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Ex-cellulose carbon fibres with improved mechanical properties

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Ex-rayon carbon yarns have been prepared according to an original route characterized by a fast pyrolysis step in the presence of an organosilicon compound. The evolution of the mechanical and physicochemical properties of the fibres throughout the transformation of cellulose into carbon showed that the organosilicon additive was necessary to obtain carbon yarns exhibiting satisfactory mechanical behaviour and to improve significantly the fracture properties of the ex-rayon carbon fibres. *© 2006 Springer Science + Business Media, Inc.*

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1. Introduction

Isotropic carbon fibres obtained from cellulosic precursors have been widely studied in the 70's [1–5]. Their low thermal conductivity makes them excellent reinforcements for phenolic-based ablative materials used in the aerospace industry. The physicochemical processes taking place during the transformation of cellulose into carbon are complex. Related papers deal with pyrolysis of natural [6] or artificial [7] cellulose fibres or, more generally, thermal degradation of biomass [8]. It is commonly assumed that this transformation follows two concurrent pathways [9]: (i) depolymerisation of the macromolecular chains produces a variety of oxygenated compounds, which represent the major mass loss of the solid residue, and (ii) dehydration of the glucopyranose units forms a polymeric intermediate that is able to convert into polyaromatic structures in the solid state.

Using empirical approaches, the ex-cellulose fibre manufacturers have progressively improved their methods of preparation. It is generally recommended to pyrolyse cellulose at slow heating rates of a few $^{\circ}\mathrm{C{\cdot}h^{-1}}$ [10, 11]. The use of organosilicon compounds has previously been patented [12, 13] and mentioned in the literature [14, 15]. However, their effects on the properties of the fibres have been poorly described and the mechanisms of their action on the pyrolysis processes of cellulose into carbon have not been established.

The aim of this work was to investigate the effects of an organosilicon additive on the mechanical properties of the fibres during the thermal transformation of cellulose into carbon. The evolution of these properties throughout the pyrolysis process, with or without the additive, was examined. Particular attention was given to mechanical properties.

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2. Experimental

2.1. Precursors

The rayon fibre yarn consists of 2000 continuous, twisted filaments, which have an average diameter of 12.7 μm. Its tensile strength is about 680 MPa. The precursor is a low-crystalline, low-oriented cellulose which has a number average polymerisation degree $\overline{DP}_n$ of 350.

The pyrolysis additive is an organosilicon compound [16].

2.2. Elaboration of the carbon fibres

2.2.1. Coating of the additive onto the cellulose yarns

The cellulose yarns were dipped into a dilute tetrachloroethylene solution of the additive, and then heated at 120°C to remove the solvent. The additive looks like a sheath around the fibres that can be observed by scanning electron microscopy (SEM) (picture not shown here). Its film-forming properties and low viscosity (a few mPa·s in tetrachloroethylene solution) help spread it out around the fibres. The additive was almost totally recovered by treating the impregnated yarns with dichloromethane, showing that these coating conditions were not appropriate for the silylation of cellulose [17].

2.2.2. Carbonisation of the yarns

The rayon yarns were suspended under very low charge in the hot section of a regulated, vertical silica glass-tube furnace, then pyrolysed under inert gas flow, at an average heating rate of 10°C·min^{-1}, up to the maximum temperature T_p, and finally cooled under inert gas before being removed from the oven.

2.3. Methods of characterisation

2.3.1. Thermogravimetric analysis (TGA)

TGA analyses were carried out under nitrogen with a Setaram TAG24 analyzer under conditions similar to the carbonisation of the yarns. Sample mass was about 20 mg.

2.3.2. Mechanical properties of the filaments

The characterisations were made at ambient temperature on monofilaments treated at different T_ps. The filaments were randomly pulled out of the strands and glued onto paper frames. The diameter of each filament was measured by laser diffractometry, assuming it had a circular cross-section. As expected, the irregularity of the section gives rise to inaccurate values of the cross-sectional area, the tensile strength σ_r and the Young's modulus E. The cross-sectional area values calculated by image analysis suggest that the average values derived from laser diffractometry measurements were overestimated by ≈2%.

Each type of fibre was subjected to tensile tests in uniaxial loading mode at two gauge lengths, 10 and 25 mm, to take into account the deformation of the device. E, σ_r and tensile strain ε_r were averaged over about 20 experiments (gauge length 10 mm). When the force-displacement curve was non-linear, the Young's modulus was derived from the slope of the linear part of the curve at low strain. Extent to failure was performed at constant crosshead speed-rate of 0.4 mm·min^{-1}. The distribution of fracture characteristics can be described by means of Weibull statistics [18, 19]. The Weibull modulus of the fibre m characterises the spreading of the tensile strength experimental values: the larger m, the narrower the distribution.

2.3.3. Mechanical properties of the yarns

The carbon yarns were subjected to tensile tests with an experimental machine. The extremities of the yarn were fixed inside metallic tubes with an epoxy-based glue. The tubes were gripped in the bits of the machine. Traction was applied on the yarn at a constant speed of the inferior traverse of 0.05 mm·min^{-1}. The elongation of the yarn was calculated from data of two LVDT-type displacement sensors and from the deformation value of the experimental device, which is 0.3 μm·N^{-1}. A 500 N force sensor measured the load applied to the yarn. The initial gauge length was 20 mm.

The parameters selected to characterise each yarn are:

- γ (%), the fraction of broken fibres before the mechanical test, assimilated to the proportion of fibres broken during the carbonization.

  $$\gamma = 1 - E_{\text{yarn}}/E_{\text{fibre}}[20]$$

  where E_{fibre} is the average modulus of the filament, E_{yarn} is the modulus of the yarn calculated from the linear part of the experimental curve, presuming that no fibre was broken before the test. This equation implies that the load is uniformly distributed over all non-broken fibres aligned in parallel directions.
- $F_{\max}$ (N), the load measured at the maximum of the experimental curve.
- $R_{\max}$ (cN·tex^{-1}), the resistance of the yarn divided by its lineic mass. This parameter allows comparing the mechanical resistance of yarns, each being constituted of a different number of fibres.
- $\sigma_{\max}$ (MPa), the stress calculated from $F_{\max}$. Its estimation requires knowing the fraction of fibres broken during the mechanical test, α. This parameter is obtained from the difference ΔF between the linear behaviour of the yarn, when no fibre is supposed to be broken, and the true behaviour of the yarn. At the maximum of the experimental curve, α is given by the equation:

  $$\alpha_c = \Delta F/(F_{\max} + \Delta F)[20]$$

  $$\text{and} \quad \sigma_{\max} = F_{\max}/(A_{\text{yarn}}(1 - \alpha_c))$$

  $$\text{with} \quad A_{\text{yarn}} = N(1 - \gamma)S_{\text{fibre}}$$

where N is the number of fibres in the yarn and S_{fibre} is the average cross-sectional area of the fibre, calculated from its average diameter measured by laser diffractometry.

2.3.4. Elemental analysis

Elemental analyses were performed by the "Service Central d'Analyse du CNRS" (Vernaison, France). No particular care was taken to handle the products, except cellulose precursor and samples heated at 285°C that were packed in sealed bottles under argon, after degassing under reduced pressure (100 Pa) to eliminate gazes adsorbed onto the fibres. For samples heated above 285°C the results include the gases adsorbed onto the fibres.

2.3.5. Solid-state ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C NMR)

The spectra were recorded on a Bruker DPX 400 spectrometer at 100.6 MHz from powdered samples put into a zircone probe (I.D. 4 mm), using cross polarisation (CP) technique and magic angle spinning (MAS) between 6 and 8 kHz.

3. Results and discussion

Notation: the rayon yarn, the organosilicon compound and the yarn impregnated with the organosilicon compound are referred to as CEL, ADD and CEL/ADD respectively.

3.1. Thermogravimetric analysis

TGA analyses of the precursor CEL and the additive ADD showed that rayon decomposed between 250 and 400°C, and the additive above 400°C. However, it is not ruled out that one could influence the degradation of the other when CEL/ADD yarns are pyrolysed. The TGA curve of the CEL/ADD yarn is almost the same as for cellulose CEL (Fig. 1). Their behaviours differ between 350 and 550°C, but the main decomposition area and the final mass losses are very similar. A possible interaction could be revealed by comparing the experimental TGA trace of CEL/ADD yarn to the calculated plot for a mixture CEL+ADD, built from the experimental curves of each constituent. This method has been previously used for mixtures of a microcrystalline cellulose with various pharmaceutical compounds [21]. In our case, the superposition of the two curves confirms that the presence of the additive at low concentration does not influence the mass loss of the rayon CEL (Fig. 2).

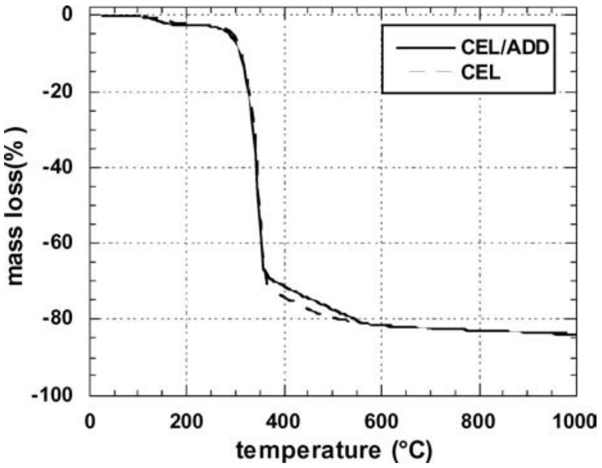

Figure 1 TGA traces of CEL and CEL/ADD yarns.

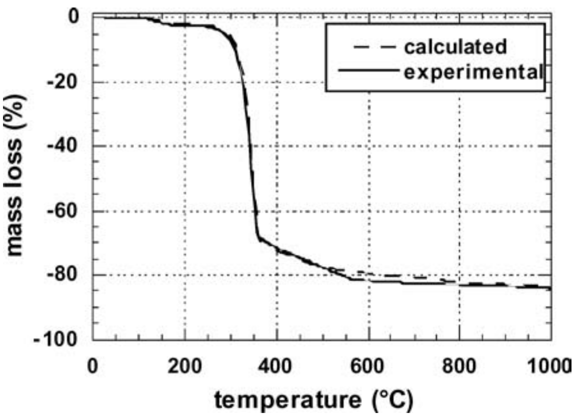

Figure 2 Experimental and calculated TGA plots of CEL/ADD yarn.

3.2. Evolution of the mechanical properties of fibres and yarns during carbonisation

Figs 3 and 4 present the tensile strengths of the rayon fibres and yarns that were pyrolysed with or without additive. Two effects of the additive are clearly identified. First, its presence prevents the mechanical resistance of carbon yarns from collapsing. Secondly, it significantly improves the tensile strength of fibres after the carbon residue is formed. Table I shows the mechanical properties of ex-CEL and ex-CEL/ADD fibres and yarns pyrolysed at 1200°C that illustrate this double effect of the additive.

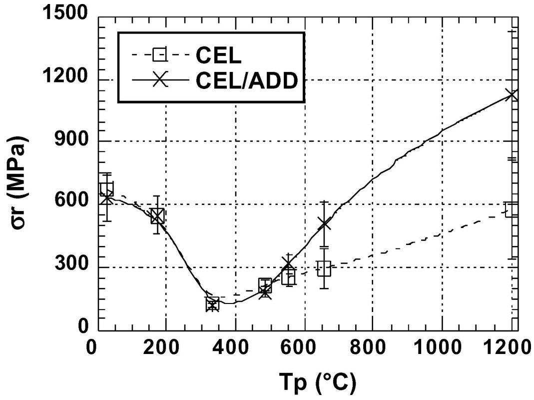

Figure 3 Variation in the tensile strength of fibres (σ_r) during the thermal treatment.

TABLE I Mechanical characteristics of fibres and yarns

	Fibre			Yarn			
	E (GPa)	σ_r (MPa)	m	F_{max} (N)	R_{max} (cN·tex^{-1})	γ (%)	σ_{max} (MPa)
ex-CEL	38 (4)	663 (235)	2.8	2.3 (0.6)	2.7 (0.8)	68.2 (10.0)	126 (4)
ex-CEL/ADD	40 (5)	1126 (305)	5.1	42.4 (2.5)	50.1 (2.9)	25.5 (0.3)	1093 (72)

Standard deviation in brackets.

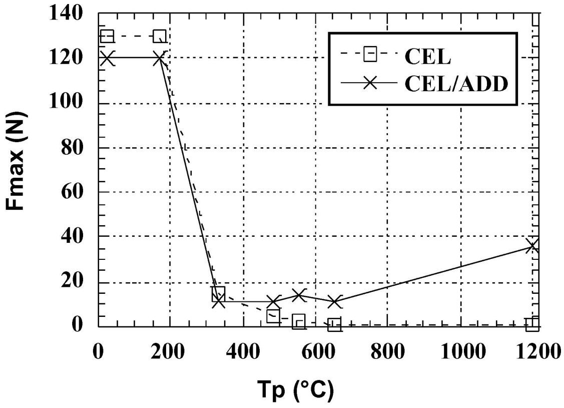

Figure 4 Variation in the maximum load supported by the yarn (F_{max}) during the thermal treatment.

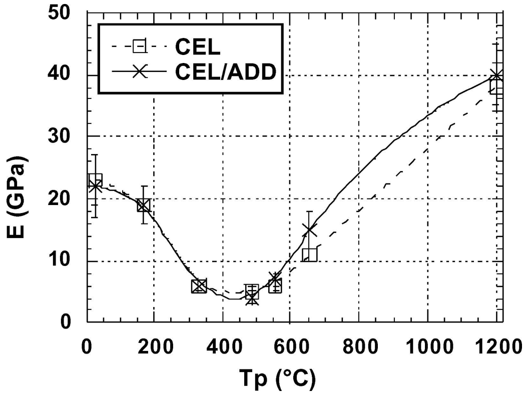

Figure 5 Variation in the modulus (E) during the thermal treatment.

The ex-CEL/ADD fibres exhibit an average tensile strength twice as high as ex-CEL fibres carbonized without additive [22]. The increase of the values is associated with a reduction of their dispersion (Weibull modulus m). The better resistance (R_{max}) of the ex-CEL/ADD yarn, compared to the ex-CEL yarn, is related to a decrease of the number of broken fibres in the yarn before the mechanical test (γ), and to an increase of the maximal stress σ_{max}.

Fig. 5 shows that the organosilicon compound has no influence on the evolution of the modulus of fibres. The increase of the tensile strength can be related to a reduction of the size of the surface flaws that cause failure. This surface effect of the additive, which does not modify the carbon of the bulk and so, does not modify the modulus of the fibre [23].

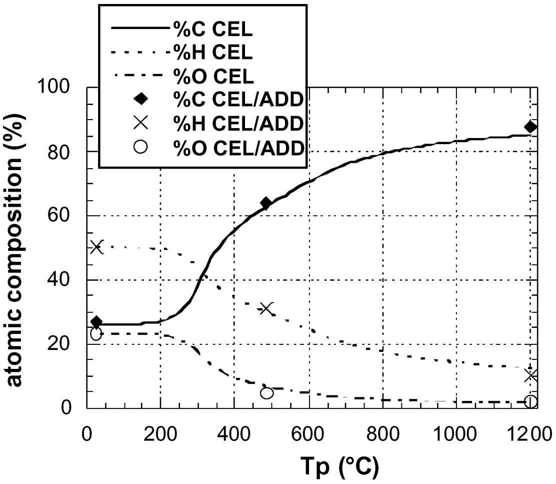

Figure 6 Changes in the relative elemental composition of CEL and CEL/ADD yarns during the thermal treatment.

3.3. Evolution of the chemical properties of the fibres and yarns during carbonisation

The changes in the relative C/O/H composition of the CEL yarns throughout the thermal treatment are presented in Fig. 6. From $T_p = 250°C$, a progressive increase in the carbon content was observed. The relative C/O/H amounts in the CEL/ADD yarns (crude or treated at 200 and 485°C) are brought together in Fig. 6. It appears that the presence of the additive has no influence on the elemental composition of the residue when rayon is pyrolysed.

The ^{13}C NMR spectra of the rayon yarns CEL heated at various T_ps are presented in Fig. 7. In the spectrum of crude cellulose, signals of carbon nuclei of the elementary glucopyranose units are observed in the region 60–120 ppm [24, 25]. The changes in the spectra of the solid residue during the thermal treatment are in agreement with the experimental results [6] and the mechanisms of transformation of cellulose into carbon [4, 7, 9, 26] reported in the literature. Dehydration of glucopyranose units is denoted by new massifs around 130 ppm (characteristic of ethylenic carbon atoms) and 170–180 ppm (carboxylic or carbonyl groups). Then, the increasing of the massif centred at 130 ppm demonstrates the formation of the carbon network. ^{13}C NMR spectra show no significant difference in the evolution of massifs attributable to pyrolysed cellulose when heated in the presence of the additive (Fig. 8). An additional signal appears around 0 ppm, assigned to

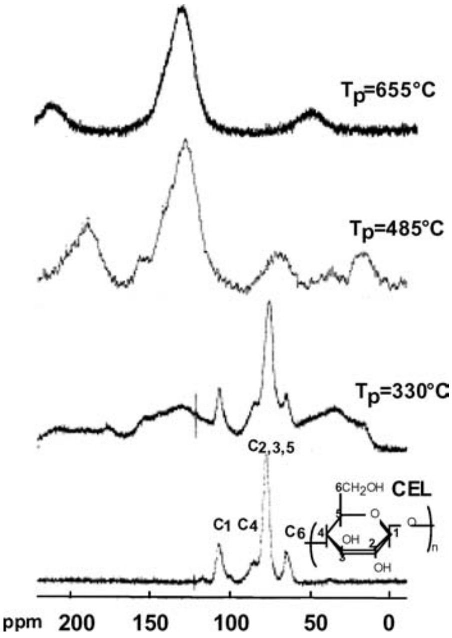

Figure 7 ^{13}C CP/MAS NMR spectra of CEL yarn heated at different temperatures.

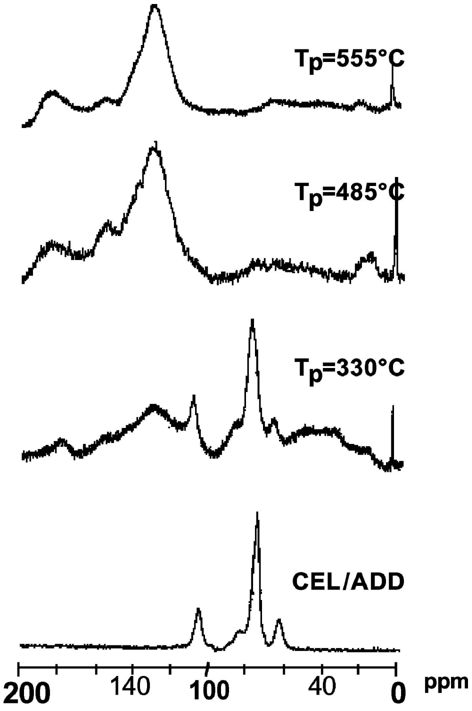

Figure 8 ^{13}C CP/MAS NMR spectra of CEL/ADD yarn heated at different temperatures.

carbon atoms bound to silicon (M and D units). It is not observed in the spectrum of the crude CEL/ADD yarn, because the additive is present at low concentration (a few mass%). Afterwards, as cellulose degrades before the additive, the relative proportion of C–Si bonds increases in the sample. The signal at 0 ppm is still present in the spectrum of the yarn heated at 555°C. TGA analyses show that the mass loss of the additive is less than 50% at this temperature.

Elemental analyses and solid-state NMR spectroscopy show that the presence of the additive does not cause significant changes in the evolution of the pyrolysis residue of the rayon CEL. These results are in agreement with the TGA conclusions (the low concentration of the additive does not influence the mass loss of the rayon), and are coherent with the interpretation of the effect of the additive on the mechanical properties (a surface modification that does not modify the bulk of the fibre).

4. Conclusion

The study of rayon yarns pyrolysed at increasing temperatures, in the presence or not of an organosilicon compound, led to observe important differences in the ultimate mechanical properties of the materials. Thus, without the additive, the carbonisation of the yarns led to a collapse of their tensile strength whatever the heating rates. On the other hand, when the yarns were heated in the presence of the additive under fast heating rate conditions (a few $^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$), the final materials obtained at $T_\mathrm{p} = 1200^{\circ}\mathrm{C}$ exhibited σ_r values around 1100 MPa. These values are about twice as high as those of fibres obtained according to a conventional pyrolysis process using slow heating rates. As an example, the WYB fibres exhibit σ_r values of 620 MPa [26]. Moreover, the use of an organosilicon compound enhanced significantly the fracture properties of the resulting carbon fibres, even when using fast thermal cycles. The role of the additive is mainly to reduce the size of the critical surface flaws that cause failure. Interestingly, this new route for the preparation of carbon fibres and yarns did not result in any appreciable change, neither in the chemical behaviour, nor in the chemical composition of the fibres.

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