

Material Properties of Poly(Propylene Carbonates)

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Abstract The material properties of poly(propylene carbonate) (PPC) are discussed with respect to thermal features, viscoelastic and mechanical properties, processability, characteristics in solution, biodegradability, and biocompatibility. Thermal decomposition proceeds in two steps: (1) backbiting at temperatures as low as 150°C in the presence of catalyst residues, giving cyclic propylene carbonate; and (2) chain scission at temperatures over 200°C with possible involvement of initial hydrolysis. PPC shows one thermal transition at a glass temperature of around 40°C. PPC is a pseudoplastic material, and a master curve constructed for frequency-dependent viscosity shows no real plateau for material of number-average molecular weight (M_n) < 50 kDa. At temperatures in the range of the glass transition, the apparent activation energy for flow changes rapidly from 500 kJ/mol to about 40 kJ/mol. The viscosity of PPC has an activation energy in the range of 5–25 kJ/mol (M_n < 50 kDa). The modulus of elasticity (around 800 MPa) and yield strength (10–20 MPa) are reminiscent of low-density polyethylene. PPC has a large elongation at break, and may be useful for the preparation of composites and blends. Biodegradation of PPC is dominated by hydrolysis, which can be accelerated by Lewis acid catalyst residues. Biocompatibility is excellent in the sense that it does not induce an inflammatory reaction in tissue.

Keywords Biodegradability · Blends and composites · Poly(propylene carbonate) · Thermal properties · Viscoelastic properties

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1 Introduction

Poly(propylene carbonate) (PPC) as the product of the “alternating” copolymerization of carbon dioxide and propylene oxide (PO) was first synthesized at the end of the 1960s with a rudimentary catalyst based on water and diethyl zinc [1]. The alternation of a carbon dioxide and PO moiety in the backbone was and is not always perfect: consecutive PO units led to ether linkages in the polycarbonate. In the course of time, better catalysts were found and known catalysts were optimized. Only very recently with the application of homogeneous catalysts, has the perfect alternating polymer routinely become accessible [2–5]. The label “PPC” is used for many types of products that result from the copolymerization of PO and carbon dioxide. The composition, regio- and stereochemistry of the products, however, may vary in a certain range, and so may the resulting material properties. In many publications dealing with the material PPC, detailed information on the microstructure is lacking, making it generally difficult to compare individual studies and to arrive at “PPC properties.” In this review, we will consider only PPC with less than 10% ether linkages in the backbone, and we will only differentiate between PPC and *alt*-PPC, the latter referring to the perfectly alternating polymer (Fig. 1).

The commercialization of the product has recently reached volumes of over 1,000 t/year [6]. For example, a PPC line of 10,000 t/year was commissioned by the China Bluechemical Ltd [7].¹ In the past, PPC was mainly used in binder applications at a volume smaller than 100 t/year [8]. The main reason for the current increase in production and capacities is the relatively smooth biological degradation, which has become of importance lately with respect to a general recognition of the need to prevent persistent pollution by plastic materials. An earlier commercialization was probably impeded greatly by the “challenging” material properties, i.e., PPC did not fit into any large existing market. Other economic constraints were tentatively

¹Other producers are the Inner Mongolia Meng Xi High-Tech Group, whose production of PPC in China apparently has a capacity of up to 9 kt [www.degradable.org.cn] and the Tianguan Enterprise Group (Henan, PRC).

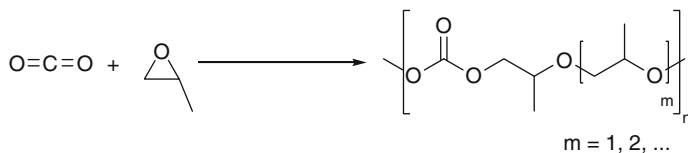


Fig. 1 PPC as the result of the alternating copolymerization of PO and CO₂

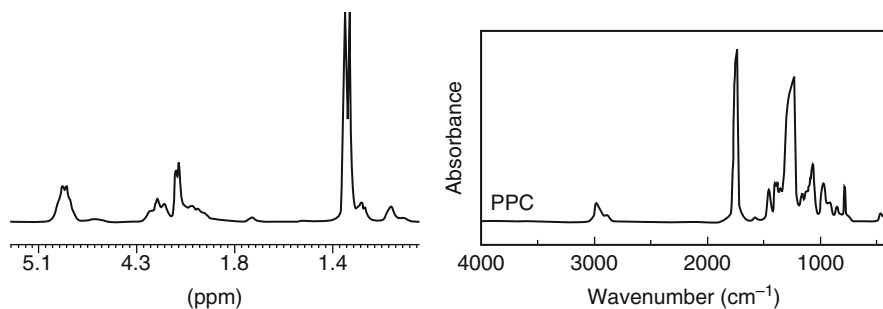


Fig. 2 NMR (*left*) and IR (*right*) [13] spectra of PPC

less decisive: raw materials are readily accessible and abundant, technology could have been developed or adapted, and an acceptable catalyst was already available in the 1980s [9]. At the appropriate volume and technology, the costs of production could thus have been in the range of poly(propylene oxide) production.

The challenges involved in the material properties of PPC relate to its thermal features, i.e., its thermal decomposition, and the glass transition temperature (T_g) of about body temperature of the otherwise amorphous polymer. These have implications for processing and application of the material. This review will discuss consecutively the thermal, viscoelastic, and mechanical properties of PPC and the experiences in processing PPC and its composites. The properties of solutions of PPC will also be presented, and the biodegradability and biocompatibility discussed. Spectroscopic properties will not be discussed. Further information on NMR data can be found in the following references [2, 10–12]. A typical spectrum is shown in Fig. 2 [13].

2 Thermal Properties

2.1 Thermal Decomposition and Stabilization of PPC

The thermal decomposition of PPC has been studied in the past using several methods, including the time-dependent viscosity of hot PPC, thermogravimetric analysis (TGA), and pyrolysis gas chromatography/mass spectrometry

(GC/MS) [10]. The conclusion of all these older and some new studies is that the main low energy thermal decomposition pathway of PPC prepared from heterogeneous zinc catalysts commencing at temperatures of about 150–180°C is backbiting or unzipping [14, 15]. The main product is cyclic propylene carbonate (cPC), which has an atmospheric boiling point of 240°C [16].² The formation of cyclic carbonate could unequivocally be secured [15]. Propylene carbonate is very compatible with PPC, and is only slowly released from it (*vide infra*). It should be noted therefore that TGA assessments of decomposition temperatures are not very sensitive below 200°C for indicating decomposition or molecular weight breakdown. In fact, loss of mass at temperatures around 240°C and higher may represent the physical desorption of cPC from the already decomposed sample. Thus, the literature data on thermal decomposition of PPCs may appear confusing, e.g., one of the highest decomposition temperatures for a PPC reported is 278°C, measured for a sample with a number-average molecular weight (*M_n*) of 50 kDa and about 92% of carbonate linkages. The decomposition point was taken as the onset of thermal decomposition, with 5% loss of mass [17]).

The thermal decomposition behavior has been newly addressed in the last 5 years. The understanding has been deepened with the objective to thermally stabilize PPC. The onset of decomposition in the range of 150–180°C is unfavorable for processing because ultrahigh molecular weight PPC is still quite viscous at that temperature and there could be substantial stress in the sample after injection molding at low processing temperature. This stress will relax at room temperature and deform the sample. A thermally more resilient PPC is thus highly desirable.

The mechanism of thermal decomposition at temperatures up to about 180°C is unzipping for a normally pure sample of PPC. Chain ends play a role in the decomposition process, as deduced from the stabilizing effect achieved by end-capping [10, 18]. It was thus established that the decomposition temperature of capped PPC is independent of the molecular weight, whereas the opposite is true for uncapped PPC [19, 20]. Lower molecular weight PPC loses mass faster because of the higher concentration of end groups [21]. In contrast to the generally observed backbiting reactions below 200°C, much more robust PPCs are occasionally reported. In an older publication on a PPC that was prepared from zinc glutarate containing a perfluorinated diacid, the onset of thermal decomposition was also found to be dependent on the molecular weight and ranged from 233 to 255°C for samples having a *M_n* of 59 and 144 kDa, respectively [22]. The NMR spectra showed broad lines prohibiting an accurate assessment of the percentage of carbonate linkages.

More insights are given in a publication by Varghese et al. in 2010 [23]. An *alt*-PPC sample prepared with a homogeneous cobalt catalyst shows that Lewis acids and water may generate hydroxide or carbonate chain ends with subsequent fast unzipping at temperatures as low as 150°C [23]. This behavior was observed for a product with catalyst residues and with thermally unstable linkages in the main

²See http://www.en.wikipedia.org/wiki/propylene_carbonate. Accessed 01 April 2011.

chain (peroxide). Hydrolysis and subsequent backbiting led to cPC. Lewis acids and water may generate hydroxide or carbonate chain ends with subsequent fast unzipping at temperatures as low as 150°C. However, a pure sample of *alt*-PPC with a molecular weight (Mw) of 330 kDa prepared from a peroxide-free catalyst was found to decompose only slowly, even at 200°C, with no formation of cPC. This is both remarkable and highly desirable. These observations should be verified with samples of PPC from other sources and with other molecular weights. Consistent with these results is a report on the stability of a commercial product from the Tianguan Enterprise Group, which was reported in 2010 [24]. Here, an onset of thermal decomposition was found at 260°C.

At temperatures higher than 200°C, chain scission sets in [16, 19, 23]. An older study of PPC of various molecular weights used the more sophisticated approach of TGA coupled to IR spectroscopy, and pyrolysis GC/MS [14]. A peak rate of decomposition (dependent on the molecular weight) was found at about 230–250°C. At such temperatures, end-capped PPC also thermally decomposes [19]. It is suggested that, at this temperature, main chain scission is in full progress and results in fast and irreversible decomposition. From these studies, it is obvious that PPC is exceedingly unstable at temperatures over 240°C. The products of decomposition are not univocally established. Cyclic carbonate and propylene glycol might also be products [14, 23], but they were not found by Lee and coworkers [23]. Lewis acids impact the unzipping reaction to some extent [25]. The formation of propylene glycol could reflect the presence of hydrolysis in the high temperature decomposition pathway.

The kinetics of the decomposition of PPC has been estimated from several studies. An analysis from TGA shows that the activation energy for end-capped PPC at temperatures over approximately 250°C is in the range of 130 kJ/mol, a relatively low value (for a chain scission process) [19]. The same analysis for uncapped PPC is complicated by non-linear behavior. Results consistently indicate that, at lower temperatures, a different decomposition reaction takes place than at higher temperatures.

In Fig. 3, the thermal decomposition of PPC is depicted according to the current state of knowledge. At lower temperatures and with samples that have not been prepared and purified with the utmost care, unzipping readily proceeds, even at

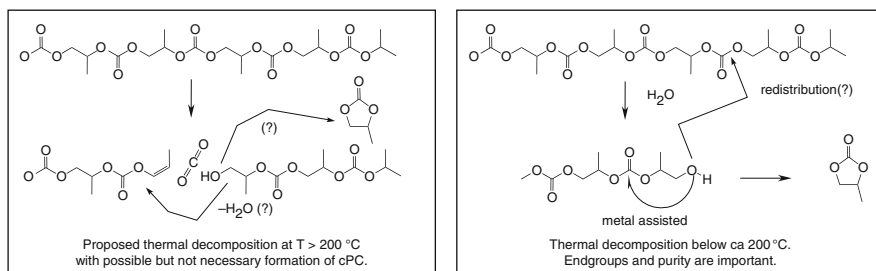


Fig. 3 Putative reactions leading to the (thermal) decomposition of PPC

150°C. At higher temperatures main-chain scission occurs, but the pathways still needs to be clarified. Cyclic carbonate may also be formed (e.g., after hydrolysis with residual water), but not necessarily. CO₂ and propylene glycol may result as products. Thermally more stable PPC may be processed at temperatures over 250°C as long as exposure time is short (minutes).

In order to thermally stabilize PPC, several approaches have been followed that are similar to the approaches used for generating a commercially useful polyacetal, which also readily decomposes by unzipping [26]. Two strategies are recognizable: effective end-capping to prevent unzipping (analogous to, e.g., Delrin production by Dupont) and incorporation of co-monomers (such as Ultraform BASF SE). The latter will also certainly affect other properties (T_g). End-capping in solution can be achieved with electrophilic reagents such as acetyl chloride, chlorophosphates, methane sulfonyl chloride [27], anhydrides [19] or chlorosilanes [28]. In addition, several reports document how the addition of anhydrides (maleic, succinic) can stabilize the high temperature melt of PPC [29, 30].

The thermal degradation of maleic anhydride end-capped PPC (MA_{end}-PPC) occurs at a temperature that is about 20 K higher than that of PPC degradation (from TGA for 5% loss of mass) [18]. In that study, viscosity change with time was also used to monitor the chain degradation [18]. The time dependence of the complex viscosity at 180°C shows how the decomposition rate of PPC and MA_{end}-PPC differ by a factor of 35. The rate of decomposition of PPC is found to accelerate with decomposition. This is attributed to an autocatalytic process involving the new species (presumably end groups or water formation, cf. Fig. 3). The decomposition rate of MA_{end}-PPC is linear with time in the smaller range of degradation studied. This does not imply that a nonlinear behavior will not also set in at a higher state of decomposition.

Thermal stabilization could also be attained by adding certain stabilizers to PPC, e.g., β -cyclodextrin. The principal effect could also be interpreted as the controlling of end-group reactivity. Due to the binding of the chain ends in the cavity, unzipping is thought to be retarded, with an apparent increase of about 30°C in thermostability [31]. A 10°C increase in thermal stability of PPC was found in a composite with MgAl layered double hydroxide [32]. An older study reports on a similar improvement of the thermal stability of PPC resulting from the use of a supported zinc glutarate catalyst on montmorillonite for PPC synthesis in neat PO. The polymer with a Mn of 20 kDa had a thermal decomposition onset of over 256°C. The origin was attributed to clay residues [33]. Surprisingly, cyclic amines additives can also be useful for thermally stabilizing PPC [34]. The origin of this effect has not yet been studied. In addition, calcium stearate, which was shown to complex to PPC, improves thermal stability at processing conditions [35]. It is corroborated that chain mobility is decreased by the metal salt.

The overall thermal stability of PPC can further be enhanced through modification of the main chain, i.e., by the incorporation of ether units, or through the terpolymerization with epoxides other than PO or ethylene oxide (EO), and with lactide, lactones and other heterocycles [36–39]. The higher the content of ether linkages in PPC, the higher the thermal stability is [40]. This seems to be a result of

several effects: the concentration of carbonate linkages decreases, backbiting with formation of cPC is interrupted, and the chain is tentatively less mobile. The latter point is implied from a study involving several aliphatic polycarbonates derived from linear monoalkyl epoxides. The study shows that the thermal instability of ethylene and propylene polycarbonate is poor in relation to other epoxide/CO₂ copolymers [41]. The terpolymerization of PO/CO₂ and cyclohexene oxide (CHO) with a salen cobalt (III) type of catalyst was reported to yield a statistical copolymer with C₃ and cyclic C₆ two-carbon building blocks between carbonate linkages. The thermal decomposition temperature (50 wt% of the sample) thus increased with the amount of CHO from 257°C for PPC to 295°C [42]. This is analogous to similar work with other catalysts to synthesize terpolycarbonates of PO and CHO or derivatives [41, 43–49]. A new report on the terpolymer of PPC with cyclohexene oxide show a higher decomposition temperature in TGA, with a 5% mass loss at 244°C with 6.7 mol% of CHO [50]. Ether linkages in the terpolymers were not specified.

A terpolymer of PPC with [(2-naphthyloxy)methyl]oxirane as further monomer could also be obtained [51]. Here, a systematic increase in the onset of decomposition temperature with termonomer incorporation was measured, despite the fact that the terpolymer had a smaller molar mass with increasing termonomer content (the higher ether content was not considered). The effect is attributed to a stiffer main chain that is less mobile and thus has higher energy vibrational modes. In a further study using this strategy, a terpolymer with *N*-(2,3-epoxylpropyl)carbazole shows an onset of decomposition at 265°C (by TGA) [52]. Yet another series of terpolycarbonates was prepared consisting of PO/CO₂ and a bifunctional glycidyl ether-type of monomer using a heterogeneous catalyst system based on diethyl zinc, glycerine, and yttrium carboxylate [53]. Several products were obtained with molecular weights ranging from 109 to 200 kDa. A 37°C increase in decomposition temperature onset (the lowest was about 190°C) was found between the two molecular weights. Here, a decrease in mobility through network formation is anticipated.

Terpolymers of maleic anhydride (MA) and PPC could be prepared using a double-metal cyanide (DMC)-type catalyst. The polymer was amorphous like most terpolymers of propylene carbonate [39]. For terpolymers with up to 50:50 (mol/mol) of PO/CO₂ and MA, it could be shown by TGA that the observed degradation temperature was again raised by about 20–30°C and that the maximum rate of decomposition even exceeded 300°C.

For recently prepared terpolymers of PO/CO₂ noticeable improvements in thermal stability were thus achieved. The rate of decomposition decreases with the termonomer content. Part of the effect obviously originates from the lower concentration of propylene carbonate entities and another part from the lower flexibility of the main chain. In addition, another explanation for the increase in thermal stability with termonomers (which is, however, not substantiated) could be found in the solubility of water in the product because every recent study indicates that hydrolysis is a major cause of the initiation of thermal decomposition [23]. Also, additives have been identified as slowing down thermal degradation.

2.2 Thermal Transitions

Several reports concern the thermal transitions of PPC. Glass temperatures for “PPC” have been determined that range from just above 25°C to about 45°C. The broad range indicates that the PPC products are only similar, not identical. The microstructure (regioregularity) is a factor. To illustrate this point, it is useful to look at PPC from a catalyst system based on diethyl zinc, glycerine, and yttrium carboxylate. It produces polycarbonate with various regioregularities as a function of the yttrium content. It is reported that the higher the concentration of head-to-tail linkages, the higher the T_g . A range was found of 37–42°C for polymers with 70–77% head-to-tail dyads, respectively [54]. An *alt*-PPC with more than 95% head-to-tail dyads and a Mn of 55 kDa had a T_g of 40°C [5, 10].

A further factor is the amount of ether linkages in the polycarbonate. For example, a polymer-supported DMC catalyst based on zinc and ferricyanates allowed the preparation of a polymer containing a substantial amount (40–60%) of ether linkages. This product had a T_g of 8°C [37]. This compares well with an ether carbonate polymer from a DMC catalyst mentioned in an older patent from the Dow chemical company with a 17% ether linkage of low molecular weight [55]. Assuming that the T_g of the polyether carbonate follows the Fox equation, i.e., $T_g = 1/(w_1/T_{g1} + w_2/T_{g2} + \dots)$ where w_i is the weight percentage of co-monomer i , and T_{gi} is the glass temperature in K of co-monomer i . Setting the glass temperature of the poly(propylene oxide) copolymer part to –65°C [56], a T_g of 38–42°C must be concluded for the polyether carbonate.

The molecular weight is obviously a determining factor [15, 17, 22]. The maximum of $\tan \delta$ in dynamic mechanical thermal analysis (DMTA) analyses as a measure for T_g was determined for PPC with various molecular weights to be 30–36°C for Mn of 29–141 kDa [21]. The corresponding data from modulated differential scanning calorimetry (MDSC) are reported as 24–37°C (the PPCs were prepared with zinc glutarate as catalyst, and should have about 5% of ether linkages). In contrast to this, a T_g of 28°C was found for a PPC prepared from zinc adipate [57, 58]. Analyzing these data according to the Flory-Fox equation, which relates the number-average molecular weight to the glass transition temperature, a T_g of 37°C results at infinite Mn. Note that these data are lower than those in a former report by the same group [15]. For the MA_{end}-PPC capped polymer, it is found that maxima in $\tan \delta$ lie at 42.0°C (5 Hz) and 40.3°C (2 Hz) for PPC [18]. The uncapped PPC has about 99% carbonate linkages in the backbone. A typical DMTA measurement of a purified PPC sample from zinc glutarate with Mn = 46 kDa is represented in Fig. 4 and shows a T_g of around 40°C.

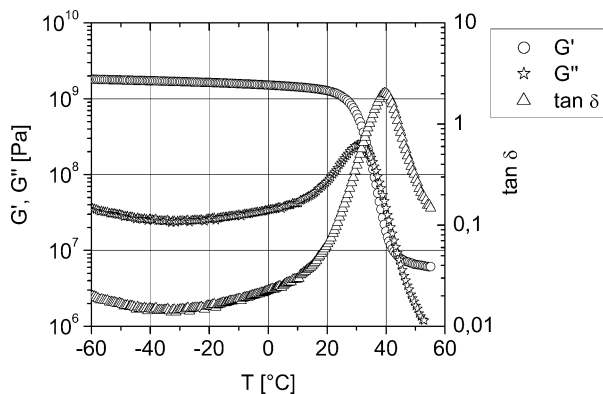
The glass temperature of PPC is readily lowered with the usual plasticizers, which tend to be compatible with the polymer (Table 1). It is easily appreciated that cPC thus lowers the T_g of PPC by about 2 K per weight percent. The glass temperatures of the terpolymers have also been recorded. In the PPC containing the (2-naphthylxy)methyl substituent, T_g increases with content according to the bulky substituent, although the poly(propylene glycol) linkages, which generally

Table 1 Plasticizing PPC with Mw of 250 kDa [8]

Plasticizer content (wt%)	Glass transition temperature ^a					
	Butyl benzyl phthalate	Dipropylene glycol dibenzoate	cPC	Acetyl triethyl citrate	Tributoxy ethyl phosphate	Dibutoxy ethyl adipate
5	38.3	32.4	25.9	21.0	27.0	30.1
15	17.6	22.7	7.5	13.5	9.5	6.9
25	6.3	10.8	-12.5	-2.7	4.7	1.7

^aMeasured by DSC following standard test method ASTM D3418-75

Fig. 4 DMTA analysis of a PPC with a Mn of 46 kDa, showing storage modulus G' , loss modulus G'' , and $\tan \delta$ as a function of temperature (Borchardt and Luinstra, unpublished data)



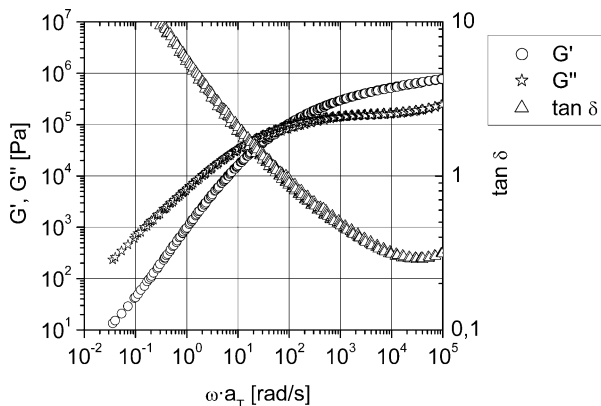
lower T_g , have a higher concentration [51]. The outcome of a similar study with a carbazole pending group gave very similar results [52]. The glass transition of the MA-PPC terpolymer was found at around 50°C [39]. There are thus several options for tailoring the intrinsic thermal properties of PPC (decomposition and glass temperature): in a limited interval via the molecular weight and regio/stereoregularity, via incorporation of more or less ether linkages, or via terpolymerization with various heterocyclic rings, such as phthalic anhydride [59], butyrolactone [37] (T_g only), or cyclohexene oxide [50].

3 Viscoelastic and Mechanical Properties and Processing of PPC

3.1 DMTA Analysis

Many fundamental material properties are accessible in rheological and mechanical testing experiments [60]. Rheological properties are not only very relevant for the processing of polymers, they are also the basis for understanding chain motion and relaxation processes in (linear) polymers. Relatively few rheological studies have been reported on PPC, often only in combination with the processing of PPC [15, 61].

Fig. 5 Master curve of storage modulus G' , loss modulus G'' , and $\tan \delta$ as a function of the reduced angular frequency ωa_T at the reference temperature of 150°C



PPC (at higher temperatures) behaves like a typical pseudoplastic non-Newtonian fluid. The activation energy of the viscosity in dependence of shear rate (284–2846 Hz) and M_n was detected using a capillary rheometer in the temperature range of 150–180°C at 3.0–5.5 kJ/mol (28,900 Da) and 12–13 kJ/mol (117,700 Da) [15]. The temperature-dependent viscosity for a PPC of 46 kDa between 70 and 170°C was also determined by DMA (torsion mode). A master curve was constructed using the time–temperature superposition principle [62] at a reference temperature of 150°C (Fig. 5) (Borchardt and Luinstra, unpublished data). A plateau for G' was not observed for this molecular weight. The temperature-dependent shift factors a_T were used to determine the Arrhenius activation energy of about 25 kJ/mol (Borchardt and Luinstra, unpublished data).

A DMA study close to the T_g of a PPC sample of about the same molecular weight ($M_w = 177$ kDa, polydispersity index, PDI = 3.71) and of MA_{end} -PPC in tensile mode gives also one symmetrical damping peak. A tensile modulus of over 10 MPa was found after passing through the T_g (ending at over 90°C). This was attributed to the high entanglement density. A master curve at a temperature of 40°C (Fig. 6) gives almost a plateau at 5 Hz for E' . An estimation of the entanglement molecular weight (M_e) from the frequency-dependent Young modulus was 17 kDa (Wang, Polymer Material Engineering Lab, Changchun Institute of Applied Chemistry, personal communication). An analysis using the Williams-Landel-Ferry (WLF) theory gave insight into the molecular motions and the activation energies involved with it. It was found that in the vicinity of T_g , PPC has a large activation energy of 500 kJ/mol, whereas MA_{end} -PPC has only half of the value. Also, the curves for PPC are much steeper with temperature than for MA -PPC. PPC is thus more sensitive to temperature changes than MA_{end} -PPC [18]. The fractional free volume near T_g was also calculated in the study. These were almost twice as high (0.045) as the universal (usual) fraction free volume of about 0.025 [63].

An essential work of fracture (EWF) analysis of PPC was performed using PPCs of various M_n [21]. It was found that, independent of the M_n , load versus displacement curves are similar and can thus be compared. A significant amount of plastic

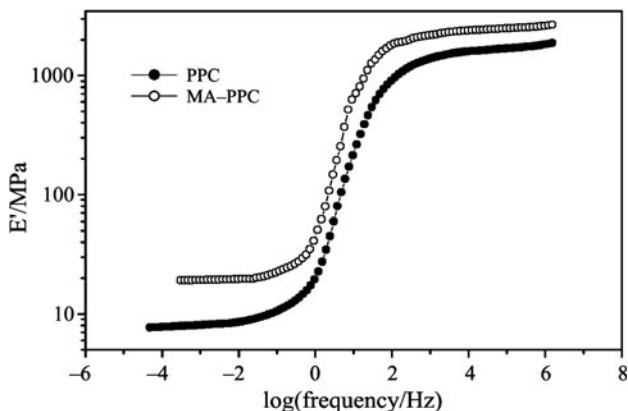


Fig. 6 Master curves of E' versus frequency of PPC and MA_{end}-PPC at a temperature of 40°C, obtained by superimposition of the data from dynamic tension experiments [18]

deformation in PPC takes place as samples are elongated and deformed, particularly in low molecular weight products. The fracture toughness of a 141 kDa PPC was determined to be 12.6 kJ/m², close to the value of PP and polyvinylchloride (PVC). The former number increases with molecular weight (9.1 kJ/m² at Mn = 29 kDa).

3.2 Mechanical Testing and Processing of Blends and Composites

Purified PPC (Mn = 50 kDa, PDI ≈ 1) was mechanically tested on dumb-bells. The T_g of the sample was not reported. The Young modulus was found to be 830 MPa, with elongation at break of 330% and a tensile strength of 21.5 MPa [32]. Incorporation of exfoliated layered double hydroxide (max. 5%) leads to a convincing increase in modulus, but a sharp decrease in elongation at break. For a commercial thermally stable PPC of Mn = 260 kDa (PDI ≈ 5), a tensile modulus of about 680 MPa (tensile strength of 17 MPa) was reported [24]. The PPC, commercialized by China Bluechemical, was reported to have a tensile strength of only 4.7 MPa (with a T_g of 20°C) [7]. This material is of lower molecular weight (Mn = 70 kDa by gel permeation chromatography; polydispersity index = 3.2).

As mentioned above, the material property profile of PPC is unlike that of any of the large-scale applied engineering thermoplastic polymers, nor does it resemble that of rubbers, i.e., with the exception perhaps of some types of PVC [64]. One favorable property of PPC of sufficient molecular weight (>4 M_c) is the large elongation at break. This makes it possible to use (inorganic) fillers to increase the elastic modulus in a range useful for the preparation of containers, and still retain an acceptable toughness. For examples, see the following references [65–72]. PPC tends to be compatible with fillers or other polymers, or can be made compatible with them using additives. A few recent examples are incorporated here. It was

found that glass fibers are well dispersed in PPC matrix [24]. The mechanical and thermal properties of PPC are improved to such an extent that they reach a Vicat softening temperature of 50°C. The elongation at break is reduced to 8% with 10% glass fibers and to 0.5% with 40%. This is typically observed for the elongation of composites with PPC. The same effect was found in a more sophisticated composite of PPC with starch, calcium carbonate, and poly(ethylene-*co*-vinyl alcohol) [73]. An older study on a composite of PPC with untreated calcium carbonate is thus improved [74, 75]. It was observed that the micrometer-sized filler disperses well into the PPC matrix, although the smaller nanoparticles showed a tendency to agglomerate. The Young modulus and the yield strength for the former increased with 10 wt% filler to 1,700 MPa and 32 MPa, respectively. The tensile strength also increased with calcium carbonate content, which is attributed to a good binding between the particles and the matrix. The elongation at break decreases linearly with the filler content to an excellent level of 300% at 30 wt% calcium carbonate of 38 μm particle size. PPC is also compatible with polybenzamide [76]. This blend shows improved thermal and mechanical properties. A further example of such a blend is that of PPC with poly (methyl methacrylate) (PMMA) and a small amount of poly vinyl acetate (PVA) for compatibilization and leads again to the same conclusions, with PVA playing an important role [77].

4 Solubility and Chain Extension

Little is known about the chain dimensions of PPC in solution. Recently, a comparison of the hydrodynamic volume of polystyrene (PS) and PPC has been reported for tetrahydrofuran (THF) as solvent in connection with a size exclusion chromatography (SEC) analysis [78, 79]. The basis for the calculation was the assumption of an immortal PO/CO₂ alternating copolymerization, and thus that absolute values of Mn relate to starter and PO/CO₂ ratios. Narrow molecular weight distributed PPCs with various molecular weights were prepared from adipic acid as starter. The absolute molecular weight has a relationship of $K M^{(\alpha+1)} = K_{(\text{PS})} M_{(\text{PS})}^{(\alpha+1)}$, where α and K are the Mark–Houwink parameters of *alt*-PPC and PS, respectively [80]. Using the calculated absolute Mn (Mn_{abs}) values, and the observation that $\log(\text{Mn}_{\text{abs}}) = \log(0.255) + 1.09 \log(\text{Mn}_{\text{rel}})$ where Mn_{rel} is the Mn value relative to that of PS. $K_{(\text{PPC})}$ was calculated to be 0.063 mL/g and $\alpha_{(\text{PPC})}$ to be 0.61 in THF. A further relationship was established for PPC in benzene: values for $K_{(\text{PPC})}$ of 0.0011 mL/g and $\alpha_{(\text{PPC})}$ of 0.8 [29, 54]. This shows that THF is a good solvent for PPC, and that benzene is an even better one as chain coils are more extended. In fact, PPC may readily be dissolved in many solvents, except chemicals such as longer chain alkanes and alkanols, water, and ethylene glycol. Substituted aromatic compounds and ester with, for example, butyl groups are poor solvents, just like methanol [8].

5 Biodegradation, Biocompatibility and Hydrolysis of PPC

5.1 Environmental Stability

The biodegradation of PPC in air, in water and in soil has been the subject of several studies. The observations and experiences are multiple, indicating that decomposition may generally be reached, but is very dependent on the conditions. Water plays a major role in all these processes. The surface and bulk interactions of PPC with water are known. PPC is not very compatible with water, and thus decomposition starts from the surface by erosion. The surface of PPC films prepared by compression molding was examined by several techniques, among them atomic force measurements [74]. Very smooth surfaces were found, illustrating that PPC is viscoelastic at room temperature. Water adsorption was measured after immersion in water; after several (4) hours, 1.5 wt% water was present in the film. The contact angle of the immersed samples did not change, showing the final hydrophobic properties.

The enzymatic degradation of PPC was studied in the form of a cast film (10–20 μm) that was exposed to an aqueous solution containing lipases from *Rhizopus arrhizus* and *Rhizopus delamar*. PPC was found to be stable in a buffer of pH 5.6–7.2 at 37°C [81]. A more elaborate research project concerned samples of PPC immersed in buffered solutions of pH 6. A weight loss at a rate of 1 wt% per month could be detected. Cavities were observed after 2 months. With time, the samples absorbed more water, increasing from 3 wt% after 1 month to 10 wt% after 6 months, and the rate of decomposition increased with the water content. A definite biodegradability was claimed in water using several lipases and also using three different fungi [82]. A new study with carefully purified *alt*-PPC of high molecular weight came to the conclusion that the material does not change its molecular weight nor distribution after keeping it in water at ambient conditions [23].

The degradation in soil can be much faster, although several different experiences have been reported. An early decomposition study with soil burial showed that PPC films (cast from chloroform, 40–50 μm , Mn = 50 kDa) are only marginally attacked after 6 months [83]. In contrast, a beaker consisting of 140 μm of a starch derivative and 25 μm of PPC was found to degrade under unspecified composting conditions in a period longer than 14 months. This is consistent with an earlier report (in Chinese) that describes the biodegradation of PPC in compost, with cell uptake, as soon as the molecular weight dropped below 6 kDa [84]. The disintegration of PPC with Mn of about 50 kDa in the form of 200 μm compressed film at 60°C in standard compost was fast [10]. These results are depicted in Fig. 7 and show that the sample was fully disintegrated within 3 months.

The weathering of *alt*-PPC in a weathering chamber was the subject of a further decomposition study, and the results are very relevant for the use of PPC in outdoor applications [23]. A thin film of PPC on a glass substrate was used and subjected to a temperature of 63°C, humidity of 50%, and light of 250–800 nm with an energy of 550 W/m². It was found that the molecular weight decreased by chain scission

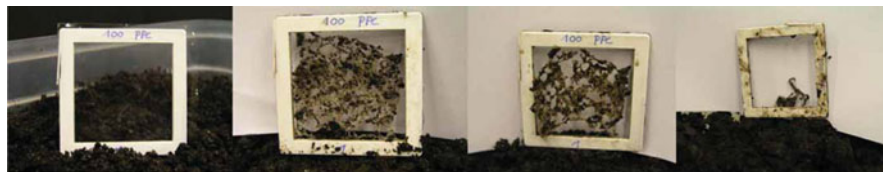


Fig. 7 Composting of PPC original and after 16, 30, and 69 days

processes involving hydrolysis of the carbonate entity by water to give carbon dioxide and two alcohol-terminated chains; cPC was not found. Also, the presence of unsaturated groups as the result of Norrish-type radical decomposition (light-induced), could not be confirmed. In another study, electron beam irradiation of PPC was found to result in a deterioration of molecular weight, concomitant with the dose [85]. When the irradiation is performed in the presence of multifunctional unsaturated isocyanurates, the formation of cPC could not be secured. The products of such experiments are indicative of radical abstraction and coupling reactions.

The hydrolysis of PPC in solution was studied as a function of the pH value [86]. The viscosity of the solution was taken to monitor the progress of hydrolysis. It was found that the hydrolysis is very dependent on the pH. At pH 5–9 little or no viscosity decrease occurs in a period of 20 days. At a pH lower than 3 or higher than 11, hydrolysis is substantial. Overall decomposition rate is faster in a basic solution (about 4,000 times faster at pH 13 than at pH 1). In this respect, PPC is more stable in acidic medium than polyester PCL or PLA. The PPC degradation experiments were not investigated with respect to the product spectrum.

Two factors seem important for a fast decomposition which is dominated by hydrolysis: a temperature above T_g , and a catalyst that catalyzes nucleophilic attack. The latter is substantiated from a study by Kuran, using Lewis acids in the form of diethyl zinc [87]. Degradation at low concentrations of diethyl zinc yields large amounts of cPC. At much higher concentrations of diethyl zinc, polymer degradation is even faster. The catalytic action of Lewis acids seems to result from activation of the carbonyl carbon. Complexation to the carbonyl oxygen atom was confirmed by IR spectroscopy. The formation of carbonato zinc species in the decomposition was inferred from new bands between 1,400 and 1,650 cm^{-1} and explained by electrophilic reactions of PPC. cPC is formed from zinc carbonato species, and forms an interesting bridge to the thermal decomposition behavior and corresponding pathways.

5.2 Biocompatibility

The *in vivo* degradation of PPC has been monitored for use as a surgical polymer, or as slow-release substrate. The degradability of PPC pellets in the peritoneal cavity of rats was found to be negligible after 2 months. The surface area was probably too small for substantial degradation [88]. No adverse reactions with respect to the health of the animals were reported. The interaction of PPC with various bacteria

Table 2 Miscellaneous properties of PPC

Property	Value	Ref
Hardness (H D)	74	[24]
Refractive index	1.463	[8]
Permeability (cc mil/m ² day atm)		
Oxygen	15–35	[8]
Nitrogen	10	[8]
Carbon dioxide	120	[8]
Water	3–18	[8]
Density (g/mL)	1.26	[8]
Dielectric constant	3	[8]
Surface charge at 10 KV and 50% relative humidity (V/cm)	850	[23]
Surface resistance (500 V) (Ω)	2×10^{-14}	[23]
Contact angle to water	76.6°	[74]
Surface energy (mJ/m ²)	42.9	[74]
Melt flow index (g/10 min)		
150°C/2.160 kg for Mn of 56 kDa	0.18	[15]
150°C/21.60 kg for Mn of 56 kDa	10.12	[15]
150°C/2.160 kg for Mn of 89 kDa	0.06	[15]
150°C/21.60 kg for Mn of 89 kDa	4.04	[15]
150°C/2.160 kg for Mn of 114 kDa	0.02	[15]
150°C/21.60 kg for Mn of 114 kDa	1.07	[15]

and cells (tissues) has been the subject of a detailed study. The bacterial adhesion to PPC after 4 h was evident for *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Staphylococcus epidermidis*, *Escherichia coli*, and *Staphylococcus aureus*, but with different intensity [74]. The number of bacteria in that time is an indicator for the ability to degrade the PPC substrate. For the first two strains, colonization is expected on the basis of their ability to deal with low nutrient surroundings and to form biofilms. The other bacteria adhere, but in a number that is one to two orders of magnitude smaller. The PPC surface does not allow human HEp-2 cells to grow on it. This is attributed to the low water content. The matter of biocompatibility with tissue was also assessed by implanting films into mice. The films were removed with the tissue after 1, 4, 8, and 12 weeks. The inflammatory reaction caused by the PPC film was weak if at all, there was no tissue necrosis, and no extended chaotic inflammation. Overall, the tissue response suggests that PPC has a good biocompatibility. Surprisingly, it was found that the implanted film had a much rougher surface, i.e., PPC films undergo degradation in vivo. Whether the mechanism of degradation is via oxidation, hydrolysis, or enzyme mediation remains without evidence. In Table 2 miscellaneous properties of PPC are listed.

6 Conclusions

PPC has become an emerging material in the landscape of thermoplastic polymers. Most of its essential properties are known. It is biocompatible and biodegradable, which makes it attractive for packaging purposes. PPC is a material with unusual

thermal properties. This holds true in particular for the glass transition at about body temperature. For application as a film, a lower T_g is desirable, whereas for application as a container a higher T_g is a prerequisite. Through the incorporation of further monomers the T_g can be increased, as well as through the preparation of composites with fillers. PPC of a molecular weight over 60 kDa has a large elongation at break. This allows the blending of solid fillers to a good extent before the composite becomes extremely brittle. PPC has a moderate-to-good affinity for common fillers. Plasticizers such as cPC lower the T_g effectively. Several indications lead to the assumption that the often-observed thermal decomposition at processing temperature (150–200°C) could be controlled as (1) more and more insight into the decomposition pathway become available (role of water and of catalyst residues), and (2) more and more reports are published of PPCs that are thermally robust at a temperature of at least 200°C.

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