), 7.93-8.29 (s, 4H; C^cH₂). The carbon labels are referred to the chemical structure reported in Fig. S5, ESI.

2.2.7 Determination of antibacterial activity

The antimicrobial properties were assessed by evaluating the survival of bacterial cells exposed to the prepared samples. The two target microorganisms (*E. coli* and *S. aureus*) were grown aerobically in NB for 16 h at 37 °C. The culture obtained was centrifuged at 7000 rpm for 10 min, washed in sterile physiological solution (0.9% w/v NaCl) and re-suspended in the same solution in order to obtain $\approx 10^5$ colony forming units (CFU) mL⁻¹. For PPI, P(PI-co-RA), PT, (PT-co-RA), according to Totaro et al. [2], pieces of each sample with a surface area of 2.5 cm² were transferred into 2 mL tubes containing 1.5 mL of cell suspension previously prepared. Regarding PRA, which had a viscous consistency, 75 mg of the polymer were inserted into 2 mL tubes containing 1.5 mL of cell suspension. Tubes were placed in a shaker at 100 rpm at room temperature (about 23 ± 1 °C) for 24 h. After the incubation, each cell suspension was serially diluted (1:10) and the dilutions were plated on PCA. After incubation of the plates at 37 °C for 24 h, the number of colonies, corresponding to the number of viable cells, was counted, after averaging using triplicates, through a modification of the equation reported by Lala *et al.* [27], as follows:

$$\text{Mortality \%} = \frac{B-A}{B} \times 100$$

where mortality % = percentage of reduction of viable cells, A= average number of viable cells obtained after 24 h of contact with samples, and B = average number of viable cells after 24 h of incubation of a bacterial cell suspension in the absence of any material also used as positive control. The microbial content was assessed to be null for each specimen, therefore no negative control has been used.

2.3 Analytical Techniques

¹H NMR spectra were recorded at 400 MHz with a Varian Mercury 400 spectrometer (chemical shifts are in part per million downfield from TMS); the solvent used was CDCl₃ or CDCl₃/TFA (trifluoroacetic acid) 80/20.

Weight average molecular weight (Mw) and polydispersity index (PD) were determined using gel permeation chromatography (GPC) performed in CHCl₃ at ambient temperature on a HP 1100 Series apparatus with a PL gel 5 μm Minimixed-C column with UV and refractive index as detectors. Polystyrene standards were used to prepare a universal calibration curve. PPT samples were dissolved in CHCl₃ with some drops of hexafluoroisopropanol (HFIP), PPI samples were dissolved in CHCl₃. The calorimetric analysis (DSC) was carried out by means of a Perkin-Elmer DSC6 under nitrogen flow. In order to delete their previous thermal history, the samples (ca. 10 mg) were first heated at 20 °C/min to 250 °C, kept at high temperature for 2 min, and then cooled to -70 °C at 10 °C/min. After this thermal treatment, the samples were analyzed by heating from -70 °C to 250 °C at 10 °C/min (2nd scan).

During the cooling scan the crystallization temperature (T_C) and the enthalpy of crystallization (ΔH_C) were measured, while the glass transition temperature (T_g), the melting temperature (T_m) and the enthalpy of fusion (ΔH_m) were determined during the 2nd heating scan. T_g was taken as the midpoint of the heat capacity increment associated with the glass-to-rubber transition.

Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere using a Perkin Elmer TGA7 apparatus (gas flow 40 mL/min) at 10 °C/min heating rate from 50 to 800 °C. The temperature corresponding to the initial mass loss (T_{onset}) and mass residues have been extrapolated.

Physical and mechanical properties were determined using a Rheometric Scientific DMTA IV Dynamic Mechanical Analysis instrument with a dual cantilever testing geometry. Typical test samples were bars obtained by injection moulding at melting using a Minimix Molder. The analysis was carried out at a frequency of 3 Hz, at 3 °C/min in the temperature range -120 °C to 120 °C, with a 0.01% of strain (PPI series); or 3 Hz, 3 °C/min, from -120 °C to 160 °C, and 0.02% of strain (PPT series).

Tensile testing was performed by an Instron 5966 tensile testing machine equipped with a 10 kN load cell (test speed 50 mm/min, room temperature 19 ± 1 °C, 70 ± 10 % relative humidity, initial grip separation 23 mm). Five samples for each composition with dimensions of 50.0 mm (length), 5.0 mm (width) and 200/300 μm (thickness) were analyzed. Such samples, obtained from the same film, were prepared by press-molding above melting and subsequently cooling down to room temperature, without releasing the pressure.

Cyclic tensile testing was performed with the same apparatus. Sample films of P(PI-co-RA)-90/10 were stretched to ε_m, 100% elongation at room temperature with a 50 mm/min stretching rate. Then the clamps began to return with a speed of 50 mm/min until the force on the sample was 0 MPa. After the above two steps, one cycle is complete. Three samples were tested to calculate mean values and

standard deviation. Every sample was subjected to 5 cycles and the shape recovery rate (R_r) was calculated according to the following equation:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N - 1)}$$

where N is the cycle number, ε_m is the maximum strain imposed on the material, $\varepsilon_p(N)$ and $\varepsilon_p(N - 1)$ are the strains of the sample in two successive cycles when the force on the sample is 0 and $R_r(N)$ is based on two successive cycles. Final data were expressed as percentage.

3. Results and Discussion

3.1 Chemical characteristics and thermal properties of homopolymers and RA-based copolymers

In this work, novel random copolymers were prepared starting from ricinoleic acid, 1,3-propanediol and dimethyl isophthalate or terephthalate according to the reaction schemes reported in Schemes 1-5. A classical two-stage polycondensation process was used for homopolymers and copolymers. In order to avoid potential degradation phenomena occurring during the syntheses, the thermal stability of RA was checked by TGA under air flow, resulting in a T_{onset} of 255 °C.

Moreover, RA is characterized by a low reactivity toward esterification reaction, because of its secondary OH group and its hindering lateral aliphatic chain. Literature reports that high molecular weights for PRA ($M_w \approx 100,000$) can be obtained only by enzymatic catalysis for very long reaction times [5]. Otherwise, authors reported low molecular weight ($M_w \approx 3000-8000$) [2, 6-7] obtained through chemical synthesis of PRA in molten state or solution.

In this work, two compositions were prepared for the two series of copolymers, using a feed ratio of 90/10 and 75/25 mol% of DMI (or DMT) with respect to ricinoleic acid, in order to have a balance between the antibacterial and thermomechanical properties, according to previous results [2]. Moreover, for PPI-based copolymers, an additional composition (82/18 DMI/RA mol%) was prepared in view of the resulting mechanical properties.

The chemical characterization data of the samples are reported in Table 1.

The molecular structures of the homopolymers and copolymers were confirmed by ^1H NMR analysis as well as the ratio RA/DMI or RA/DMT with respect to the feed (Table 1). Some representative spectra are reported in ESI, Figures S1-S5. In addition, from the ^1H NMR spectra the double bond content was also evaluated. By focusing on the ratio between two distinct peaks related to the protons of the double bond (range 5.25-5.60 ppm) and the protons of the RA methylene unit at lower chemical shift, it can be noticed that almost all samples have a high double bonds content (Table 1: 92 mol% for PRA, 95 mol% P(PT-co-RA)-90/10). The copolymers containing the highest amount of PRA,

present lower values of double bonds content (around 60 mol%): this could be due to partial degradation reactions that occurs when the polymerization time is longer. However, it is possible to observe that the polymerization process almost occurs without a significant double bond decrement. The molecular weights, measured by GPC, show that the final M_w values are higher for the copolymers than for PRA, due to the higher reactivity of PD with respect to the hydroxyl group of ricinoleic acid. It is notable that a relatively high M_w is obtained for the PRA homopolymer, with respect to the data previously reported by same authors [2]. This can be probably ascribable to the higher purity of the RA (> 80%) used in the present work respect to that of the monomer employed in ref. 2 (\approx 80%) in fact, the presence of impurities could act as chain stoppers limiting the growing of the macromolecular chains.

In Table 2, the thermal data of all the samples prepared are summarized. PRA, which is a viscous liquid at room temperature, is an amorphous polymer, with very low T_g (-67 °C). The presence of cis double bond, which causes kinks and disturbs the symmetry of the chains, as well as the long lateral sequence of six methylene groups for each monomeric unit, do not allow the achievement of an ordered arrangement. PPI is an amorphous polyester, with glass transition temperature at 40 °C, while PPT is a semicrystalline polymer, with melting temperature of 230 °C and T_g at 54 °C, while. These calorimetric data for homopolymers are consistent with literature [19].

For the PPI/PRA copolymers, only a single T_g is observed for all the samples in the DSC scans, indicating the presence of a homogeneous amorphous phase. The rigid chains of PPI achieve a notable level of flexibility with the addition of a small amount of RA units, inducing a significant decrement of T_g , which decreases from 40 to 17 °C with the presence of 10 mol% of RA units. With the increment of the RA-unit content, T_g decreases accordingly with the composition.

For the PPT/PRA copolyesters, the crystallization, melting and glass transition processes are present in the DSC scans, as expected for random copolymers able to crystallize. PPT homopolymer crystallizes at 170 °C during the cooling scan from the melt. The presence of the amorphous RA chains, randomly distributed along the main chain, can be a hindrance to the crystallization process of the PPT units, producing a decrement of T_c to 162 °C (with 10 mol% of RA units), up to 123 °C (with 25 mol% of RA units). The crystallization and melting enthalpies decrease accordingly to the composition. Finally, also for PPT/PRA copolymers, the presence of a single glass transition indicates a homogeneous amorphous phase characterized by a T_g which significantly decreases from 54 °C to 5 and -31 °C with 10 and 25 mol% of RA.

The thermogravimetric results (Table 2) show that PPI and PPT have almost the same thermal stability (\approx 400 °C) under nitrogen atmosphere. This can be explained, taking into account that the

main thermal degradation pathway of polyesters is highly dependent on the nature of the diol subunit, whose decomposition is due to a β -scission mechanism [19]. PPI shows one main weight loss, as well as PPT, but the latter has a residue of less than 10 wt% (Figures 1-2): indeed an intermolecular condensation was reported to occur, forming carbonaceous char [28]. PRA begins its degradation process at temperature of 354 °C: then, its weight loss occurs in two main processes. The copolymers show lower T_{onset} with respect to the PPI and PPT homopolymers, in agreement with composition. By observing the derivative curves (Figures 1b and 2b), it is notable that the main weight loss of copolymers present a shoulder at lower temperatures, in correspondence with the initial degradation process of PRA. This shoulder becomes more intense with the increment of the RA unit content.

Dynamic mechanical analysis was carried out on PPI, PPT and the copolymers with the lower amount of RA unit because the other compositions resulted too fragile probably due to a lower molecular weight. In Figure 3 the storage modulus E' , which indicates the elastic response of a material, and $\tan \delta$, the ratio of the loss modulus (E'') respect to the storage modulus, were plotted as a function of temperature. Pure PPT shows the dynamic mechanical viscoelastic relaxations β and α , respectively around -70 °C and 75 °C. The α transition corresponds to the glass transition. The β relaxation, occurring at low temperature and characterized by a small intensity, is attributed to the reorientation of the hydroxyl groups and to the local motions of the carboxyl groups in the amorphous phase [29]. The P(PT-co-RA)-90/10 copolymer presents a DMTA spectrum that is very similar to that of the PPT homopolymer: as expected the transition temperatures are lower due to the presence of the flexible aliphatic RA-units.

In comparison to PPT, in PPI curve (Figure 3b) the maximum value of the $\tan \delta$ peak is more pronounced, because the amount of amorphous phase is higher and the movements of the amorphous PPI chains cause a great energy loss around glass transition temperature [30]. The P(PI-co-RA)-90/10 copolymer is characterized by a mechanical behavior similar to that of PPI, where the differences are due to the presence of the flexible RA-chains.

3.2 Tensile properties of RA-based copolymers

Tensile properties of PPI and its copolymers were carried out on film samples. PPT films were not tested because they resulted too fragile. Fig. 4 shows the strain-stress curves of all the samples, while the data are collected in Table 3. The presence of soft segments of RA determines huge changes in the mechanical behavior of the PPI chains. A substantial decrease of both tensile modulus E and tensile strength σ_{max} is present in copolymers, while the elongation at break ε_b increases with respect to the homopolymer, showing a huge increase to over 1000% with 10 mol% of PRA. Such P(PI-co-RA)-90/10 sample indeed (Figure 4b) evidences the typical behavior of a thermoplastic elastomer:

no yield, high toughness and excellent ϵ_b (higher than 1000 %). Therefore, it was subjected to cyclic stress-strain tests, whose curves are shown in Fig. 5. The shape recovery ratios at 100% of strain during five cycles are collected in Table 4 and the results are characterized by an increase of the shape recovery according with the cycle numbers. During the first cycle, which is named “training cycle”, the weak net-points are destroyed and a reorientation of the molecular chains occur, according to the direction of deformation. This behavior is known as softening, and it can be due to rearrangement of the macromolecular chains. After the first cycle, an ideal orientated elastic network is formed, therefore, the samples show higher recovery ratios (80-90%). Starting from the second cycle, the stress-strain curves follow a fixed path, but the hysteresis area becomes much smaller than the previous cycle. It is reported that this behavior is due to the rearrangement of the macromolecules together with the crystallization during straining [31-32]. It must be underlined that the copolymers with higher amount of PRA, do not present significant elastic properties, therefore the soft characteristic of RA unit, able to impart elastic properties to the backbone of PPI, find the optimal composition just if the molar ratio PPI/PRA is 90/10.

3.3 Antibacterial properties of RA-based copolymers

The characterization of the new materials also included the evaluation of their antimicrobial activity, which were determined as cell mortality after incubation of the specimens with a suspension of *S. aureus* ATCC 6538 and *E. coli* ATCC 8739. These strains, used as Gram positive and Gram negative targets, may cause serious infections in the food industry as well as in hospitalized patients [33]. The results of the antibacterial tests are summarized in Table 5 and supplementary Table S1: PRA causes 100% mortality against *S. aureus*, as expected by already reported data [2-3]; the same mortality is also observed for *E. coli*, differently from Totaro et al. (2014) [2]. This difference could be ascribed to the higher purity of the monomer used for the PRA synthesis (> 80% in the present work respect to that of the monomer employed in ref. 2, \approx 80%). PPI and PPT do not show any antibacterial activity against *E. coli* and a negligible inhibition against *S. aureus*. Concerning the copolymers, the two compositions richest in RA unit, P(PI-co-RA)-75/25 and P(PT-co-RA)-75/25, are characterized by a significant antibacterial activity, close to 100% of mortality against *S. aureus*. Against the gram negative *E. coli* only P(PI-co-RA)-75/25 is able to exert an antimicrobial effect. The activity is probably due to the long lateral aliphatic segments of RA along the macromolecular chains, which can damage the cytoplasmic membrane after passing through the cell wall, causing cell death [2,3,35]. The different response against *E. coli*, could be due to the amorphous nature of PPI with respect to the semicrystalline PPT: the presence of organized regions, with well-ordered PPT chains indeed, could act as a permeability barrier, reducing the uptake into the cell or also inhibiting the mobility of the long lateral chains of RA units. In PPI amorphous regions, such RA lateral chains are free to move

and penetrate the cell walls, exerting their lethal action. This hypothesis is consistent with previously reported data: RA was copolymerized with another semicrystalline polymer (PBS), resulting in a lower antibacterial activity against *E. coli* with respect to the Gram positive strain [2]. In general, the effect is higher versus *S. aureus* because Gram negative bacteria have an additional outer lipopolysaccharide membrane on the cell wall, acting as a permeability barrier, so the uptake into the cell is reduced.

In the conditions tested, the lower amount of ricinoleic acid was not as efficient as the higher concentration in exerting the activity, neither with PPI nor PPT. In the case of P(PI-co-RA)-82/18, the mortality data obtained are affected by a high standard deviation that can be ascribed to non-homogeneous sample preparation for antibacterial tests, affecting the bioavailability of ricinoleic acid units.

4. Conclusions

Random copolymers synthesized starting from PD, RA and DMI or DMT, were successfully prepared with different molar ratio of RA units. Thermal data indicates that PPT-based copolymers are semicrystalline with a homogenous amorphous phase, whereas PPI-based samples are in a fully homogeneous amorphous phase. DSC and DMTA analyses show that the presence of the flexible RA-units along the main chains determine a notable decrement of the glass transition temperature, according to the composition. The tensile properties show a significant decrease of both tensile modulus E and tensile strength σ_{\max} in PPI copolymers with respect to the homopolymer, while the elongation at break ε_b increases, showing a huge enhance to over 1000% with 10 mol% of PRA. The cyclic stress-strain tests carried out on such film sample denote a shape recovery ratios (at 100% of strain during five cycles) increasing up to 95%.

Concerning the antibacterial properties, the copolymers containing 25 mol% of RA have a significant antibacterial activity, showing a great potentiality for being used in several industrial applications. In conclusion, by tuning the RA amount it is possible to obtain elastomeric or antibacterial materials, suitable for textiles and/or film engineering applications.

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2020.106719>.

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Table 1. Chemical Characterization of PRA, PPI, PPT and their copolymers.

Sample	DMI (DMT)/RA ^{a)}	DMI (DMT)/RA ^{b)}	Double bond content (mol%)	$M_w \times 10^{-3}$ ^{c)}	PDI ^{c)}
PRA	/	/	92	17	3.8
P(PI-co-RA)-75/25	75/25	74.5/25.5	60	21	4.3
P(PI-co-RA)-82/18	82.5/17.5	82/18	80.5	34	2.9
P(PI-co-RA)-90/10	90/10	90/10	86	50	3.3
PPI	/	/	/	57	1.9
P(PT-co-RA)-75/25	72/28	73/27	59	34	2.9
P(PT-co-RA)-90/10	88.5/11.5	87/13	95	24	2.3
PPT	/	/	/	52	2.1

^{a)} Molar feed ratio of dimethyl isophthalate (DMI) or dimethyl terephthalate (DMT) and ricinoleic acid (RA).

^{b)} Molar ratio DMI or DMT/RA determined by ¹H NMR.

^{c)} M_w and polydispersity (PDI) determined by GPC in CHCl₃.

Table 2. TGA and DSC results of PRA, PPI, PPT and their copolymers.

Sample	T_{onset} (°C) ^{a)}	T_g (°C) ^{a)}	T_c (°C) ^{c)}	ΔH_c (J/g) ^{c)}	T_m (°C) ^{b)}	ΔH_m (J/g) ^{b)}
PRA	354	-67	/	/	/	/
P(PI-co-RA)-75/25	383	-8	/	/	/	/
P(PI-co-RA)-82/18	391	0	/	/	/	/
P(PI-co-RA)-90/10	394	17	/	/	/	/
PPI	401	40	/	/	/	/
P(PT-co-RA)-75/25	394	-31	123	28	187	24
P(PT-co-RA)-90/10	393	5	162	38	216	36
PPT	402	54	170	41	230	51

^{a)} Determined by TGA under nitrogen flow;

^{b)} Determined by DSC during the 2nd heating scan;

^{c)} Determined by DSC during the cooling scan from the melt at 10 °C/min.

Table 3. Tensile properties of PPI and its copolymers.

Sample	E (MPa)	σ_{max} (MPa)	ϵ_b (%)
P(PI-co-RA)-75/25	128 ± 7	7.4 ± 0.5	17.1 ± 1.4
P(PI-co-RA)-82/18	302 ± 21	10.1 ± 1.2	7.8 ± 2.0
P(PI-co-RA)-90/10	36.5 ± 17	2.8 ± 0.08	1262 ± 79
PPI	2246 ± 13	50.1 ± 1.8	3.6 ± 0.1

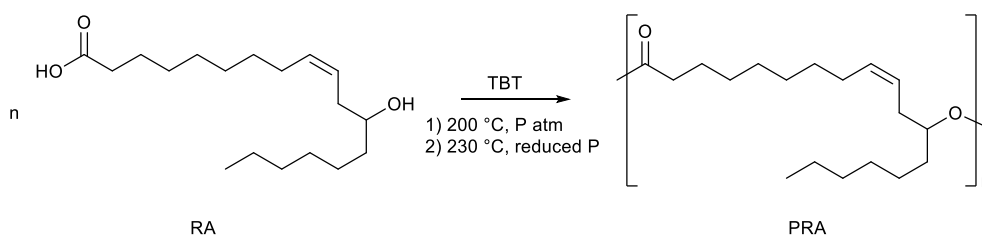
Table 4. Elastic properties of P(PI-co-RA)-90/10, demonstrated by shape recovery ratio at 100 % strain using cyclic tensile testing.

Sample	R _r (1)	R _r (2)	R _r (3)	R _r (4)	R _r (5)
P(PI-co-RA)-90/10	44.7 ± 3.1	82.1 ± 0.8	89.2 ± 3.5	89.1 ± 3.4	95.4 ± 3.9

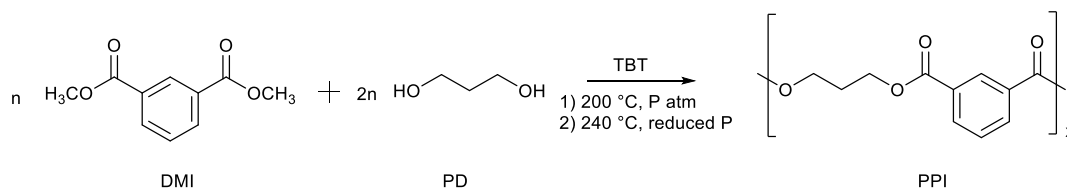
Table 5. Antibacterial properties of PRA, PPI, PPT and their copolymers against *E. coli* and *S. aureus*. The % of mortality has been calculated considering as positive control a bacterial suspension in the absence of any material, as described in section 2.2.7.

Sample	<i>E.coli</i> (% mortality)	<i>S.aureus</i> (% mortality)
PRA	100	100
P(PI-co-RA)-75/25	99.6 ± 0.2	98.0 ± 1.8
P(PI-co-RA)-82/18	31.9 ± 18.4	42.9 ± 34.2
P(PI-co-RA)-90/10	0	0
PPI	0	24.7 ± 0.8
P(PT-co-RA)-75/25	30.2 ± 10.5	97.9 ± 2.6
P(PT-co-RA)-90/10	0	23.6 ± 8.5
PPT	0	13.2 ± 1.5

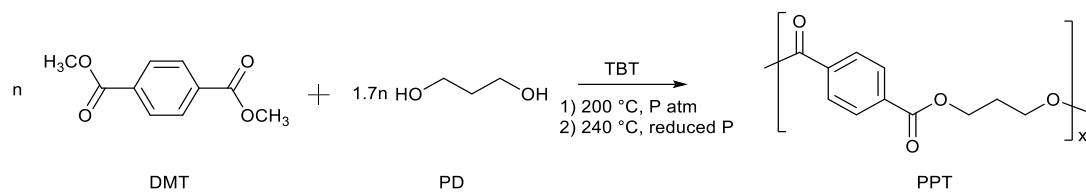
Scheme 1: Polymerization reaction of poly(ricinoleic acid) (PRA).



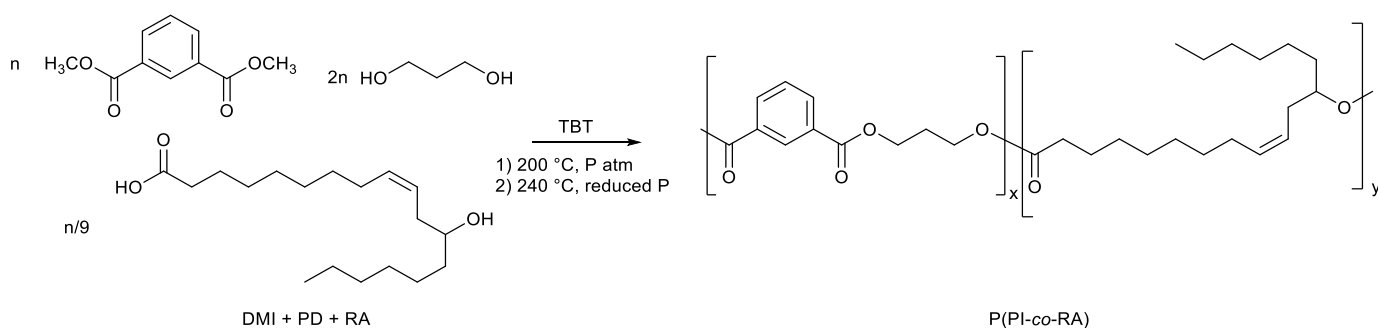
Scheme 2: Polymerization reaction of poly(propylene isophthalate) (PPI).



Scheme 3: Polymerization reaction of poly(propylene terephthalate) (PPT).



Scheme 4: Polymerization reaction of poly(propylene isophthalate-*co*-ricinoleic acid) (P(PI-*co*-RA)).



Scheme 5: Polymerization reaction of poly(propylene terephthalate-*co*-ricinoleic acid) (P(PT-*co*-RA)).

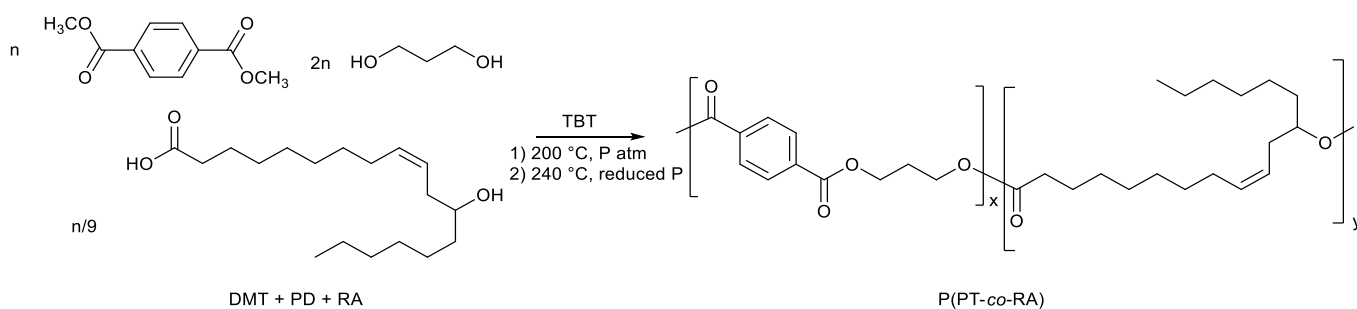


Figure 1. a) TGA and b) DTGA curves of PPI, PRA and copolymers.

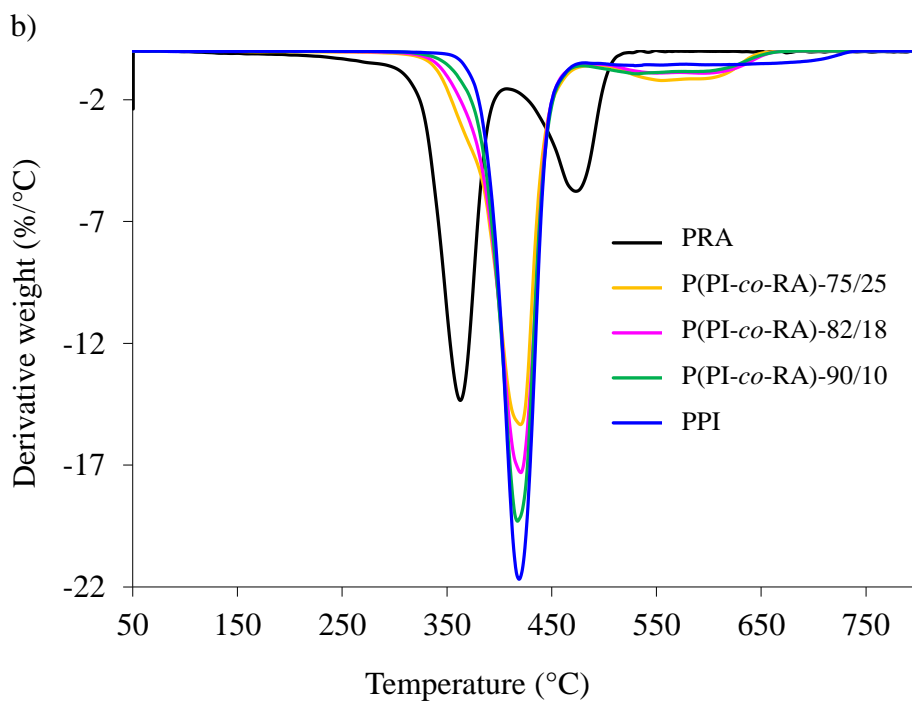
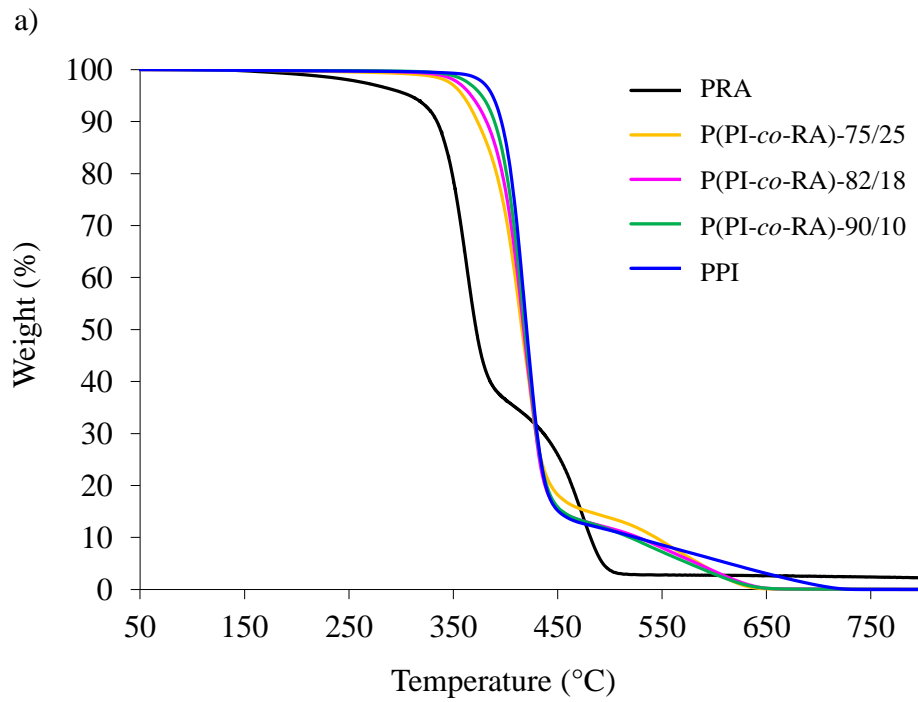


Figure 2. a) TGA and b) DTGA curves of PPT, PRA and copolymers.

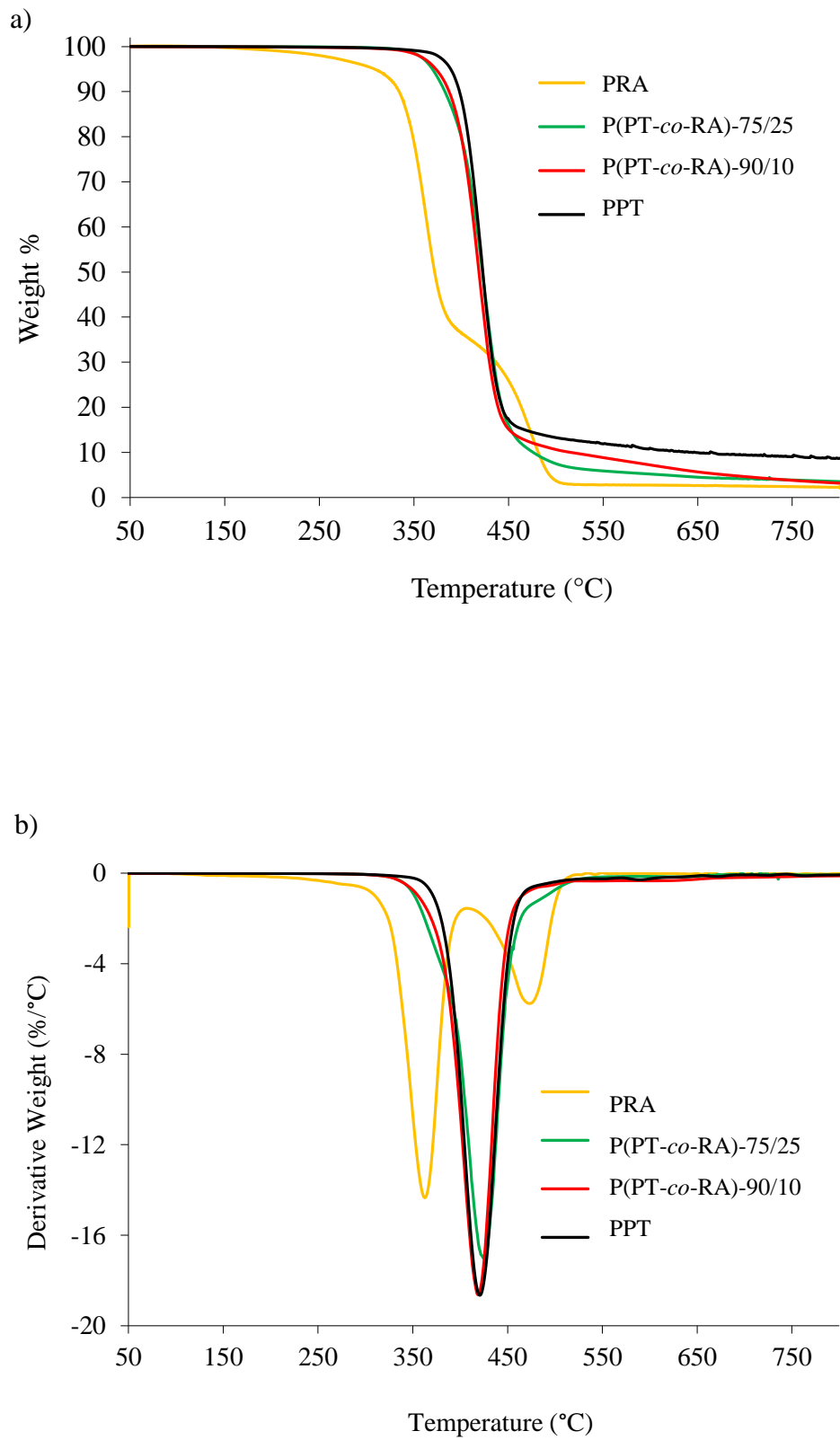
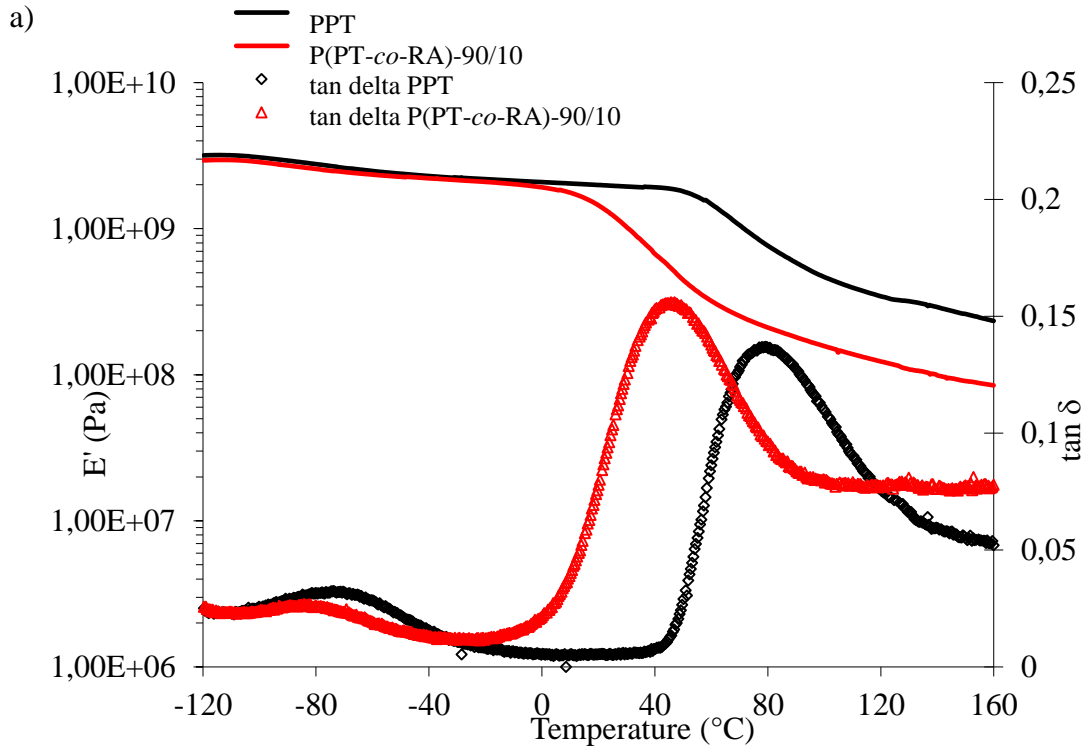


Figure 3. Dynamic mechanical curves of a) PPT and P(PT-co-RA)90/10 and b) PPI and P(PI-co-RA) 90/10.



b)

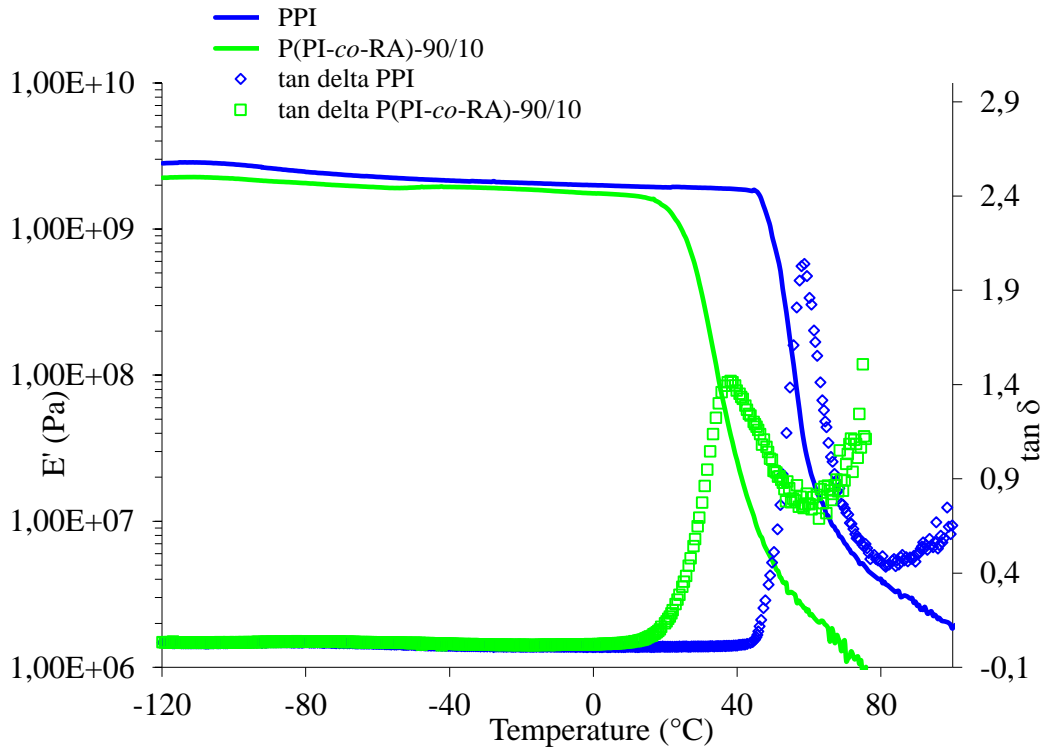


Figure 4. a) Tensile stress-strain curves of PPI and copolymers; b) Stress-strain curves of P(PI-co-RA)-90/10.

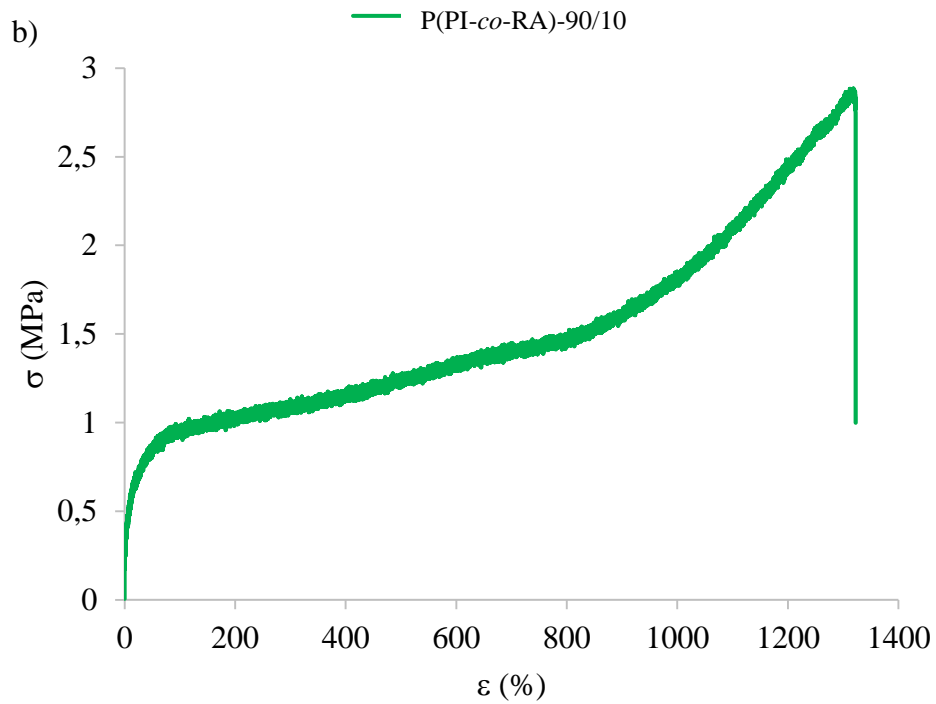
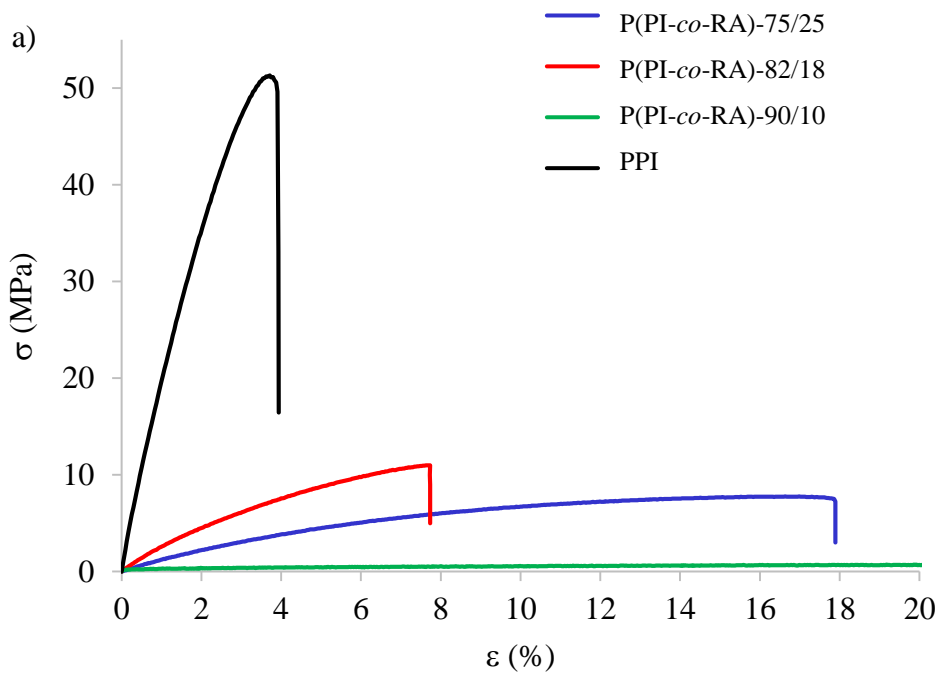


Figure 5. Cyclic tensile testing stress-strain curves of P(PI-co-RA)-90/10.

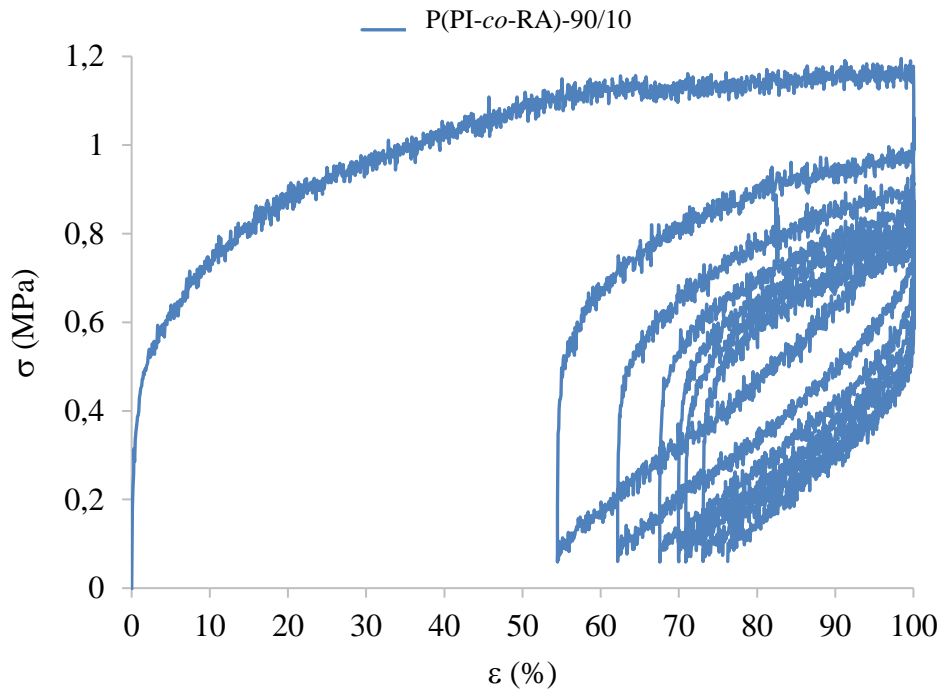


Figure 6. Antibacterial properties of all samples.

