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Fully biobased poly(propylene 2,5-furan dicarboxylate) for packaging applications: excellent barrier properties as a function of crystallinity

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High molecular weight, amorphous poly(propylene 2,5-furan dicarboxylate) has been aged at 135°C for different times. The crystal phase contributes to achieve exceptionally low oxygen transmission rate and also good impermeability to water vapors, making PPF one the most interesting fully biobased polyesters for packaging applications.

Today, academic and industrial research in the field of polymers is strongly oriented towards bio-based alternatives to petroleum-derived plastics with enhanced properties for advanced applications. In this context, 2,5-furan dicarboxylic acid (FDCA), a monomer readily accessible from sugars, is one the most high-potential bio-based building blocks for polymers[1] and the first candidate to replace the petro-derived terephthalic acid. The polyesters, obtained by combining FDCA (or the corresponding derivatives) with diols at different -CH_2- length,[2] have already shown interesting properties, mainly in the field of high barrier performances. In this context, some preliminary studies focused on poly(ethylene furandicarboxylate) (PEF) [3-5] as an interesting, viable bio-sourced alternative to poly(ethylene terephthalate) (PET), which is now dominating in the packaging market, mainly in the soft drink bottle area. Oxygen permeability in PEF is reduced by a factor of about 10 with respect to PET. The reasons of the impressive performance of PEF as compared to PET can be ascribed mainly to the reduction of chain flexibility in the presence of furan rings. Therefore, furan-based polyesters seem to be good candidates for new excellent barrier materials.

Moreover, some examples of the dependence of permeation on the number of methylene groups are reported in literature:[6,7] although the even/odd effect is not completely clear, sequences of three –CH_2–in the aliphatic chains generally achieve good barrier performances, such as in poly(propylene terephthalate) (PPT), featuring an oxygen barrier which is 35% higher than PET.[8] Therefore, all things considered, poly(propylene 2,5-furan dicarboxylate) (PPF), which is a fully biobased material, has good chances to combine sustainable features with good barrier properties. Moreover, taking into account that crystallinity further enhances the polymer barrier properties, some thermal ageing experiments can induce a certain crystal degree and further promote the barrier performance of PPF. The present paper aims at describing early experiments that were carried out to investigate barrier properties in virgin and aged PPF samples.

Synthesis, structure and barrier properties of PPF

The first syntheses of FDCA-based polyesters were described in a US patent[9] in the 1950s and then further explored by Moore and Kelly in the 1980s.[10] Afterwards, Gandini prepared several poly(2,5-furan dicarboxylate)s, mainly by solution or interfacial polycondensation.[2] However, from an industrial point of view, bulk polymerization is more suitable. To this purpose, some papers report the preparation of such polyesters by melt polycondensation starting from the FDCA-dimethyl ester [5,11-12] and, recently, from FDCA, thus avoiding the methyl-esterification step and the production of methanol.[13-15] Sometimes the polymerization protocol requires a very long reaction time (over 15 hours), but the choice of favorable molar ratios for the reagents and suitable catalysts, reaction times and temperatures produce furan-aromatic polyesters characterized by high average molar mass.[15]

The present work shows how, starting from the synthetic procedure described in ref. 15 and fairly changing such protocol, a PPF polymer was prepared in about 6.5 hours (procedure in the Supporting Information). Molecular weight is remarkably high (Mn=18200, Mw= 54600, D=3.0), as obtained by GPC analysis.

The ^1H NMR spectrum confirms the PPF molecular structure, highlighting the presence of a moderate amount of ether bridges (2.91 mol%), not previously reported for PPF by other authors, but already described for PEF.[14]

DSC scans show that PPF is a tendentially amorphous sample, with a T_g at 54°C (See Table 1 in Supporting Information), in agreement with the values reported in literature.[16] During the cooling scan

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† Electronic supplementary information (ESI) available: details on synthesis of PPF, films preparation and ageing experiments are provided. ^1H NMR, DSC, WAXD and DMTA characterizations, density and permeability measurements are described. See DOI: 10.1039/x0xx00000x

from the melt at 10°C·min^{-1} PPF is unable to crystallize; it only presents, during the second heating scan, a cold crystallization process, with very low intensity (1 J·g^{-1}), at 138°C. The melting process is positioned at 170°C.

The comprehension of the thermal behaviour and tendency to crystallize of furandicarboxylic polyesters is really important as it influences barrier properties.[17-19] Comparing thermal data of PPF with those of the analogous poly(propylene terephthalate) (PPT), determined in the same conditions, it results that PPT is a semicrystalline material, with a relatively high crystallinity degree (T_m = 230°C with ΔH_m = 54 J·g^{-1}, measured at 10°C·min^{-1} after a cooling from the melt at 10°C·min^{-1}).

Papageorgiou *et al.*[12] compared the thermal behaviour of PPF and PPT and found that PPF is characterized by a slower crystallization rate than PPT, due to a lower flexibility and symmetry of the furandicarboxylate ring with respect to the terephthalate unit. Similarly, PEF and PET, [20] which are both semicrystalline with T_m = 214 and 245°C (measured at 20°C·min^{-1} after quenching), respectively, have a similar behaviour: PEF crystallization rate was found to be remarkably slower than that of PET. Accordingly, PBF (T_m= 172°C, ΔH_m=34 J·g^{-1}, measured at 10°C·min^{-1} after cooling from the melt at 10°C·min^{-1})[13] is characterized by a lower T_m and crystallinity degree than PBT (T_m=220°C, ΔH_m=55 J·g^{-1}, same experimental conditions than PBF). Therefore, it is possible to assume that the crystallizing ability of furandicarboxylate polyesters is lower than that of the corresponding terephthalates. In this sense the furandicarboxylate unit seems more similar to the isophthalate one, as discussed in ref. 14. For example, PEI and PPI, like PPF, are amorphous or polymers with low crystallinity.

With the aim to test the barrier performances of PPF, thin films were prepared by compression moulding. The virgin sample, corresponding to the film with ageing time t_a=0 min in Table 1, is characterized by a very low level of crystallinity (ΔH_m= 0.4 J·g^{-1}, see also Figure 1). The WAXD spectrum, shown in Figure 2, only highlights the halo of the amorphous phase. Indeed, a series of reflections, including the most intense at 27.85 °2θ is due to the crystals of Sb_2O_3, used as catalyst.

The amorphous PPF features a high density (Table 1), despite the presence of ether bridges (2.91 mol%) that can reduce the density value itself.[21] It is notable that terephthalate polyesters (PET and PPT, Table 1) show lower density values with respect to PPF. Amorphous PEI, instead, and semicrystalline PEF have similar and higher density values, respectively. As density, for many polymers, is directly proportional to gas barrier properties,[17] the high value found for PPF suggests good performances in terms of impermeability.

Finally, Table 1 reports the oxygen transmission rate (OTR) data at two different values of relative humidity (RH= 50 and 90%) and the water vapour transmission rate (WTR). Table 1 also gathers some data, measured in the similar conditions, for significant polyesters.[3,15,19,22-26] It is worth noting that PPF is characterized by a very low OTR and WTR value as compared to all these polymers, which are known for their good performances in packaging applications.

Such a behaviour is unusual: polymers with high gas-barrier levels often have very low barrier performances towards polar solvents such as water. It is so for EVOH, PVOH, PA, due to the moisture-induced disruption of intermolecular self-associations favoured by hydrogen bonds. On the other hand, polyolefins, such as PE and PP, show low gas barrier properties (OTR =6.85 (RH85, 20°C) and 7.87 (RH75, 23°C) cm^3·cm·m^{-2}·day^{-1}·atm^{-1}, respectively), but high water barrier (WTR =0.39 (RH90, 40°C) and 0.59 (RH90, 38°C) g·mm·m^{-2}·day^{-1}·atm^{-1}, respectively)[23] due to their hydrophobic character.[17] PPF is found to feature both characteristics.

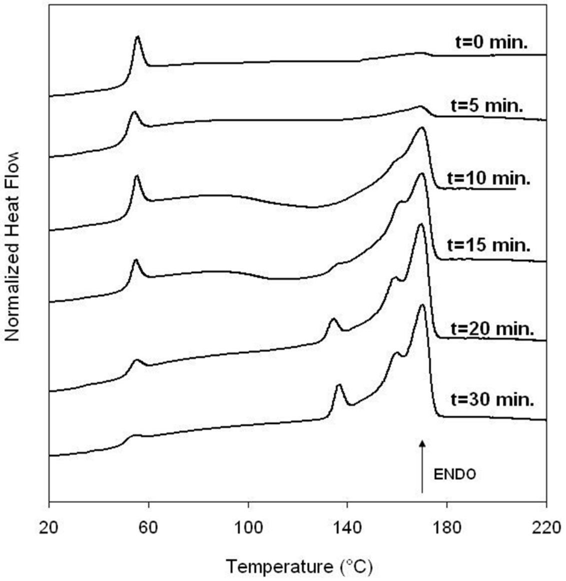

Fig. 1 DSC thermograms (1st scan) carried out on PPF films aged at 135°C for different times

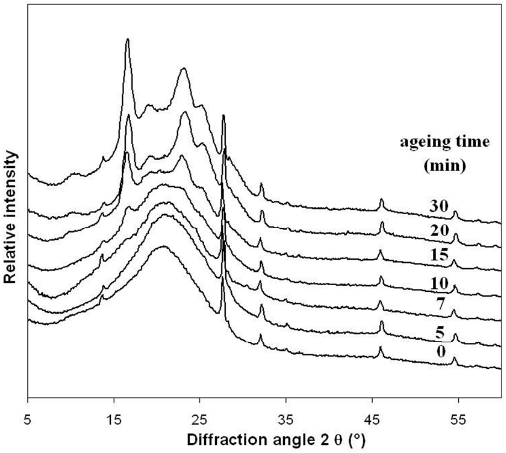

Fig. 2 WAXD spectra of PPF films aged at 135°C for different times

The improved barrier of furandicarboxylate (PEF) with respect to terephthalate polyester (PET) is attributed to the higher rigidity of the furan rings.[3] Indeed, the phenyl ring-flipping mechanism present in PET is suppressed in the presence of the furan ring. This causes a reduction of the segmental motions in PEF, also detectable in a decrement of the intensity of the β-relaxation in DMTA spectra.[3] These characteristics are strictly connected to a reduced diffusion inside the material, in the amorphous phase as well.[25]

Table 1 Characterization data of aged PPF films and comparison with other polyesters

Sample	Ageing times [min]	ΔH$_m$$^{a)}$ [J·g^{-1}]	X$_c$$^{b)}$ [%]	ρ$^{c)}$ [g·cm^{-3}]	OTR 50 RH $^{d)}$ [cm^3·cm·m^{-2}·day^{-1}·atm^{-1}]	OTR 90 RH $^{d)}$ [cm^3·cm·m^{-2}·day^{-1}·atm^{-1}]	WTR 100 RH $^{e)}$ [g·mm·m^{-2}·day^{-1}·atm^{-1}]
PPF	0	0.4	0	1.355	0.0472	0.0458	0.762
	5	1	9.5		0.0398	0.0484	-
	7	1	10.1		0.0315	0.0413	-
	10	6	12.7		0.0273	0.0368	-
	15	18	18.8		0.0254	0.0329	0.757
	20	33	27.3		0.0079	0.0171	0.303
	30	33	31.0	1.377	<0.005	<0.005	0.243
PET				1.338^{f}	0.363$^{f)}$ 0.748$^{i)}$ 0.354$^{m)}$	0.390 $^{g)}$	1.6$^{h)}$ 1.2$^{l)}$
BOPET$^{n)}$					0.129$^{n)}$		0.48$^{n)}$
PEI				1.346 $^{m)}$	0.090$^{m)}$ 0.098$^{o)}$		
PEF				1.4299 $^{i)}$ 1.36$^{p)}$	0.0702$^{i)}$		
PLA					1.58-1.74$^{q)}$		1.46-1.60 $^{q)}$

$^{a)}$Calculated by subtracting cold crystallization enthalpy from melting enthalpy, measured in DSC, 1st heating scan, 10°C min^{-1}; $^{b)}$crystallinity degree, measured by WAXD; $^{c)}$density, measured by helium pycnometer; $^{d)}$Oxygenum Transmission Rate, at 23°C, 50 and 90 % Relative Humidity; $^{e)}$Water Vapor Transmission Rate, at 37.8°C; $^{f)}$ref.22, RH43, 23°C; $^{g)}$ref.22, RH85, 23°C; $^{h)}$ref.23; $^{i)}$ref.3, 35°C; $^{l)}$ref.24; $^{m)}$ ref.25, 30°C; $^{n)}$bi-oriented PET, Tetrapak internal data; $^{o)}$ref.19, RH0 23°C; $^{p)}$ ref.15 $^{q)}$ref.26, RH50 23°C.

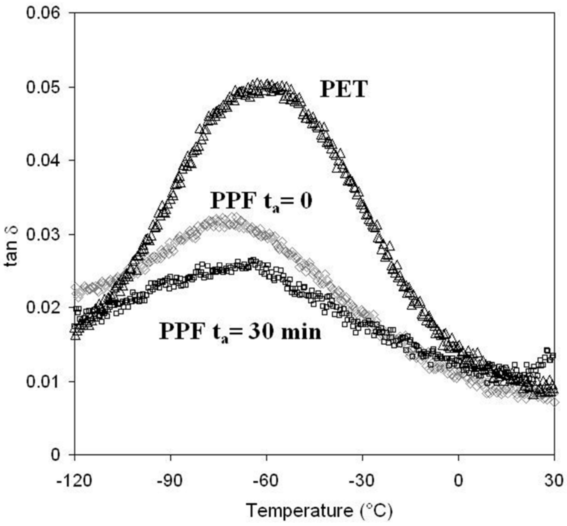

Fig. 3 β-relaxation in PET and PPF DMTA spectra.

The same observations can be applied to PPF polymers. Figure 3 reports the DMTA spectra for PPF and a commercial PET sample.

It is worth noting that the β-relaxation, centred at about -70°C, for the original PPF (t_a=0) is characterized by a remarkably lower intensity with respect to the analogous process in PET. Additionally, concerning the WTR data, the polarity of the furan ring imparts an increased water solubility and a decreased water diffusivity, resulting in an average permeability reduction with respect to the analogous terephthalic polymers.[27]

Finally, considering the effect of the length of the aliphatic chain in the diol, it is known that oxygen permeability increases with the increase of the number of methylene units and proves higher for odd methylene numbers, due to a lower crystallinity of the materials.[6] At low -CH$_2$- number, the odd/even effect seems less significant and the permeability data are low and similar. Therefore, the good performances of both PPF and PEF are expected, even if PPF is an amorphous sample and does not benefit of the favourable effect of the crystallinity.

Therefore, thanks to such observations, PPF seems a very good candidate as a material with enhanced properties for packaging applications.

Ageing experiments and barrier properties

PPF is able to crystallize in some specific conditions, for example during the DMTA scan at 3°C·min^{-1}, after the glass-rubber transition. It was observed that also a thermal treatment at 135°C induces the PPF crystallization. Therefore, some PPF films were oven-aged for periods varying from 5 to 30 min. They did not show degradation phenomena during ageing, as their molecular weight does not change. Moreover, their solubility is maintained, indicating that crosslinks do not occur. In Figure 1, it is worth noting that PPF slightly crystallizes at temperatures higher than T_g and then shows a complex melting process, whose intensity increases as a function of the ageing periods. Table 1 reports the effective film melting enthalpies, (ΔH_m-ΔH_{cc}). It must be noted that melting enthalpies vary from 0.4 (t_a=0) to 33 J·g^{-1} (t_a=30 min). Moreover, in the WAXD spectra (Figure 2) it is possible to identify the reflections due to the crystalline phase of PPF at 16.65, 19.05, 23.15, 25.25 degrees, according to literature.[15,16,28] The other reflections can be ascribed to the catalyst crystals. The degree of crystallinity, calculated by subtracting the amorphous halo, is reported in Table 1 and shows an increment from 0 to about 30%. Ageing treatments also induce an increment in density (Table 1), due to the highly packed chains.

Finally, Table 1 shows the permeability data of the annealed samples. It is notable that permeability with respect to oxygen gas and water vapor strongly decreases as the ageing period increases and, then, as crystallinity and density increase. It is surprising that the OTR value decreases until the detectable threshold of the instrument for the film annealed over 30 minutes. A significant decrement is also observed for WTR data.

The strong decrement of permeability in the annealed samples can be attributed to the presence of polymer crystals, that are highly packed and conformationally ordered, characterized by high density and low free volume. Due to this rigid architecture, the molecular diffusion is largely hindered. Accordingly, in Figure 3 the β-relaxation of the sample annealed for 30 minutes is characterized by a further low intensity, confirming a reduction of the segmental motions in the semicrystalline sample.

Conclusions

A high molecular weight PPF sample was synthesized starting from sustainable bio-based monomers. The material is amorphous and characterized by high density and excellent barrier properties to both oxygen and water vapor. Films were prepared by compression molding and treated in an oven at 135°C over different time-lengths in order to promote PPF crystallization. After 30 min of ageing, PPF presents 30% of crystallinity. The OTR and WTR measurements carried out on aged films show exceptional barrier performances. Impermeability to oxygen and water vapor was correlated to the chemical characteristics of PPF, which derives from the combination of two monomers characterized by high rigidity and low symmetry. Moreover, the crystal phase, highly packed and dense, improves the impermeability of the structure.

Despite relatively long crystallization times observed in our compression molded samples, we believe that industrial techniques for manufacturing mono- or bi-oriented films could induce much faster crystallization under appropriate conditions. If this will be confirmed, PPF could become an outstanding material for packaging applications such as shrinkable films, multilayer barrier containers, thermoformable blister packs.

Works are in progress to better understand the PPF phase behavior, tendency to crystallize and relationships between crystal phase and barrier effect.

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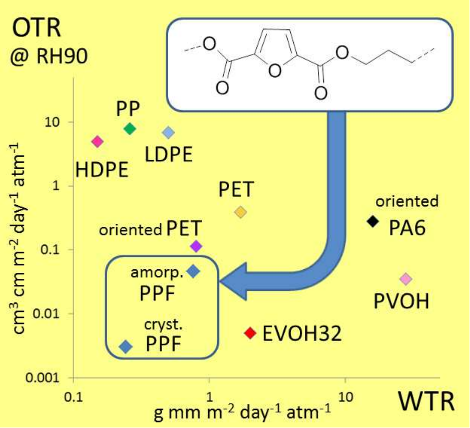
Graphical and Textual Abstract



Data from ref 27

Excellent performances in barrier properties against both oxygen and water vapor have been obtained in poly(propylene 2,5-furandicarboxylate) by forcing the crystallization in appropriate conditions.