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TENSILE PROPERTIES OF POLYPROPYLENE FIBRES

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ABSTRACT

As soon as it appeared on the market, one half century ago, polypropylene (PP) appeared as a promising fibre-forming polymer but with some difficulties in processing due to a lack of control of its viscoelastic properties and in durability due to its low stability to oxidation. These difficulties were progressively resolved in the last decades by a sharper control of synthesis conditions e.g. of stereoregularity and molar mass distribution, and by a better knowledge of oxidation and stabilization mechanisms. These research efforts allowed PP to invade a very wide range of fibre applications, from disposable diapers to geotextiles.

KEYWORDS: Polypropylene, Structure, Processing, Mechanical Properties, Embrittlement, Durability, Stabilization

SUMMARY

INTRODUCTION

Polypropylene was known before the Second World War, but only in its non-crystalline (atactic) form which displays the characteristics of an unvulcanized rubber with the inconvenience of being practically unvulcanizable. Polypropylene became an industrially interesting polymer when Natta discovered a way to obtain a stereoregular structure using stereospecific catalysts (1954). Polypropylene is thus the last commodity polymer (the others being polyethylene, poly(vinylchloride) and polystyrene) to appeare on the market. Its fibre

forming properties were rapidly recognized. It was first used to replace vegetal fibres such as hemp in cordage. However, it invaded progressively other important markets: carpets, filters including cigarette filters, geotextiles, agriculture bays and other applications, camouflage technology, disposable diapers, prosthetic mesh etc [1,2,3,4,5]… In 2005, the world consumption increased at an average rate of about 100 000 tons per year and PP fibres ranked at the second place after polyester fibres [6,7]. Its growth could be slowed down, in a more or less remote future, by the increase of petroleum price and the revival of natural fibres but these trends are, in reality, very difficult to predict.

I. POLYPROPYLENE STRUCTURE AND PROPERTIES

Polypropylene (PP) results from the polymerization of propylene. The structure of the repetitive unit is shown in Fig 1a. Some properties of the three polypropylenes are recalled in Table 1, and will be commented in what follows.

		atactic PP			isotactic PP			syndiotactic PP	
Density	g cm^{-3}	0.854-0.863		[8]	0.850	amorphous phase	[9]	0,856	[11]
					0.931-0.936	α crystalline phase	[9,10]	0,93	[11]
					0.921-0.931	β crystalline phase	[9,10]		
Thermal expansion coefficient	10^4.K^{-1}	6.1-9.4	80-120°C	[8]	1.4-1.5		[12]		
Glass transition temperature	K	238-283		[13-15]	263-283	DSC	[15-17]	270-278	[18,19]
Mark-Houwink parameters	K (ml g^{-1})	2.7×10^{-4}	benzene (23°C)	[20]	1.1×10^{-4}	decaline	[21]		
	a (none)	0.71		[20]	0.80		[21]		
Solubility parameters	MPa$^{1/2}$	15.14		[22]	15.11-18.8		[22,23]		
Heat of fusion	J g^{-1}				138-209	α crystalline phase	[24-31]	109-207	[29-31]
					113-170	β crystalline phase	[33-37]		
Melting temperature	K				459-465	α crystalline phase	[22,38]		

Table 1. Physico-chemical properties of atactic, isotactic and syndiotactic PP [8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37].

Among possible chain configurations, only stereoregular ones (syndiotactic and isotactic PP, Figures 1b and 1c) are able to crystallize and have interesting mechanical properties. Isotactic PP is, by far, the most commonly used stereoisomer.

In the latter, the equilibrium chain configuration is a helix having a period of three monomer units. iPP is able to crystallize into three distinct forms: α, β, γ, the most thermodynamically stable being the monoclinic (α) one. Hexagonal (β) and orthorhombic (γ) are developed under specific crystallization conditions. Crystalline unit parameters [38,39], as well as crystal layer thickness [17] can be found in literature, but they depend on processing conditions and will not be discussed here. Table 1 recalls values of melting temperature of an infinite crystal but melting point of a commercial isotactic PP is close to 165°C (its is found to be lower for syndiotactic PP) and can be lowered by the introduction of comonomers. PP copolymers with melting points as low as 148°C are used in fibres technology. The PP amorphous phase is characterized by a glass transition temperature close to 0°C.

The respective densities of amorphous and crystalline phase of isotactic PP are 0,850 and 0,936. The melting heat ΔH_M of the 100% α-crystalline phase is given with some scattering in literature, but the most frequently retained value is 209 kJ kg^{-1} [40], and still is higher than the one of β-crystalline phase [33-36]. It is also still considered that ΔH_M for a 100% crystalline PP is higher for i-PP than for s-PP [30-31].

Its apolar character makes PP hydrophobic (water equilibrium concentration lower than 0.1%), not easily wettable or dyeable. In contrast, it is easily washable. The surface polarity can be improved by a wide variety of treatments generally consisting in superficial oxidation [41] or plasma treatment [42,43].

Due to its hydrocarbon structure, especially the presence of a tertiary C-H bond, PP is relatively sensitive to thermal and photochemical oxidation. It cannot be processed, stored or used without stabilizers [44].

There is a wide variety of polymerization processes differing by the physical state of the monomer (gas or liquid) and the nature of catalysis (Ziegler-Natta, metallocene…) [45]. The polymerization conditions determine the degree of chain steroregularity, the molecular weight distribution, the powder morphology and, finally, the comonomer content and its distribution into the chains.

II. POLYPROPYLENE FIBRE PROCESSING

There is also a wide variety of fibre processing methods for PP. Melt spinning is a common method in which fibres are extruded through a die and then drawn [46]. Two processes can be distinguished depending on crystallization rate: short spinning (fast crystallization) and long spinning (relatively slow crystallization). In long spinning, drawing is mostly possible from the molten state. In short spinning, drawing is mostly performed in the solid state. Using a second drawing stage in the solid state, it is possible to obtain very high strength fibres (620 MPa e.g. 15 times the strength of isotropic PP samples).

The relatively low melting point of PP allows non woven cloth to be made from staple PP fibres by welding them together without the aid of chemicals and this is interesting for certain application, for instance diapers.

Melt spinning requires a relatively low viscosity e.g. a melt index typically higher than 10 dg min^{-1} [47]. Classical Ziegler-Natta PP grades cannot be processed at high spinning rates due to their wide molar mass distribution (MMD). In the 80's, polymers with sharper MMD were obtained using controlled peroxide initiated thermal degradation [48]. At the end of the 20th century, metallocene catalysis allowed the polymer polydispersity to be controlled during its synthesis leading to an increase in spinning rates and in fibre toughness [49,50].

It is noteworthy that, compared to classical polar fibres forming polymers such as polyamides or PET, PP must have higher average molar mass (typically $M_W > 100$ kg mol^{-1}) to have good mechanical properties (see below). As a result, PP is more visco-elastic than polyamides and PET in molten state, that carries some advantages and drawbacks. The advantage is that it is the visco-elastic behavior which permits to obtain fibres of very small diameter (few micrometers) at very high rate. The inconvenient is that visco-elasticity is responsible for shear rate dependence, eventually die resonance, e.g. a periodic diameter fluctuation, and melt fracture above a critical shear rate. These defects can be avoided with a rigorous control of rheological properties, which is only possible with a not less rigorous control of MMD.

Another common industrial method of PP fibres processing is the melt blown process in which short fibres (3 to 7 μm) are blown at high temperature (50 to 100°C above the melting point) and high rate (6000 m min^{-1}) leading to non woven clothes in which the cohesion results from fibrils entanglement. This process needs very high fluidity PP grades.

III. INITIAL TENSILE PROPERTIES

Usually, mechanical properties of fibres are evaluated by tensile testing (see Chapter 2). From this test, different mechanical properties can be assessed: Young modulus, stress at yield, and strain at break. Typical values [51] depending of draw ratio, are given in Table 2:

	Tensile Modulus (GPa)		Tensile strengh (MPa)		Strain at break (%)	
	iPP	sPP	iPP	sPP	iPP	sPP
Draw ratio $\lambda = 4$	3	0.8	200	130	150	100
Draw ratio $\lambda = 7$	6	1.7	400	280	50	50
Draw ratio $\lambda = 10$	15.5	*	600	*	20	50

Table 2: Tensile properties as a function of draw ratio for iPP ans sPP having similar molar masses [51].

These properties depend on temperature and deformation rate used for the test, PP molar mass, chains orientation and crystalline morphology. The latter characteristics are sharply dependent on the processing conditions [52]. As it has been previously shown, there are several processing methods: gravity spinning, melt spinning, and melt blowing. Furthermore, for each processing conditions, different parameters values as temperature, pressure, extrusion rate and draw ratio lead to different crystalline morphologies.

III.1 Stress-strain curve

In order to illustrate the mechanical behavior of PP fibres, a stress-strain curve is shown in Figure 2. This curve characterizes the mechanical behavior of a PP geotextile fibre having a diameter close to 30 μm loaded with at a constant crosshead displacement rate at 50 mm min^{-1} and using a 100 N cell. As the same manner than isotropic PP samples, initial part of the curve exhibits a pseudo-linear behavior followed by a yield. This yield corresponds to the beginning of plastic deformation associated to a necking process. The necking process is often more diffuse than in isotropic PP samples so that no knee can be observed on the stress-strain curve. In this case, yield stress (σ_y) value can be assessed as the beginning of non linear behavior.

III.2 Mechanical properties

Compared to isotropic i-PP samples, fibres mechanical properties exhibit higher Young modulus (E) and yield stress (σ_y) but lower strains at break (ε_R). However, depending on processing methods and conditions, Young moduli of PP fibres can be quite different. For instance, the methods based on melt spinning and drawing under peculiar conditions (slow stretching on a tensile testing machine or in an oven) lead to elastic modulus values in the range from 10 to 22 GPa, whereas, by using solid state extrusion (hydrostatic extrusion, die drawing followed by slow stretching or spinline stress), elastic modulus values range from 17 to 20 GPa [53].

This increase of modulus is often attributed to a specific oriented morphology called shishkebab. Indeed, for melt spinning process for instance, macromolecules are highly extended prior crystallization and the latter, when it occurs, does not change the macromolecules orientation. In these conditions, lamellar surfaces would be normal to the fibre direction leading to high modulus. According to this, many modeling approaches have been proposed to relate elastic properties of crystalline phase to elastic modulus of PP fibre [54]. Crystalline phase and orientation degree are responsible for yield stress increase: typically its value can reach up to 100 MPa compared to 27 MPa for isotropic i-PP.

Concerning UHMW-PP, a maximum modulus value of 40.4 GPa has been obtained by Matsuo et al. by using the gel-casting method [55]. This value approaches the theoretical crystal modulus of i-PP (35-42 GPa) [56].

At last, fibres of s-PP display a rubber-like mechanical behavior when fibres are submitted to successive elongation and relaxation cycles [57,58]. This is the most important characteristic and unusual physical property for s-PP fibres. For this latter, the maximum achievable tensile

modulus value is remarkably lower than for i-PP, since this latter is characterized by higher crystal modulus, crystallinity ratio and drawability compared to the former. As a result, the maximum tensile modulus of oriented s-PP is close to 3 GPa.

III.3 Fracture properties

Fracture properties of iPP fibres depend on intrinsic parameters as molar mass, crystallinity ratio, morphology and orientation. This latter is linked to processing conditions especially draw ratio. This aspect has been extensively studied in the literature [21]. But these properties are also highly dependent on defects induced by the processing at the surface or in the core of the fibre.

Classically, stress at break is close to 150 MPa and strain at break values range from 150 to 300%. An annealing process would lead to increase stress at break but to decrease strain at break.

On fibres made by melt spinning, it has been observed that strain at break is determined by the spinline stress provided that weight average molecular molar mass is higher than 180 kg.mol^{-1}. [59]. Below this critical value, fibre fails in a brittle manner with a strain at break close to 10% and without strain hardening. Figure 3a shows strain at break as a function of weight average molar mass for fibres having different molar masses: below 150 kg/mol, fibres are brittle. It is noteworthy that a molar mass decrease is always accompanied by a crystallinity ratio increase (Figure 3b) [60].

Fracture properties, i.e. stress and strain and break, are often interpreted by using tie molecule concept. Indeed, it has been common to consider that the fibre structure is based on "microfibrils" or "nanofibrils". These fibrils are formed from shish-kebab structures as previously seen. In order to obtain good fracture properties, the crystalline regions have to be

interconnected by chains or entangled chains through amorphous region, called "tie-molecules" [61]. In the case of melt spinning fibres, one can assume that a lack of interconnections is responsible for brittle failure below the critical molar mass close to 150 kg.mol^{-1}.

IV. FIBRE DURABILITY

IV.1. Failure processes

Fibre failure can result from mechanical loading, from physical polymer-solvent interactions, or from chemical interaction between the polymer and reactive species (water, oxygen, etc…) present in the environment or from a combination of these cases.

Mechanical failure can result from creep, fatigue or accidental overloading resulting from instance from earthquake in case of geotextiles. Efficient rules for mechanical design are in principle available [62,63,64] to avoid anomalous mechanical failure.

Polymer-solvent physical interactions can considerably reduce the time to failure when the material is submitted, at the same time, to mechanical loadings [65]. In the case of PP, however, polymer-solvent interactions are strongly limited by the apolar character of the polymer and by its crystallinity. It is well-known that PP is soluble only at high temperature, e.g. practically in molten state, in a small number of aromatic solvents. PP fibres can not be recommended in applications where they are submitted to mechanical loading in the presence of aromatic chlorinated solvents.

Chemical interactions between PP and reactive species present in the environment are sharply determined by the hydrocarbon structure of the polymer. This type of structure is totally unreactive with water and with most of the water soluble species: acids, bases, salts, except the case of oxidizing ones such as nitric acids, potassium permanganate, hydrogen peroxide, etc …

Thus the only significant ageing process in PP is oxidation with the above mentioned reactants, or simply with atmospheric oxygen. The rest of this paragraph will then be devoted to oxidation and its consequences on mechanical behaviour of PP fibres.
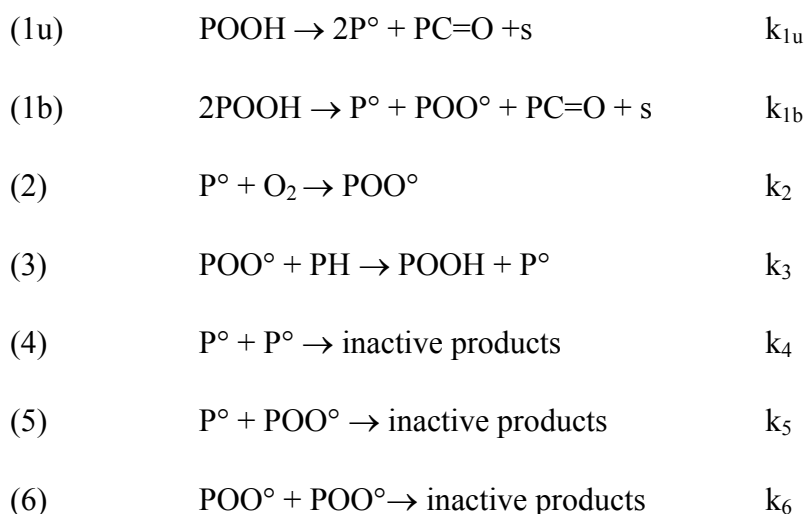
IV.2. Oxidation mechanism

After the pioneering works of Semenov in the former USSR [66] and Bolland and co-workers in England [67,68], it was widely recognized that oxidation occurs through a radical chain mechanism of which the main peculiarity is that it generates hydroperoxides (POOH) which decompose easily to give new radicals inducing thus a catastrophic auto-acceleration of the reaction. The propagation of the radical chain involves two steps: first the oxygen addition to an alkyl radical (P°) to give a peroxy radical (POO°) and second the abstraction of an hydrogen to the substrate to give an hydroperoxyde and a new alkyl radical. The second step is at least one million time slower than the first one so that it plays a key role in the oxidation kinetics.

The PP monomer units contain a tertiary C-H bond especially reactive in hydrogen abstraction processes that partially explains the relatively high sensitivity of the polymer to oxidation.

Another very important characteristic of PP oxidation is that termination by bimolecular combination of peroxy radicals is not very efficient, that contributes to increase the oxidizabily of the polymer.

Hydroperoxide decomposition can be unimolecular (1u) or bimolecular (1b) and catalyzed by transition metals (Ti, Cu, Fe, Cr, Co, etc…). In all the cases, it produces alkoxy radicals of which the peculiarity is to rearrange easily by β-scission (see Figure 4).

As it will be seen below, chain scission is the direct cause of embrittlement. Finally, most of the important features of PP oxidation can be well predicted from a standard mechanistic scheme:

(1u)	$POOH \rightarrow 2P° + PC=O + s$	k_{1u}
(1b)	$2POOH \rightarrow P° + POO° + PC=O + s$	k_{1b}
(2)	$P° + O_2 \rightarrow POO°$	k_2
(3)	$POO° + PH \rightarrow POOH + P°$	k_3
(4)	$P° + P° \rightarrow$ inactive products	k_4
(5)	$P° + POO° \rightarrow$ inactive products	k_5
(6)	$POO° + POO° \rightarrow$ inactive products	k_6

The kinetic behavior depends essentially on initiation mode, as illustrated by Figure 5.

In the case of radiochemical ageing at relatively high dose rate, initiation results essentially from polymer radiolysis, hydroperoxide decomposition can be neglected for short exposure times at low temperatures. In this case, oxidation proceeds at a constant rate.

In the case of thermal ageing at low temperature, since k_{1u} is relatively low, the hydroperoxides concentration reaches rapidly a level where bimolecular decomposition becomes predominant. In this case, oxidation kinetics displays an induction period followed by a catastrophic auto-acceleration. Whatever the chosen endlife criterion, lifetime is always of the order of the induction time.

In the case of photochemical ageing, with the commonly used light intensities, hydroperoxides react by the unimolecular mechanism with a k_{1u} value several orders of magnitude higher than for thermal ageing at the same temperature. As a result, induction time is reduced to zero and auto-acceleration is considerably less marked than in thermal ageing.

IV.3. Oxidation induced embrittlement

Embrittlement due to oxidative ageing results from the fact that the polymer looses its capacity to undergo plastic deformations. It occurs suddenly that indicates the existence of a critical state separating ductile and brittle regime of deformation. The most probable causal chain can be ascribed: oxidation → chain scission in amorphous phase → molar mass decrease → easier chain disentanglements → chemical crystallization → embrittlement.

At the present state of our knowledge, it is difficult to choose between two embrittlement mechanisms: a purely micro-mechanical one in which the key factor would be a critical interlamellar distance l_a or a molecular mechanism in which the key factor would be critical concentration of tie chains interconnecting crystalline lamellae. In both cases however, for a given starting morphology, this critical state corresponds to a critical value of the weight

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average molar mass: $M_W = M'_C$. For PP, M'_C is of the order of 200 kg mol^{-1} for quasi-isotropic samples and 150 kg mol^{-1} for fibres.

IV.4. Stabilization

Since oxidation almost results from a radical chain process with relatively low initial rate and high initial kinetic chain length (number of propagation event per initiation event), it is possible to envisage efficient ways for its inhibition:

① Radical scavenging (e.g. chain interruption) by aromatic amines, hindered phenols or hindered amines of the tetramethylpiperidine type (HALS).

② Decrease of the initiation rate by hydroperoxide destruction by non-radical way, using sulfides or phosphites, and suppression of eventual catalytic effect of metallic impurities using metal chelatants.

③ In the specific case of photo-oxidation: decrease of the photo-initiation rate using UV absorbers (but they are not very efficient in thin samples), pigments such as TiO_2 with adequate surface treatments (otherwise, they would have a deleterious photo-catalytic effect) or quenchers to desactivate photo-excited states responsible for photo-initiation.

Polyolefins stabilization has raised up a very abundant literature [69,70,71,72,73,74,75,76]. Very efficient recipes, exploiting the synergistic effects between distinct stabilizers families, are commonly used.

IV.5. Lifetime prediction methods

Unstabilized PP cannot be processed or even stored at ambient temperature where its lifetime wouldn't exceed a few years, even in dark. Considerably longer lifetimes can be obtained with adequately chosen stabilizers systems. Lifetimes on the order of 100 years are for example expected in the case of PP geotextiles. The problem, for users is to try to determine this lifetime from accelerated ageing tests. Two ways are possible: the empirical way in which one key condition is a good simulation of natural ageing conditions and the scientific way in which the key condition is a good scientific model to represent ageing effects. The empirical way has largely predominated in the half past of century, despite its low reliability [77,78,79,80]. The emergence of numerical tools to solve very complex kinetic schemes has recently given an impulsion to the scientific way [81]. In this latter case, accelerated ageing tests are not aimed to simulate natural ageing but only identify model parameters. It appears then that tests at variable oxygen pressures, which were rarely used in the past, are especially interesting [82].

CONCLUSIONS

As soon as the method for its stereospecific synthesis was discovered, one half century ago, polypropylene appeared as a very interesting fibre forming polymer owing to its low cost, easy processability, hydrophobicity and relatively high tenacity. Considerable worldwide efforts, in the elapsed period, allowed to control more and more sharply the degree of stereoregularity and the molar mass distribution and to reduce the oxydizability that is the weakest PP characteristic. As the same time, new processing methods profiting by the peculiarities of the PP rheological behavior, especially its high visco-elastic character in molten state, were created. As a result, a wide variety of PP fibres, offering a broad range of

diameters, stiffnesses, tenacities, photo and thermal stabilities, etc … is now available in the market. It is thus not surprising to find PP fibres in an unequalled variety of applications, from geotextiles to diapers.

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