

# INFLUENCE OF NATURAL FIBRE REINFORCEMENT ON MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE.

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## ABSTRACT

Influence of spruce fibre reinforcement on the polypropylene matrix has been studied in terms of microstructural and mechanical properties. Pure PP properties have been compared with PP reinforced by different spruce fibre weight fractions. Results have shown that addition of spruce fibres causes the appearance of a  $\beta$  crystalline phase and an increase of the PP degree of crystallinity. It leads simultaneously to a higher Young's modulus and an important loss in tensile strength and elongation at break. Fracture tests coupled with digital image correlation technique for measuring strains in the crack tip vicinity have put in light the better accommodation of overstrains in the composite material, which explains its higher toughness.

## 1. INTRODUCTION

Over the past decade, the high modulus fibres such as glass, kevlar, carbon ...were used in numerous technical fields where high strength and stiffness are required. However, these classic fibres often cause considerable problems in terms of reuse and environmental impact [1]. Their composites end up in landfills, while some are incinerated after use and may contribute to pollution.

In recent years, manufactured industries have shown environmental awareness in choosing materials and fibre reinforcements. The tendency to selecting biodegradable fibres has been a natural choice for reinforcing polymers to make them "greener". These fibres offer several advantages such as cheapness, low weight, easy degradability, low abrasion, good acoustic and thermal insulation properties; they may turn out to be one of the material revolutions of this century [2-4].

The further effort aims at the development of "fully biodegradable" composites by combining natural fibres with biodegradable resins [1]. At the end of their life, they can be easily disposed of or composted without harming the environment.

Currently, polypropylene is used for a large number of applications because it is cheap, lightweight, easily recyclable and modifiable to achieve specific requirements [5,6]. Polypropylene has been the fastest growing major plastic at some 7% per year [7]. In order to be able to meet the high demands on stiffness and strength, polypropylene must often be reinforced. A variety of natural fibres are available for reinforcement in polypropylene, for example: flax, hemp, sisal, bamboo [8]...In this study, spruce fibres have been incorporated into polypropylene with different fibre weight fractions in order to investigate their effects on this polymeric matrix.

The influences of spruce fibres on polypropylene have been examined in terms of mechanical and microstructural properties.

The addition of spruce fibres in PP matrix modifies microstructural properties of the polymer. These modifications have been studied by using two different experimental techniques: DSC and WAXS.

Mechanical properties of pure polypropylene and polypropylene reinforced with short spruce fibres have been studied in both tensile and fracture tests. The tensile behaviour has been studied as a function of fibre weight fraction and experimental results are compared with some theoretical models. In addition, a particular investigation on fracture mechanisms has

also been carried out on CT (Compact Tension) specimens made of pure polypropylene and of polypropylene reinforced by 30% of spruce fibres.

A recent study in fracture behaviour of polypropylene has shown the complexity of the crack tip damage zone [9] but the influence of natural fibres on fracture behaviour of this material is still a new subject. In order to compare fracture mechanisms in the two materials, digital image correlation method [10] has been used to obtain whole-field strain measurements around the crack tip.

## 2. MATERIALS AND SAMPLE PREPARATION

The used polypropylene (PP) is the APPRYL 3400 MA1 supplied by ATOFINA. It is an homopolymer polypropylene obtained by controlled rheology and presenting an isotacticity of 90% with the crystal form  $\alpha$ . This polymer has a density of  $0.905 \text{ g/cm}^3$  and a Melt Flow Index of  $42\text{g}/10 \text{ min}$ .

Spruce fibres come from industrial waste, with length and diameter about respectively  $800 \mu\text{m}$  and  $400 \mu\text{m}$ . Fibres have a powder form, a cream colour and a density of  $0.4 \text{ g/cm}^3$ .

Polypropylene and spruce fibres were extruded in a twin screw extruder. The extruded strands were quenched in cold water and then granulated in a cutting mill. Five proportions of fibre weight have been prepared: 1%, 5%, 10%, 30% and 40%. PP with or without fibres was then injected into two kinds of panels with thickness of 4mm or 8mm. Tensile specimens were cut out from 4mm thick-panels. Compact Tension (CT) specimens for fracture tests were cut out from 8mm thick-panels and a pre-crack was created by forcing a razor-blade into the notch root. The initial length of the pre-crack was about  $400 \mu\text{m}$  depending on the specimen.

## 3. MICROSTRUCTURE CHARACTERISATION

### Experimental conditions

Two techniques have been used in order to characterise the material microstructure: the differential scanning calorimetry (DSC) and the wide-angle X-ray scattering (WAXS).

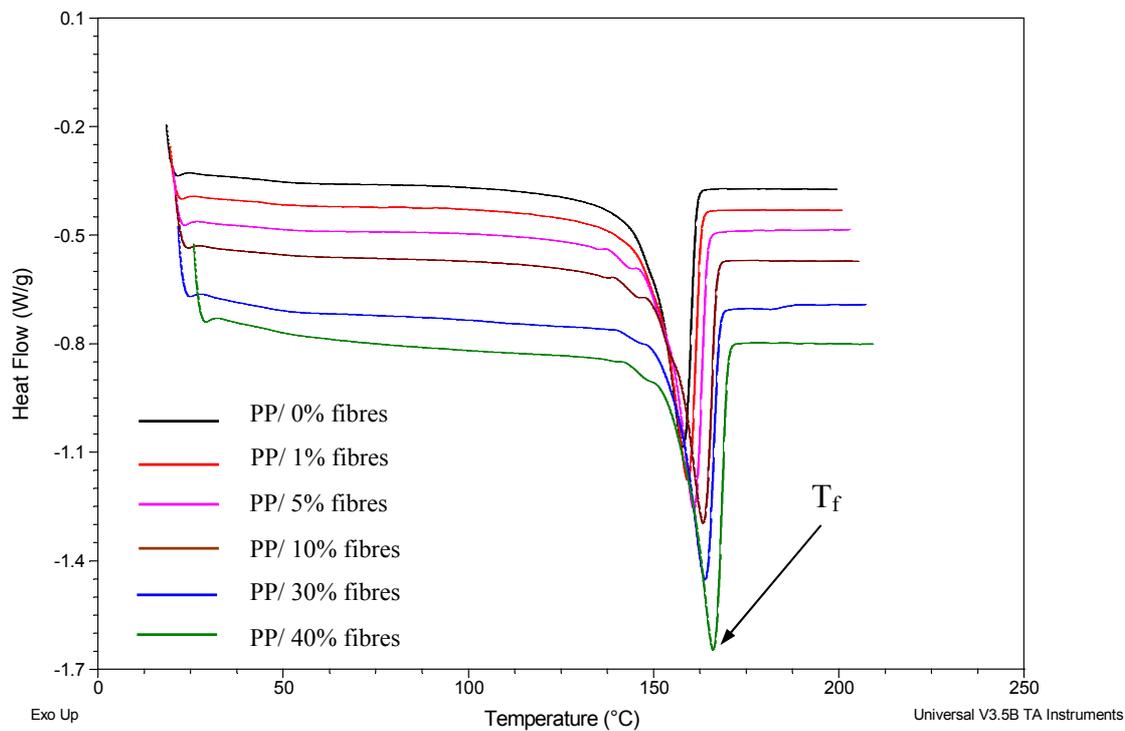
For DSC testing, we used the MDSC 2920 from TA Instruments. All samples were heated at a rate of  $5^\circ\text{C}/\text{min}$  in nitrogen atmosphere. Thermograms show endothermic peaks of crystalline phase melting. By measuring peak areas, it is possible to determine the degree of crystallinity of polypropylene and peak minima give the melting temperature values.

WAXS patterns were taken by a goniometer using Cr radiation with a step of  $0.015^\circ$ . X-ray diffraction patterns show diffracted peaks that can be associated to crystalline planes, by using the Bragg law. Presence of  $\beta$  phase crystal, which did not exist in the pure PP, has been detected in WAXS scans. The relative content of  $\beta$  phase, note  $k_\beta$ , can be calculated according to equation (1), suggested by A.Turner Jones [11].

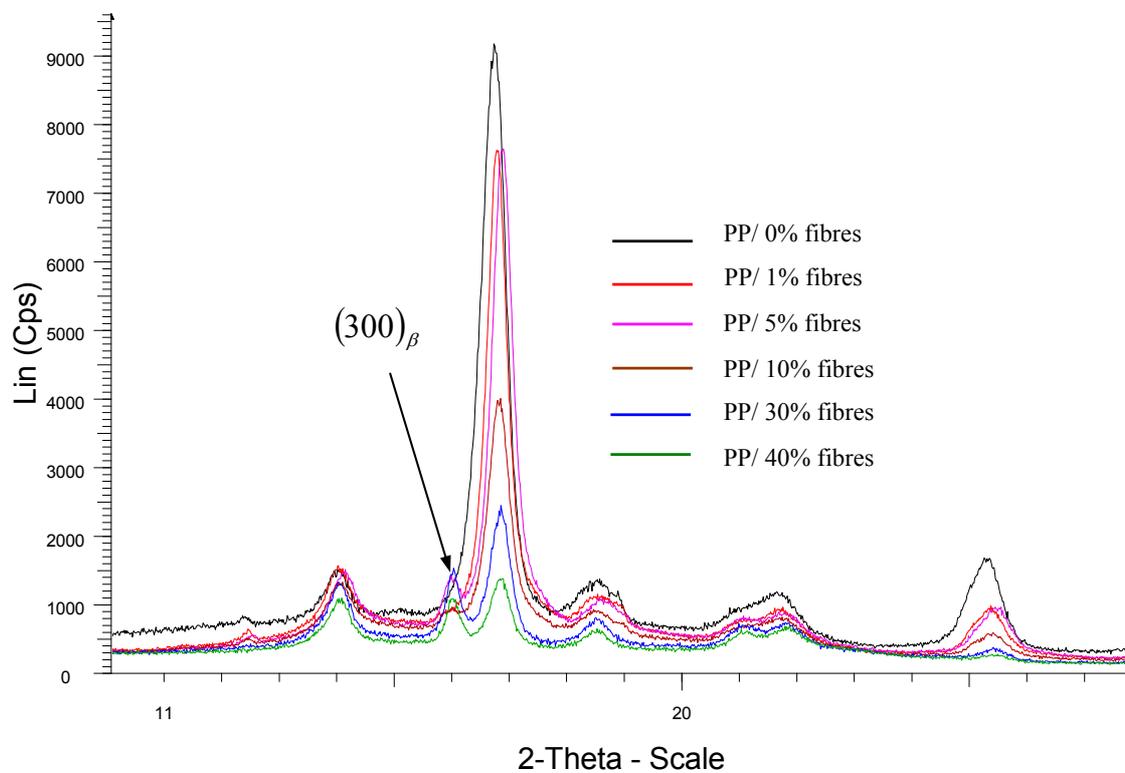
$$k_\beta = \frac{H_{\beta(300)}}{H_{\beta(300)} + (H_{\alpha(110)} + H_{\alpha(040)} + H_{\alpha(130)})} \quad (1)$$

where  $H_{i(j)}$  denotes the peak height corresponding to crystalline plane  $j$  in phase  $i$ .

## Results



“Fig. 1. Thermograms obtained by DSC at 5°C/min.”



“Fig. 2. WAXS patterns of PP and spruce fibres/PP composites.”

Thermograms obtained by DSC from PP and PP reinforced with spruce fibres are presented in figure 1 and results are listed in table 1. All thermograms show a large endothermic peak due to the  $\alpha$  phase melting. Melting temperature values measured for this large peak are slightly smaller in composite materials than in pure PP (table 1). A small peak located at about 147°C has also been detected in thermograms of the composites for a fibre weight ratio greater than 5%. This second endothermic peak corresponds to the melting of  $\beta$  phase in polypropylene [12]. Measurements of the total degree of crystallinity have shown that the higher the fibre weight fraction, the higher the crystallinity degree of the PP matrix.

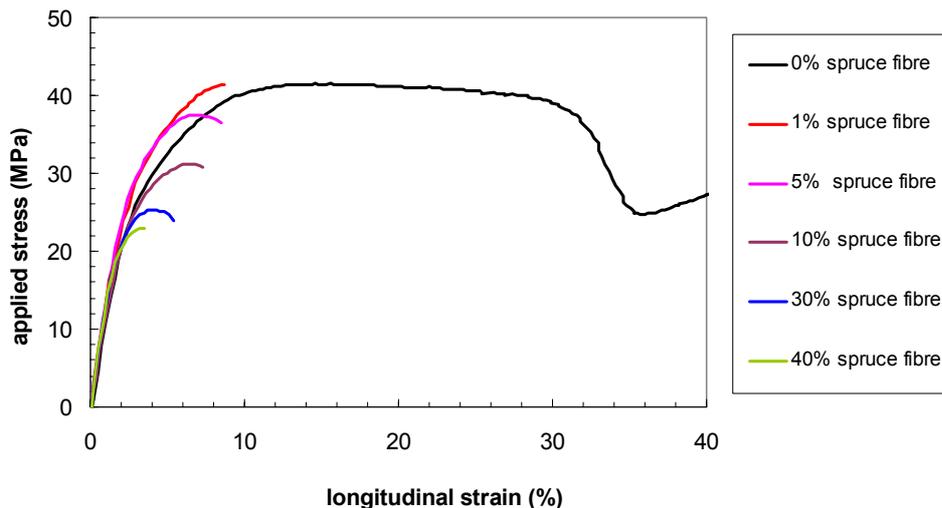
The WAXS data obtained from different samples are presented in figure 2. The highest peaks corresponding to the  $\alpha$  phase can be found at scattering angles of 14°(110), 17°(040), 18,5°(130), 21°(111) and 22°(131 and 041). The  $\beta$  phase can be detected thanks to the presence of a peak located at 16°(300). The proportion of  $\beta$  phase has been measured by formula (1) and was found to increase with the fibre weight fraction: from 9.2% for 5% of fibres to 20.4% for 40% fibres (see in table 1).

“Table 1. Microstructure properties of PP with and without spruce fibres ( $T_f$ : melting temperature,  $X_v$ : degree of crystallinity,  $k_\beta$ : proportion of  $\beta$  phase).”

Materials	$T_f$ (°C)	$X_v$ (%)	$k_\beta$ (%)
PP/ 0% spruce	167.4 ± 0.8	61.4 ± 0.4	0
PP/ 1% spruce	166.3 ± 0.1		0
PP/ 5% spruce	166.3 ± 0.1		9.2 ± 0
PP/ 10% spruce	166.8 ± 0.5	61.3 ± 0.5	8.7 ± 0.8
PP/ 30% spruce	166.8 ± 0	66.2 ± 2.2	19.7 ± 4.5
PP/ 40% spruce	166.6 ± 0	68.9 ± 2.1	20.4 ± 3.6

## 4. MECHANICAL ANALYSIS

### Tensile behaviour



“Fig. 3. Tensile behaviour of pure PP and spruce fibre/PP composites.”

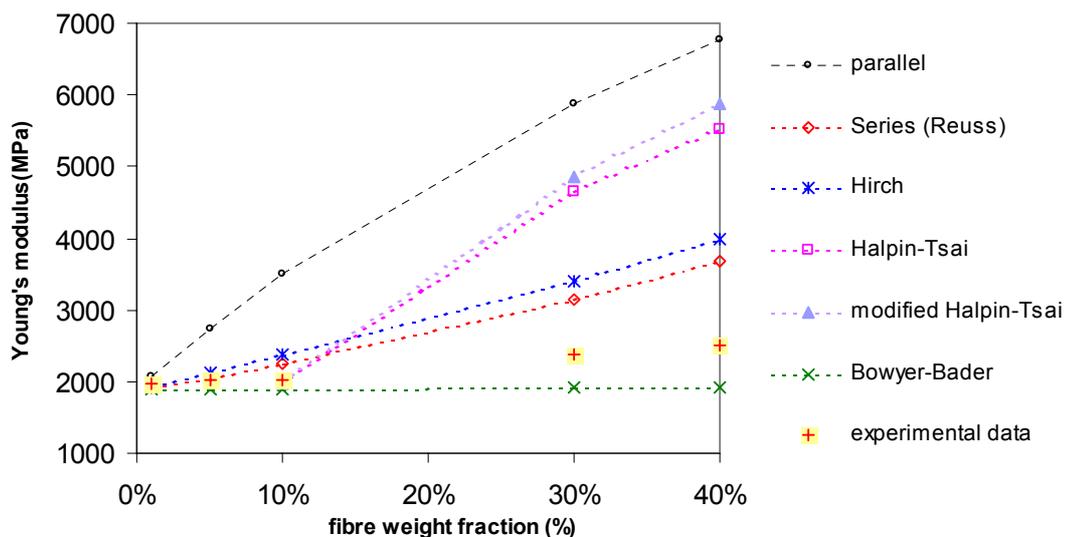
Tensile tests have been carried out with an Instron machine at a constant crosshead displacement rate of 20mm/min at room temperature. Experimental stress-strain curves for pure PP and spruce fibres reinforced PP materials are plotted in figure 3. The elastic modulus

has been obtained from the initial slope of the true stress-strain plot measured by a clip-on extensometer. Experimental values of tensile properties are summed up in table 2.

“**Table 2.** Tensile properties of materials ( $E$ : Young’s modulus,  $\sigma_y$ : yield stress,  $\sigma_f$ : tensile strength,  $\varepsilon_f$ : elongation at break).”

Materials	$E$ (MPa)	$\sigma_y$ (MPa)	$\sigma_f$ (MPa)	$\varepsilon_f$ (%)
PP/ 0% fibre	$1880 \pm 51$	$41.5 \pm 0.03$	$49.5 \pm 14.50$	$88.5 \pm 31.5$
PP/ 1% fibre	$1967.6 \pm 4.3$	$41.25 \pm 0.05$	$41.25 \pm 0.05$	$8.55 \pm 0.1$
PP/ 5% fibre	$2015 \pm 1.7$	$37.44 \pm 0.02$	$36.95 \pm 0.52$	$7.5 \pm 1.0$
PP/ 10% fibre	$2013 \pm 1.0$	$31.5 \pm 0.45$	$31.1 \pm 0.50$	$7.1 \pm 0.1$
PP/ 30% fibre	$2370 \pm 6.0$	$25.2 \pm 0.05$	$24.5 \pm 0.65$	$4.6 \pm 0.7$
PP/ 40% fibre	$2505 \pm 50$	$22.5 \pm 0.25$	$22.9 \pm 0.10$	$3.25 \pm 0.2$

Experimental results show that tensile mechanical properties (Young’s modulus, yield stress, tensile strength, and elongation at break) depend strongly on the spruce fibre weight fraction. Young’s modulus increases with the fibre weight ratio. Otherwise, tensile strength, yield stress and elongation at break decrease sharply when the fibre content increases. These results put in light that spruce fibre addition in PP matrix makes the material stiffer but considerably more brittle.



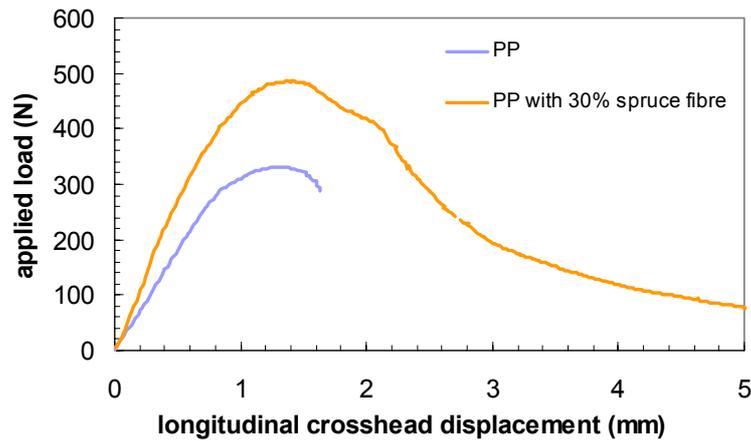
“**Fig. 4.** Comparison of theoretical and experimental Young’s modulus for spruce fibres/PP composites.”

Experimental values of Young’s modulus have been compared with modulus obtained by several predictive models in which the influences of fibre content and fibre aspect ratio were taken into account [13-17]. In figure 4, experimental and calculated values are presented. One can see that many predictive models overestimate the Young’s modulus values. Experimental values come in between the “series” model and the “Bowyer-Bader” model values.

## Fracture mechanical behaviour

### Global fracture behaviour

Fracture behaviour has been studied by testing a CT specimen in mode I crack propagation. Tests have been performed at a 1mm/min crosshead velocity with normalised specimens [18] made of pure PP and PP reinforced with 30% spruce fibres.



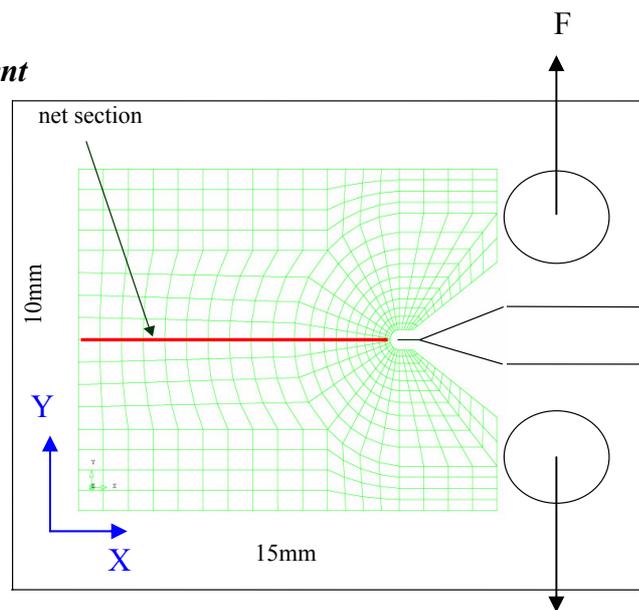
“Fig. 5. Global fracture behaviour of unfilled PP and PP with 30% of spruce fibre.”

Comparison of their global fracture behaviours is shown in figure 5. One can see in this figure that spruce fibre addition allows the maximal applied load to be increased and the total failure just after the maximum loading to be avoided, as is the case for the pure PP. Toughness  $K_{IC}$  have been found to increase from  $2.2 \text{ MPa}\sqrt{m}$  in pure PP to  $2.8 \text{ MPa}\sqrt{m}$  in 30% spruce fibre/PP composite.

#### ***The digital image correlation method***

The optical technique developed in our laboratory [10] has been applied to obtain displacement fields and consequently strain fields around the crack tip. The principle of this technique is to record the random grainy pattern created on the specimen surface before and after loading the sample. Then, at each of measurement point, by correlating sub-windows in these two pictures, it is possible to determine the in-plane displacement vectors resulting from the difference in loading. We have developed in our laboratory a GRANU.EXE program to correlate directly the two pictures based on calculation of direct correlation of the two sub-windows. The strain measurement is obtained by using a finite-element-method software to calculate the spatial derivative of the displacement. Each measurement point becomes a node of the finite-element mesh and the measured displacement vectors are imposed as boundary conditions.

#### ***Local strain measurement***

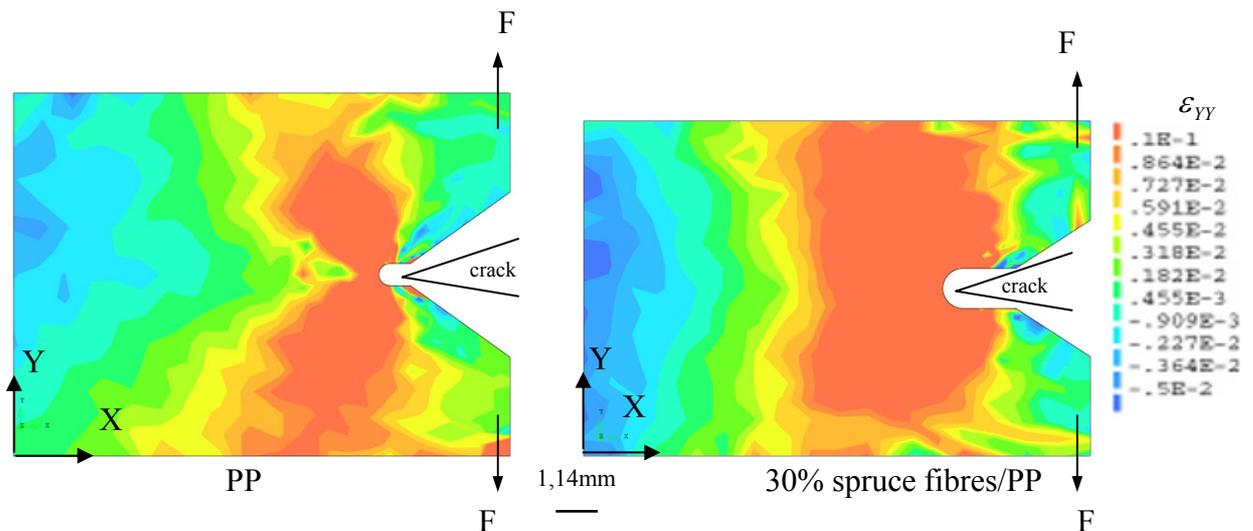


“Fig. 6. Mesh used for correlation calculation.”

The digital image correlation method has been applied to the CT specimens in pure PP and in PP with 30% spruce fibres. An optical and mechanical assembly was designed and mounted in testing machine in order to record digital images.

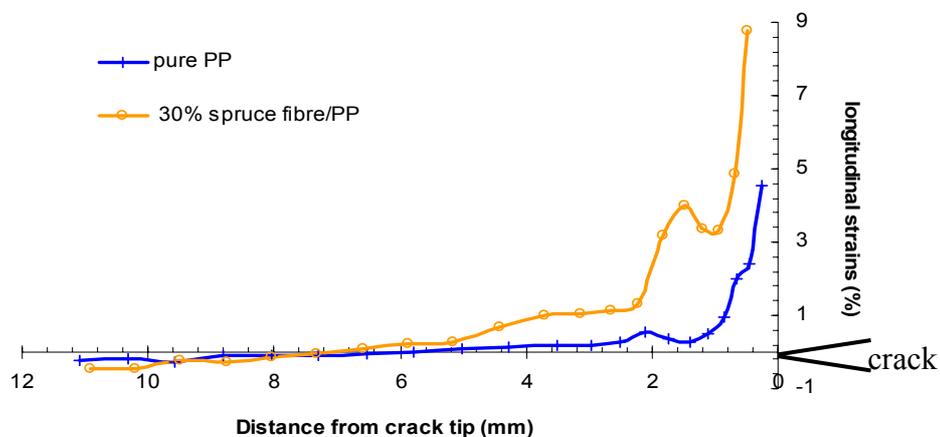
Figure 6 presents the mesh used for correlation calculations around the crack tip. Each node is a measurement “point” covering a small square of  $360 \mu\text{m} * 360 \mu\text{m}$  area. The nearest point from the crack tip is located at a distance of about 0,375 mm from it.

Experimental longitudinal strain maps measured at the maximal applied loads are presented in figure 7 for both materials. Comparison of the two maps highlights the differences in strain distribution at the crack tip in PP and in PP reinforced with 30% spruce fibres. It can be seen on figure 7 that for pure PP, zones of high strain values are oriented in  $\pm 45^\circ$  directions ahead of the crack tip. In contrast, the presence of spruce fibres modifies this distribution and leads to a larger zone of strain concentration around the crack tip.



“Fig. 7. Experimental longitudinal  $\epsilon_{YY}$  strain maps measured in front of the crack tip by digital image correlation method at maximal applied loads: 335N for pure PP and 464 N for spruce fibre/PP composite.”

In order to compare more precisely longitudinal strain values measured at the crack tip in the two materials, we have also plotted the measured longitudinal strain  $\epsilon_{YY}$  values along the net section (figure 8).

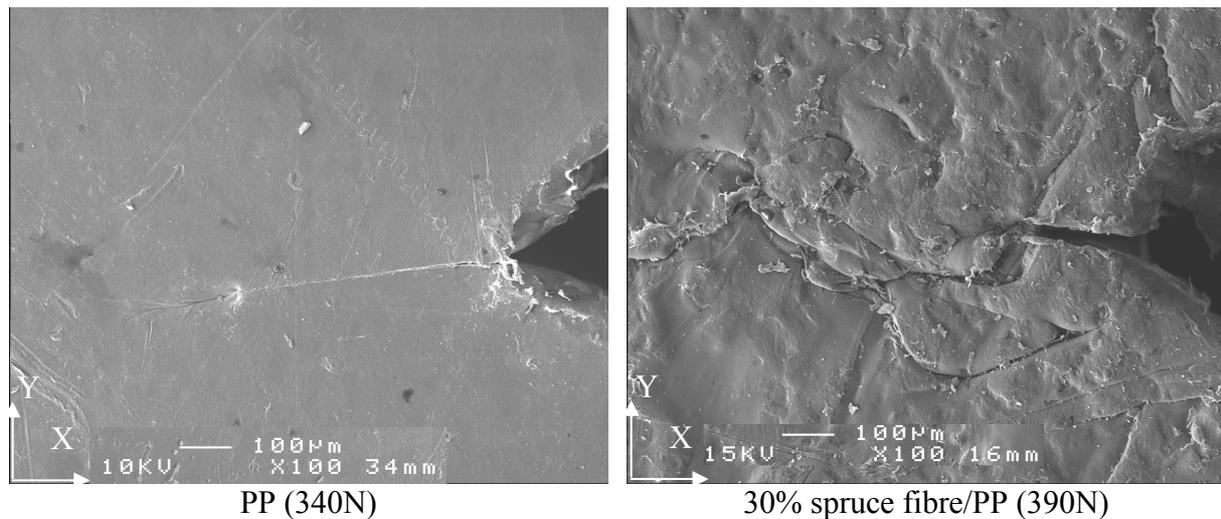


“Fig. 8. Longitudinal  $\epsilon_{YY}$  strains measured by digital image correlation technique on the CT specimen net section for the PP with and without spruce fibres.”

Figure 8 shows that the longitudinal strain values measured at the maximal applied loads are higher in the composite material than in the pure PP. At the crack tip, the longitudinal strains reach the value of 8.7% in the composite material and only 4.5% in the unfilled PP. Moreover, it can be seen in figure 8 that negative strain values have been measured at a distance greater than 7 mm from the crack tip. It corresponds to the compressive zone in the CT specimen due to the global bending effect.

All these results show that the ability of the PP reinforced with 30% of spruce fibres to accommodate overstrains at the crack tip is better than that of the unfilled PP. This explains the higher toughness of the composite material.

### *Crack observation by SEM*



“Fig. 9. Crack views obtained by SEM imaging at specimen surface just before reaching the maximal applied loads.”

The crack aspect at the specimen surface has been recorded by SEM imaging just before reaching the maximal applied loads for each material. As can be seen in figure 9, the process zone ahead of the crack tip is totally different for the two materials. For the unfilled PP, the process zone in which craze-like damage has developed, is linear, as has already been described in literature [9]. A close inspection of the crack aspect in the pure PP shows a whitening zone, which corresponds, to the high strain value zone measured by digital image correlation (figure 7).

The process zone in the PP reinforced with spruce fibres is completely different. It can be seen in figure 9 that, in this material, the presence of spruce fibres has prevented a linear damage development; on the contrary a very tortuous damage zone can be observed on the SEM image.

## **5. CONCLUSION**

The addition of spruce fibres in polypropylene was studied in terms of microstructural and mechanical properties. It has been shown that the presence of spruce fibres in polymer matrix causes the appearance of crystalline  $\beta$  phase and increases the polymer crystallinity. It leads to a stiffer but more brittle material in tension and it increases its toughness, modifying the distribution of the high strain zone in front of the crack tip.

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