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Priamine 1075 and catechol carbonate, a perfect match for ecofriendly production of a new renewable polyurea for sustainable flexible food packaging

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Abstract

New homopolyurea with enhanced functional properties was synthesized by combining a bio-based vegetable oil derived diamine, Priamine 1075, with catechol carbonate as carbonylating agent employing an ecofriendly synthetic strategy. The synthesis, carried out in catalyst-free and solventless conditions, allowed obtaining a transparent rubbery material soluble in chloroform and processable in form of film. The polyurea was firstly subjected to molecular characterization by ¹H-, ¹³C-NMR, ATR-FTIR spectroscopy and GPC analysis, to check molecular structure and weight ensuring the good control of synthesis process. Afterwards, the film was subjected to thermal characterization, DSC analysis confirming the amorphous rubbery nature and TGA revealing the outstanding thermal stability.

Tensile tests showed low elastic modulus and exceptional elongation at break together with shape-recovery capability.

Permeability tests revealed good gas-barrier properties regardless the amorphous rubbery nature, in particular to CO₂ molecules. The measured values were better than polyolefins ones, to date the most used materials in food packaging.

Keywords: catechol carbonate, Priamine 1075, ecofriendly synthesis, sustainable food packaging, gas barrier properties, mechanical properties, polyurea.

Introduction

Polyureas (PUs) are very versatile polymers, with tunable solid-state properties, usually used as multi-component systems in form of fibers, films and coatings in various fields. PUs are employed in anti-corrosion, waterproof and wear-resistant linings[1], in the preparation of energy-absorption coatings[2,3] able to improve the stability and cycle life of lithium metal batteries[4]. Thanks to the adjustable mechanical properties and excellent biocompatibility, polyureas are also emerging as promising biomaterials in biomedical applications[5–7] . Interestingly, urea-based materials have shown the ability to absorb CO₂ molecules. Thus, the use of PUs can be further extended to the realization of devices for CO₂ reduction in the atmosphere[8,9]. Aliphatic polyureas, in particular, are also known to have high UV stability, good resistance to degradation and high transparency due to the absence of aromatic moieties[10,11] and for these reasons they are particularly suitable for rolling and coating applications[12]. Polyureas can be synthesized starting from diamines, whose varied chemical structure and architecture allow deeply varying the final functional properties. The most known and spread PUs production routes involve the use of toxic and high environmental impact phosgene and isocyanate reagents as well as hazardous solvents[13–17]. Thus, the current approach aims toward phosgene/isocyanate-free synthetic pathways[15,18–20]. PUs can be synthesized by polycondensation of diamines and dicarbamates with different substitute groups[21–26] by ring-opening reaction of diamines with cyclic carbonates[9,27,28], by reaction of diamines and urea[29,30], through polycondensation of diamines and CO₂ with or without catalysts[31–34]. Recently, some of us have presented an ecofriendly one-pot solventless and catalyst-free method for the synthesis of ureas and polyureas by using an aromatic cyclic carbonate, catechol carbonate (CC), as carbonylating agent. Moreover, throughout this synthetic pathway, catechol can be easily recovered by sublimation as pure crystals ready to be recycled for the synthesis of new CC[35]. Worth of note, CC can be easily and efficiently obtained by the transcarbonation reaction between catechol

and dimethyl carbonate (DMC) by a dedicated reactive distillation system with the use of molecular sieves, with isolated yield of around 90%[36]. Catechol is a low value by-product of the hydroquinone production or could be achieved from lignin depolymerization[37–39] while DMC can be obtained by direct condensation reaction between CO₂ and methanol[40,41]. Moreover, CC have already proved its peculiar reactivity in the reaction of alcohols and polyols for the production of complex organic carbonates or benzodioxanes[42,43].

The need to contain the environmental impact does not only pertain to the synthesis step but also the source of raw materials. Despite the great concern for bio-based monomers and polymers very few natural amines and diamines, mainly derived from chitosan and poly(lysine), are currently available[44]. In addition, polyureas obtained from the most known diamines (butanediamine, pentanediamine, hexamethylene diamine) are characterized by high crystallinity degree and melting temperature reducing their workability window, as well as by poor solubility in most organic solvents limiting their processability[19,35]. Moreover, from the mechanical point of view these materials present very high stiffness[19] which prevents their application in fields where flexible materials are required.

In this context, Croda is producing a truly bio-based vegetable oil derived diamine: Priamine, a new kind of apolar and hydrophobic diamine[45] widely used in automotive, 3D printing and for the realization of adhesives, sealants and engineering plastics. Thanks to its low viscosity, it can be used solely and in solvent-free formulations. Besides thermo/oxidative stability and water resistance, Priamine provides good barrier properties and superior flexibility as well as impact resistance. Moreover, Priamine-based materials present self-healing capability.

Priamine, proposed in four versions (1071, 1073, 1074, and 1075, purity increasing with the reference number), has been employed for the realization of polyureas[18], polyepoxide foams[46] and poly(ether-urethane-urea)s[17]. In particular, Kebir et al. have prepared polyurea-Priamine 1074 by a multi-step methyl carbamate metathesis polymerization process involving catalysts[18], while Włoch et al. have synthesized partially bio-based poly(ether-urethane-urea)s containing Priamine 1071 by using isocyanate reagents[17]. Several authors evidenced microstructure and solid-state properties deeply depend on molecular chains interactions that in turn are affected by the density of hydrogen bonding established between urea linkages[10,15,19,47]. More in detail, owing to the high density of hydrogen bonds, most polyureas are insoluble or partially soluble in common organic solvents and extremely stiff and brittle. As a consequence, a proper reduction of H-bonding could be an efficient tool to improve processability and enhance mechanical toughness.

From the chemical structure point of view Priamine is a cycloaliphatic diamine containing long linear aliphatic segments with PE-like side chains[44]. By using Priamine as a monomer a particular kind

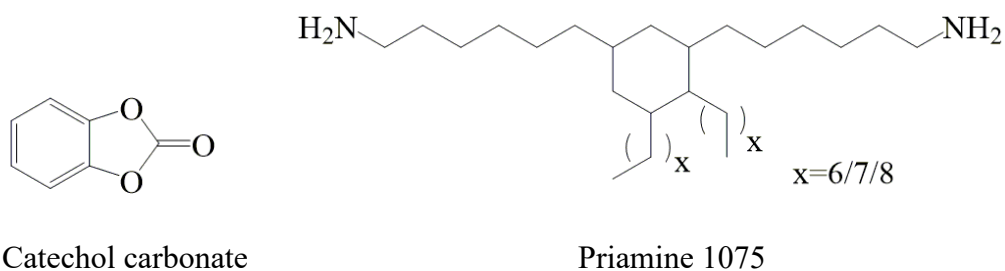
of homopolyurea can be obtained, in which the long sequences of methylene groups are thought to promote flexibility and decrease the density of urea functional groups, this way limiting the formation of H-bonds, thus enhancing the thermo-chemical stability, flexibility as well as solubility in organic solvents of the final material.

In this work, we have combined the bio-based Priamine 1075, the purest diamine produced by Croda with catechol carbonate employing an ecofriendly strategy for the synthesis of a new homopolyurea with enhanced functional properties. Besides molecular characterization, thermal, mechanical and gas-barrier properties have been studied and correlated to polymer chemical structure.

Experimental section

Materials

Catechol carbonate (CC) (Scheme 1) was prepared as recently reported by some of us[36]. Priamine 1075 (Scheme 1) was kindly supplied by Croda Italiana S.p.A. (Mortara Italy).



Scheme 1. Molecular formulas of catechol carbonate (CC) and Priamine 1075.

Methods

Molecular characterization

Polymer chemical structure was verified by: ¹H- and ¹³C- nuclear magnetic resonance spectroscopy (Varian Inova 400-MHz Instrument) at room temperature using deuterated chloroform (CDCl₃) as solvent, containing 0.03 vol% tetramethylsilane (TMS) as an internal standard, as solvent; attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (FTIR) analysis has been performed using an Agilent Technologies Cary 630 FTIR. The spectra were collected between 650 and 4000 cm⁻¹, recording 128 scans with a resolution of 2 cm⁻¹.

Polymer number molecular weight (M_n) and polydispersity index (D) were determined by a HPLC instrument (Waters 1525 pump and 410 differential refractometer) equipped with PLgel 5 μ m Mixed-C 300 x 7.5 mm column. The measurements were performed at 30 °C using chloroform as eluent (1mL/min). The instrument was previously calibrated with polystyrene standards in the range of 800–100000 g/mol.

Thermal characterization

Differential Scanning Calorimetry (Perkin Elmer DSC6) was used to analyze the thermal transitions by heating from -70 to 300 °C at 20 °C/min. The glass transition temperature (T_g) and heat capacity (Δc_p) were taken as the midpoint and the height, respectively, of the glass to rubber transition step.

Thermogravimetric analysis (Perkin Elmer TGA7), was employed to evaluate the thermal stability by heating from 50 to 800°C at 10°C/min under nitrogen atmosphere. The onset (T_{onset}) and maximum degradation rate (T_{max}) temperatures were calculated.

Film preparation

100 μ m films were obtained by compression moulding the synthesized material with a laboratory press Carver C12. The polymer was heated to 100 °C, kept under 5 ton/m² pressure for 2 min and ballistically cooled down to room temperature.

Mechanical characterization

Tensile tests were performed on rectangular specimen (5 mm x 50 mm) by means of an Instron 5966 testing machine with a transducer-coupled 1kN load cell, at a stretching rate of 10 mm/min. Elastic modulus (E) was calculated from the initial slope of the stress-strain curve.

Barrier properties characterization

Gas barrier capability to oxygen and carbon dioxide was evaluated by a manometric method using a Brugger Permeance Testing Device, type GDP-C, according to ASTM 1434-82 protocol. The measurements were performed on a film with a surface area of 78.4 cm², at 23 °C and 0 % relative humidity (dry food grade gases).

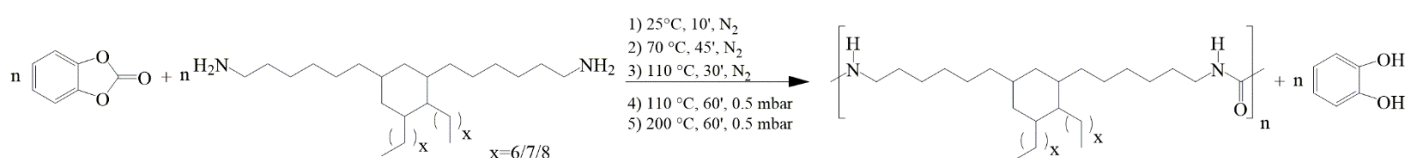
Results and discussion

Synthesis

Polyurea-P has been prepared through a solvent-less and catalyst-free synthetic process as described in Scheme 2. The main outcomes are summarized in Table 1. Equimolar amounts of Priamine 1075 (4.6 mmol; 2.5 g) and CC (4.6 mmol; 0.63 g) have been introduced in a 30 ml thermostated and mechanically stirred glass reactor. The reaction started at 25 °C, temperature at which CC is already reactive, as evidenced by mass densification. Afterwards, temperature has been progressively raised to favor the molecular weight growing, this latter proved by the progressive viscosity increase. After 85 min, pressure has been reduced to promote recovering by sublimation of catechol, accumulating in form of pure crystals and being effectively and ecofriendly recycled (84% average recovery). The discharged polymer, isolated with a 95% yield, looks like a lightly colored freestanding rubber at room temperature, soluble in chloroform. The outcome of polymerization was confirmed by ^1H -/ ^{13}C -NMR (Figure 1) and ATR-FTIR spectroscopy (Figure 2a), while the molecular weight M_n and the polydispersity index D were determined through GPC analysis (Table 1).

Afterwards, polyurea-P has been compression molded, as reported in the Experimental Section, obtaining a transparent light-colored free-standing film (Figure 3a).

The so-obtained polyurea-P film was also subjected to thermal characterization: DSC analysis to determine the polymer characteristic transition temperatures and the possible presence of crystalline phase (Figure 2b); TGA analysis to check the thermal stability (Figure 2c).



Scheme 2. Catechol carbonate and Priamine 1075 reaction conditions.

Table 1. Catechol carbonate and Priamine 1075 reaction results.

| Yield NMR % | Polymer isolated yield % | Catechol isolated Yield % | Polymer M _n g/mol | Polymer D |
|-------------------|--------------------------------|---------------------------------|------------------------------------|--------------|
| >99 | 95 | 84 | 7000 | 1.5 |

Molecular characterization

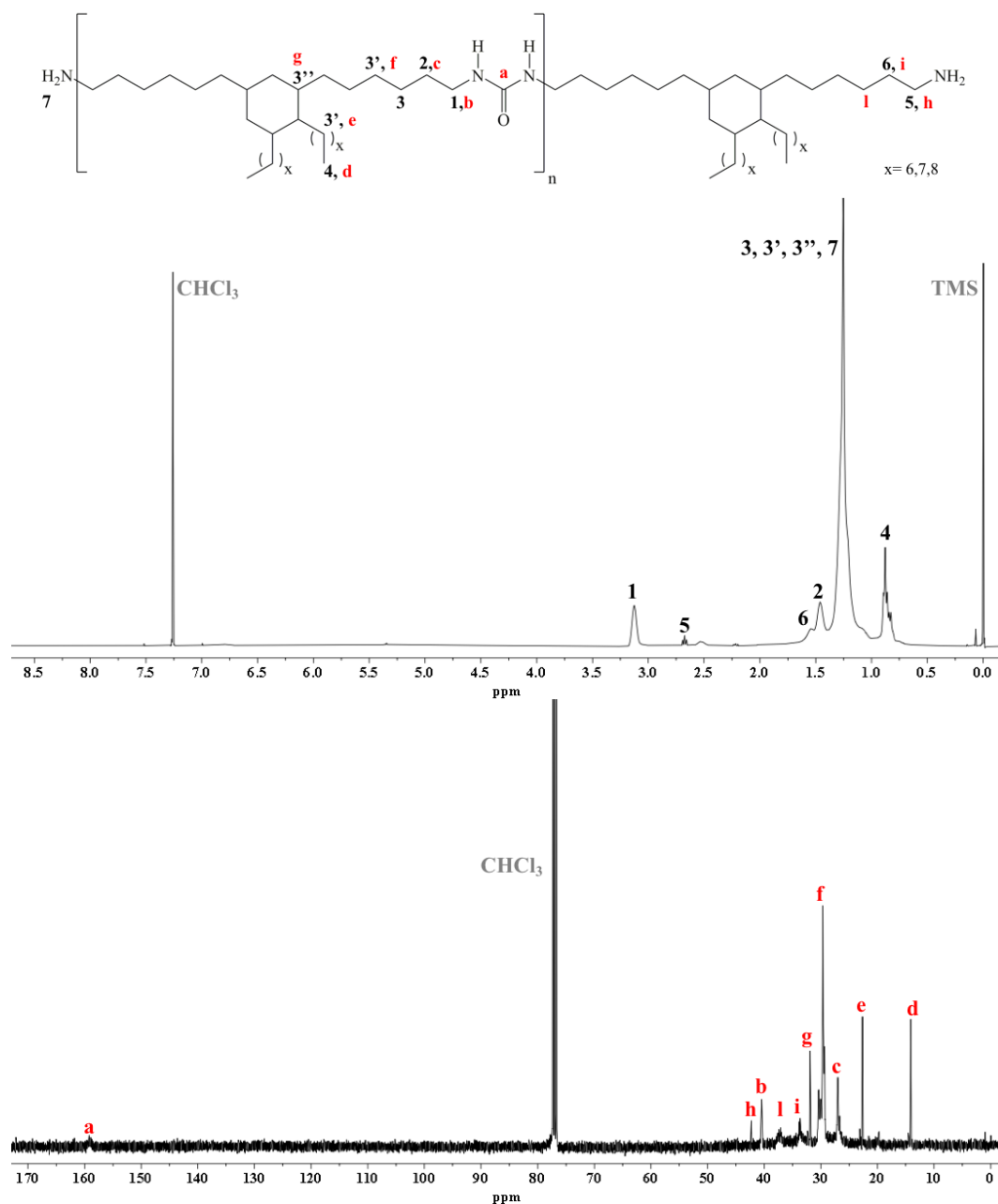


Figure 1. ^1H -NMR and ^{13}C -NMR spectra of polyurea-P, in CDCl_3 . Numbers referring to H atoms and letters relating to C atoms, respectively.

Figure 1 shows the ^1H -NMR and ^{13}C -NMR spectra of polyurea-P with the relative peak assignment.

More in detail, the resonance peaks of the methyl (**4**) and methylene/methine (**3**, **3'** and **3''**) groups belonging to the Priamine moiety are located at 0.86 and 1.22 ppm, respectively. In addition, the occurrence of the condensation reaction between CC and Priamine is evidenced by the presence of the signals at 3.16 and 1.45 ppm, ascribed to the hydrogen atoms in α - and β -position to the ureic group (**1** and **2**), respectively. The less intense peaks of the $-\text{CH}_2-$ protons of the external repeating units (**5** and **6**) are located at 2.65 and 1.55 ppm, respectively. The signal coming from $-\text{NH}_2$ group (**7**) is probably overlapped with the signals located in the region 1.10-1.60 ppm. Finally, it is worth noticing that at 7.00 ppm no peaks, due to unreacted CC or some catechol residue, are observed. This result evidences the total conversion of the monomers (> 99%) as well as the efficiency of catechol recovery (Table 1).

As concerns ^{13}C -NMR spectrum, no unexpected peaks were detected other than those due to the polyurea-P repeating unit. In particular, the methyl (**d**) and methylene (**e**) carbon atoms of the Priamine moiety branches resonate at 14.0 and 22.2 ppm, respectively, while the inner primary and secondary C atoms (**g** and **f**) are located at 30 and 32 ppm. The formation of ureic bonds leads to the appearance of the peaks at 158.8 ppm due to the quaternary C (**a**), and the signals at 40 and 27 ppm due to the carbon atoms in α - and β -position to the ureic group (**b** and **c**), respectively. Less intense peaks related to the external repeating units rise at 42.2 (**h**), 37 (**l**) and 34 (**i**) ppm.

Concerning ATR-FTIR analysis, the spectrum in Figure 2a of the synthesized polymer, in addition to the fingerprint region (from 1550 to 700 cm^{-1}) typical of each individual species, revealed the appearance of urea bands at around 1620 cm^{-1} arising from stretching vibration of $\text{C}=\text{O}$ bonds and at around 1560 cm^{-1} arising from N-H bending vibration. The stretching vibration of N-H bonds was observed at around 3300 cm^{-1} . Finally, the peaks in between 3000 and 2800 cm^{-1} are attributed to the C-H bonds of the alkyl segments.

Thermal characterization

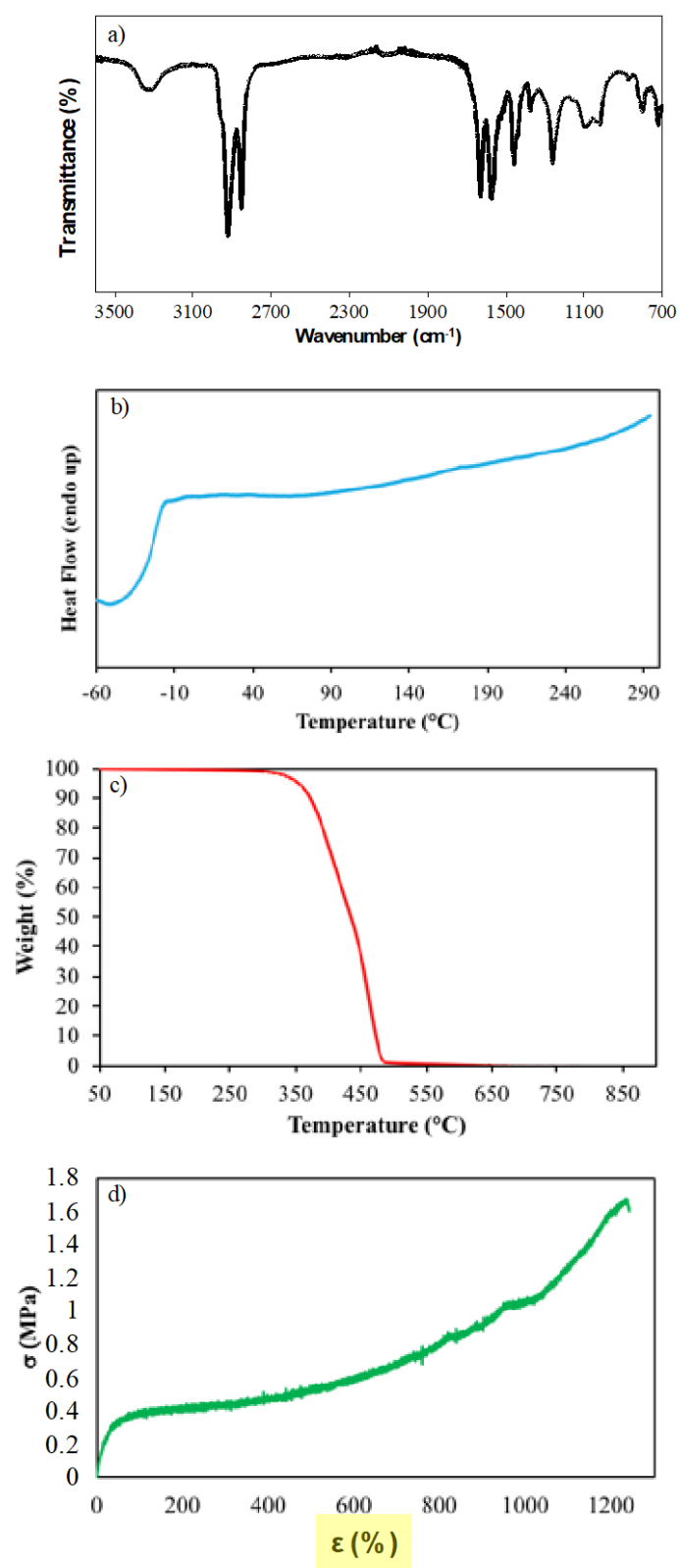


Figure 2. FTIR spectrum (a), DSC trace (b), TGA thermogram (c) and stress-strain curve (d) of polyurea-P film.

In Figure 2 and Table 2, respectively, are reported the DSC trace and the corresponding data of polyurea-P. As one can see, the calorimetric curve is characterized just by the endothermic baseline deviation of the glass to rubber transition (T_g), located at -25 °C, indicating the completely amorphous rubbery nature of the synthesized polyurea-P. This result is quite surprising for an ureic bond-containing material. Polyureas, in fact, are typically glassy and highly crystalline polymers characterized by very high melting temperatures[19,35]. In this case, it could be hypothesized the long PE-like segments of Priamine moiety confers high mobility to the macromolecular chain and, at the same time, the long side branches hinder the crystallization capability. It is also worth noting that in polyurea-P the ureic bond density, normally favoring crystals development, is much lower than in other more known poluyeras[19,35].

As corroborated by TGA analysis results (Figure 2c and Table 2), polyurea-P shows outstanding thermal stability, higher than other aromatic and aliphatic polyureic systems[12,14,19,26], in line with the Priamine 1075 chemical structure mainly composed of single C-C bonds, making polyurea-P suitable for high temperature applications. No weight loss was detected up to 300 °C, being T_{onset} located at 363 °C. Moreover, polyurea-P presents a two-step weight loss curve with maximum degradation rates at 405 and 465 °C. A multimodal weight loss could suggest different degradation mechanisms take place as temperature rises, the first one related to the main degradation process involving isocyanate group formation[48–50], the second one at higher temperature due to the cleavage of the more stable PE-like segments.

It is worth highlighting polyurea-P is thermally stable at temperature much higher than the temperature range of use of commercial polyureas (typically -50/150 °C)[51].

| DSC | | TGA | | Tensile | | | Gas barrier | |
|-------------|------------------------|-------------------|-----------------|----------|-----------------|-----------------|---|--|
| T_g °C | ΔC_p J/g °C | T_{onset} °C | T_{max} °C | E MPa | σ MPa | ϵ % | O ₂ -TR cm ³ cm/m ² d atm | CO ₂ -TR cm ³ cm/m ² d atm |
| -25 | 0.450 | 363 | 405 465 | 1.5±0.2 | 1.6±0.2 | 1000±100 | 12±0.5 | 30±12 |

Table 2. Thermal, mechanical and gas barrier characterization data of polyurea-P film.

Mechanical and gas barrier characterization

Regardless its rubbery amorphous nature, it was possible to prepare compression molded films of polyurea-P. The obtained films, lightly colored and transparent (see Figure 3a), were afterwards subjected to mechanical and gas barrier characterization.

From the stress-strain curve and the mechanical data reported in Figure 2 and Table 2, respectively, one can appreciate the very high flexibility, i.e. low elastic modulus (E) (~ 2 MPa) and stress at break (σ), in line with the materials currently used as wrapping packaging, mainly polyethylene- and polyvinylchloride-based films, whose elastic modulus values start from a few megapascals [52], together with high toughness and elongation at break (ϵ) $> 1000\%$ of polyurea-P. The mechanical response evidenced is clearly due the high polymer chain mobility ($T_g = -25$ °C) as well as to the absence of crystalline phase. It is worth mentioning the lack of yielding for polyurea-P and, even more important, the fact that just after breaking the polyurea-P specimen immediately recovered its initial shape (Figure 3b), evidencing an elastomeric behavior. As well known, an elastomeric response comes from the simultaneous presence of flexible rubbery amorphous segments, responsible for elongation, and of chemical/physical crosslinks causing shape recovery. In the particular case of polyurea-P, the net-points could be the interchain hydrogen bonds ($-N-H\cdots O=C-$) established between the ureic bonds (Figure 3). In polyurea-P, the low ureic link density allows decreasing the material stiffness, since no crystals developed, and permits achieving flexible elastomeric films thanks to the presence of hydrogen bonds. A similar behavior has been recently detected by some of us for amorphous furan-containing polyesters, for which it has been proposed the shape recovery capability is related to interchain hydrogen bonds[53–56].

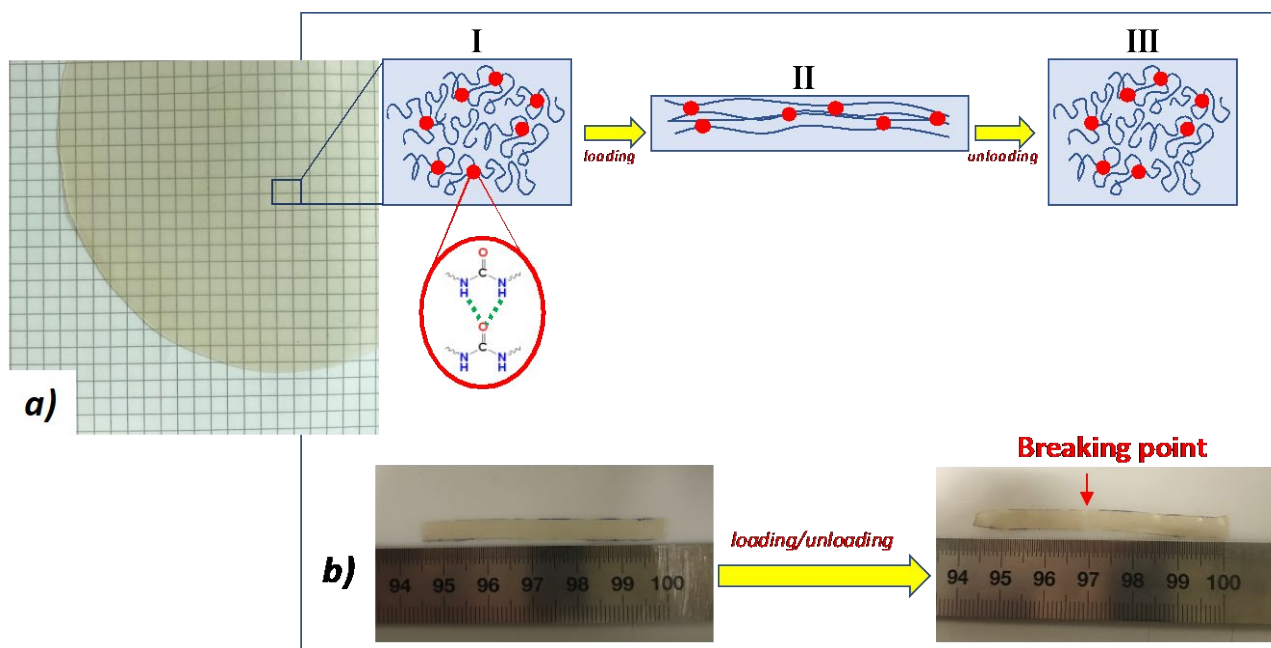


Figure 3. a) Polyurea-P compression molded film; b, top) schematic representation of intermolecular H-bonds in the neat (I), stretched (II) and released (III) polyurea-P film; b, bottom) polyurea-P strip before (left) and after (right) tensile test.

As concerns the gas barrier performance of polyurea-P, very interesting results have also been obtained. As well known, rubbery amorphous polymers are supposed to show very modest gas barrier capability since gas molecules move easier and faster through it with respect to glassy and/or semicrystalline materials[57]. Nevertheless, this is not the case of polyurea-P for which, analogously to the mechanical properties, the barrier performance is surely influenced by the $-N-H\cdots O=C-$ interchain interactions present in the polymer matrix. Gas transmission rate (GTR) values to dry oxygen and carbon dioxide, normalized by the film thickness, are reported in Table 2. From these data, it is evident the higher capability of polyurea-P film to block the O_2 molecule passage with respect to CO_2 ones ($O_2\text{-TR} < CO_2\text{-TR}$). This behavior has been evidenced for other polymeric materials[57,58] and it is mainly due to the larger CO_2 molecule size which allows a less tortuous passage through the polymer film, i.e. higher diffusion rate. The results obtained for polyurea-P have been also compared with polyolefins[59] (Figure 4), the most widely used polymers in the food packaging market. As it is evident, polyurea-P response to O_2 gas is comparable to the one of polypropylene (PP), high density polyethylene (HDPE) and low density polyethylene (LDPE). It is

worth noting the reduced CO₂-TR/O₂-TR ratio, i.e. the improved CO₂ barrier capability of polyurea-P, with respect to polyolefins (Figure 4). As well established, the diffusion path depends on the gas molecule size as well as on the affinity between permeating species and the permeable matrix. In the case of polyurea-P, the bond polarity of ureic groups could enhance the affinity between polymer matrix and carbon dioxide, thus determining lower CO₂-TR values. In this view, the polymer under study can be envisioned for applications in the flexible food packaging, with the advantage, compared to the polyolefins currently used, of being fully bio-based.

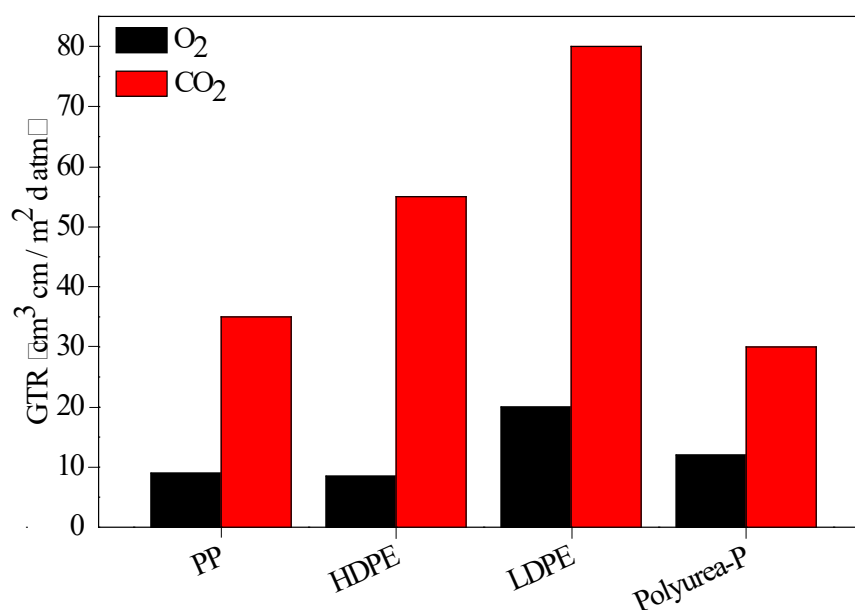


Figure 4. GTR-O₂ and GTR-CO₂ for the polymer under investigation and polyolefins[59].

The high flexibility and elastic properties make polyurea-P an interesting candidate in soft tissue engineering, in particular of cardiac tissue[60,61]. Further studies have to be conducted to test its suitability in this field.

Conclusions

In this work, the use of bio-based Priamine 1075, the purest diamine purchased by Croda, has been combined with catechol carbonate as carbonylating agent to realize a new homopolyurea with enhanced functional properties. An ecofriendly synthetic strategy has been employed. Besides molecular characterization, thermal, mechanical and gas-barrier properties have been analyzed and correlated to polymer chemical structure.

In particular, we have chosen an apolar and hydrophobic cycloaliphatic diamine containing long linear aliphatic segments with PE-like side chains to: *i)* reduce the average amount of ureic functional groups and, in turn, the density of intermolecular hydrogen bonds established between urea linkages; *ii)* provide mobile and flexible segments to the macromolecular chain; *iii)* decrease polymer crystallization capability.

The proper reduction of ureic functional groups reveals to be an efficient tool to improve thermal stability and enhance polymer solubility in organic solvents, thus widening the processability temperature window and conditions.

At the same time, the presence of a certain degree of -N-H---O=C- bonds acting as net-points, together with highly mobile long aliphatic moieties, provide flexibility, toughness and elastic behavior to polyurea-P.

The hydrogen bonding establishment is also the basis of the good oxygen and carbon dioxide barrier properties.

The solid-state properties revealed by polyurea-P make it suitable for applications in sustainable flexible food packaging as well as in soft tissue engineering.

The results obtained confirm material design as the key parameter to tune the final properties in view of the envisioned final application.

Acknowledgments

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