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Self-reinforced composites obtained by the partial oxypropylation of cellulose fibers. 1. Characterization of the materials obtained with different types of fibers

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ABSTRACT

The in-depth oxypropylation of different types of cellulose fibers, namely Avicel, Rayon, Kraft, and Filter Paper, was investigated. New biphasic mono-component materials were obtained, which could be hot-pressed to form films of cellulose fibers dispersed into a thermoplastic matrix. The success of this chemical modification was assessed by FTIR spectroscopy, X-ray diffraction, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis and contact angle measurements. The optimization of this process led to the establishment of the optimal molar ratio between the cellulose OH groups and propylene oxide, which varied as a function of the specific morphology of the fibers.

1. Introduction

The interest in cellulose fibers as reinforcement agents in composite materials with polymer matrices has increased dramatically in the last decade, as detailed in recent reviews (Belgacem & Gandini, 2005, 2008, in press; Dufresne, 2008). The main reasons associated with this upsurge are their renewable and ubiquitous character, good mechanical properties, low density, low cost and recyclability. Given the highly polar character of cellulose, the incorporation of these fibers in composites with non-polar matrices like polyolefins, requires a chemical modification of their surface in order to improve their interfacial adhesion to the matrix and minimize their moisture uptake, i.e. preserve their mechanical strength. The numerous strategies implemented to achieve these goals have also been thoroughly reviewed (Belgacem & Gandini, 2005, 2008, in press; Dufresne, 2008).

Two alternative approaches have been put forward in recent years aimed at using cellulose fibers as the sole precursors for such composites, i.e. to generate a matrix which is either precipitated, or chemically modified cellulose. The former strategy implies the use of pristine cellulosic materials and calls upon the construction of the composite by either the partial dissolution of the fibers, followed by film casting to provide the cellulosic matrix (Gindl & Keckes, 2005, 2007), or the preparation of a cellulose solution to which appropriate insoluble crystalline fibers are added and thereafter coagulating the two-phase material (Nishino & Arimoto, 2007; Nishino, Matsuda, & Hirao, 2004; Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008; Soykeabkaew, Arimoto, Nishino, & Peijs, 2008). The latter approach is different in that it is based on the chemical modification of the outer shell of the fibers by esterification (Mutsumura & Glasser, 2000; Mutsumura, Sugiyama, & Glasser, 2000; Freire, Silvestre, Neto, Belgacem, & Gandini, 2006; Freire et al., in press) or etherification (Lu, Zhang, Rong, Shi, & Yang, 2003; Lu, Zhang, Rong, Yue, & Yang, 2004a, 2004b; Zhang, Rong, & Lu, 2005) in order to create a thermoplastic sleeve which allows a continuous composite film to be hot-pressed. The interest of these alternative strategies is related to the fact that the natural fibers are now exploited as the source of both the matrix and the reinforcing element.

Our contribution to this novel approach called upon a chemical modification which had been first studied by one of us in terms of the bulk transformation of various natural polymers through their total oxypropylation which turned them into viscous polyols (Gandini & Belgacem, 2008). Its application in a controlled and limited fashion to cellulose fibers (Gandini, Curvelo, Pasquini, & de Menezes, 2005), and later to starch granules (de Menezes, Pasquini, Curvelo, & Gandini, 2007), was described succinctly and shown to generate precisely the morphologies described above, namely the creation of a thermoplastic sleeve around the unmodified inner cores of the fibers and granules, which allowed the processing of the corresponding single-component composites.

The present investigation deals with a detailed study of the partial oxypropylation of cellulose fibers, with special emphasis on its optimization with respect to the formation of the composite and on the role of different pristine and regenerated substrates.

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2. Experimental

2.1. Substrates and their oxypropylation

The cellulose substrates used in this work were Avicel microfibers (AV) (Sigma–Aldrich), Regenerated Rayon fibers (RY) (kindly provided by Cermav-Grenoble/France), Kraft Pulp (KR) (Votorantin Celulose e Papel) and Filter Paper (FP) (Hexis). The procedure for their partial oxypropylation consisted in impregnating ~2 g of a given cellulose sample with an ethanol/KOH solution ([KOH]/[cellulose OH] ~0.1) which was then left for ~12 h before evaporating the ethanol. Thereafter, the thus activated cellulose was soaked with commercial propylene oxide (PO, ACROS) under nitrogen in a 100 ml stainless steel autoclave. The variable explored in these reactions was the [PO]/[cellulose OH] molar ratio, viz. 1, 3 and 5 and the corresponding oxypropylated samples were identified as PO1, PO3 and PO5.

The closed autoclave, equipped with a manometer, a calibrated temperature measuring thermocouple and a controlled heating system, was then heated to the desired temperature (135 °C for AV, KR and FP, and 150 °C for RY), while monitoring the corresponding pressure increase. In some systems, the onset of the oxypropylation reaction was revealed by an increase in both temperature and pressure, and its final stage was associated with the system returning to atmospheric pressure, indicating the total consumption of PO. Since in some instances the reaction was too slow to generate a detectable temperature increase, the reaction time became the relevant parameter in terms of the extent of PO conversion. At the end of all the reactions, the autoclave was allowed to return to room temperature before opening it and removing the ensuing materials which were then submitted to a soxhlet extraction with *n*-hexane in order to remove the PO homopolymer (PPO) accompanying the oxypropylated fibers (Pavier & Gandini, 2000). This operation was carried out with the specific purpose of assessing the behavior of the different systems tested in terms of relative contribution of both reactions, but was not necessary in the context of the actual use of the composites, since we found that modest amounts of PPO did not modify their basic features.

The materials obtained were characterized by weight gain, content of PO homopolymer, and the additional techniques described below.

Fourier transformed infrared (FTIR) spectra were recorded in KBr pellets (1:100 w/w) with a BOMEN-MB102 spectrometer. Since the preparation of the pellets required grinding, the fibers were partially fragmented, but this operation did not influence the overall evolution of the spectra as a function of the oxypropylation conditions.

X-ray diffraction (XRD) diffractograms were recorded with a Carl-Zeis-Jena–UDR6 diffractometer. The scattered radiation was detected in the angular range of 5–40° (2θ) at a speed of 2° min^{-1}. The crystallinity index (*CI*) was estimated by the height ratio between the diffraction peaks in I_{CR} ($2\theta = 22–23°$ for cellulose type I and $2\theta = 18–22°$ for cellulose type II) for the crystalline phase, and I_{AM} ($2\theta = 18–19°$ for cellulose type I and $2\theta = 13–15°$ for cellulose type II) for the amorphous counterpart. This approach was utilized considering two-phase models for these materials (Hermans & Weidinger, 1948, 1949, 1951; Thygesen, Oddershede, Lilholt, Thomsen, & Stahl, 2005), using the standard relationship

$$CI = [(I_{CR} - I_{AM})/I_{CR}] \times 100$$

Differential scanning calorimetry (DSC) thermograms were obtained in a nitrogen atmosphere using a Shimadzu-TA-50WSI analyzer at a scanning rate of 10 °C min^{-1} between −100 and 180 °C.

Thermogravimetric analyses (TGA) were conducted in a nitrogen atmosphere with a Shimadzu-TA-50 analyzer, working in the temperature range of 25–1000 °C and a heating rate of 20 °C min^{-1}.

Contact angle measurements were carried out with an OCA–Dataphysics Contact Angle System using two liquids of very different polarity, viz. water and diiodomethane. The dispersive and polar contributions to the surface energy of each tested sample were obtained using the approach proposed by Owens and Wendt (1969).

Scanning electron microscopy (SEM) images were obtained with a Leo Scanning Electron Microscope after the conventional vacuum coating the fibers with a gold film.

3. Results and discussion

The oxypropylation reaction initiated from the OH groups present in natural polymers (solid substrates) consists in their activation with a Brønsted or Lewis base. The oxianions thus generated induce the anionic polymerization of PO through a "grafting from" process that is always accompanied by some PO homopolymerization arising from chain transfer reactions (Gandini & Belgacem, 2008).

As expected, all the products extracted with *n*-hexane displayed the typical FTIR, DSC and ^{1}H NMR features of PPO macrodiols (data not reported here). The number-average molecular weights of these oligomers ranged between 400 and 1000, which agree with previous studies carried out on other substrates (Gandini & Belgacem, 2008).

Fig. 1 shows the FTIR spectra of the RY samples before and after modification by partial oxypropylation (RYPO1, RYPO3 and RYPO5) and after the removal of the PO homopolymer. The relevant features here are (i) the overall absorption increase in the aliphatic CH stretching region (2800–3000 cm^{-1}), with the appearance of a new peak around 2970 cm^{-1}, associated with the methyl groups of the grafted propylene oxide units; (ii) the increase and shift in absorption in the C—O stretching region (1000–1100 cm^{-1}), associated with the ether moieties borne by those same units; and (iii) a new peak at 1375 cm^{-1}, confirming the presence of CH_3 groups. Another relevant feature of these spectra is the relative increase in intensity related to these new peaks as a function of the extent of oxypropylation. The same trends (spectra not shown here) were observed for all the other cellulose substrates before (AV, KR and FP) and after the modification (AVPO1, AVPO3, AVPO5, KRPO1, KRPO3, KRPO5, FPPO1, FPPO3 and FPPO5).

Table 1 gives the values of weight gain registered in all the experiments. At low [PO]/[cellulose OH] ratio, i.e. PO1, the weight gain for the FP and KR samples was higher than that for the AV and RY counterparts. Given the fact that the former substrates dis-

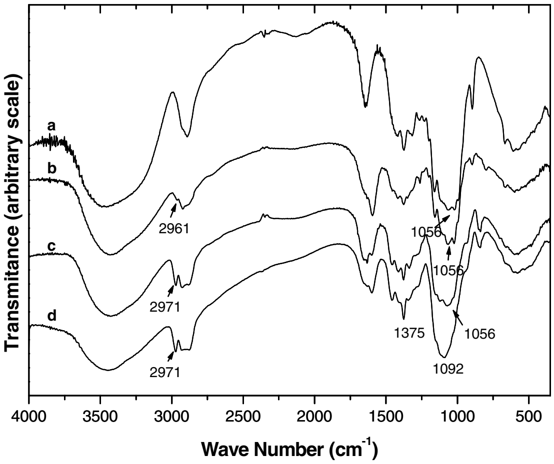

Fig. 1. FTIR spectra (KBr pellets) of cellulose samples (a) RY, (b) RYPO1, (c) RYPO3, and (d) RYPO5, after extraction of the PO homopolymer with *n*-hexane.

Table 1
Weight gain values for the different cellulose substrates versus the [PO]/[cellulose OH] molar ratio employed in the oxypropylation reactions.

Samples	Weight gain (%)		
	PO1	PO3	PO5
AV	8.1	43.4	188.0
FP	56.8	58.7	58.6
KR	31.5	55.1	57.1
RY	8.1	104.1	106.2

Table 2
Values of the crystallinity index (CI) estimated for the different cellulose substrates versus the [PO]/[cellulose OH] molar ratio employed in the oxypropylation reactions.

Samples	Crystallinity index (%)			
	Unmodified	PO1	PO3	PO5
AV	92	92	74	28
FP	85	85	80	25
KR	84	76	78	61
RY	90	83	75	48

played a lower CI than the latter ones (Table 2), this result was to be expected since, as with all heterogeneous chemical reactions of cellulose, the initial oxypropylation occurred preferentially at the amorphous regions. With increasing [PO]/[cellulose OH] ratio, the crystalline regions of RY and AV were also progressively attacked, as shown by their corresponding substantial increase in weight gain (Table 1). The much higher value observed for AV at PO5, was accompanied by a visual degradation of the fiber structure, which was confirmed by the corresponding SEM images.

Fig. 2 shows the X-ray diffractograms of the rayon cellulose samples before (RY) and after oxypropylation reactions carried out with different [PO]/[cellulose OH] ratio (RYPO1, RYPO3 and RYPO5). The changes in the X-ray pattern were attributed to the progressive decrease in the proportion of crystalline cellulose and the corresponding increase in the amorphous oxypropylated material. The same behavior was observed with the other substrates, as clearly evidenced in Table 2. In conclusion, the highest [PO]/[cellulose OH] ratio of 5 was too severe in the case of most systems, in terms of an excessive extent of oxypropylation, i.e. it left an insufficient amount of cores of crystalline fibers to insure a proper composite morphology.

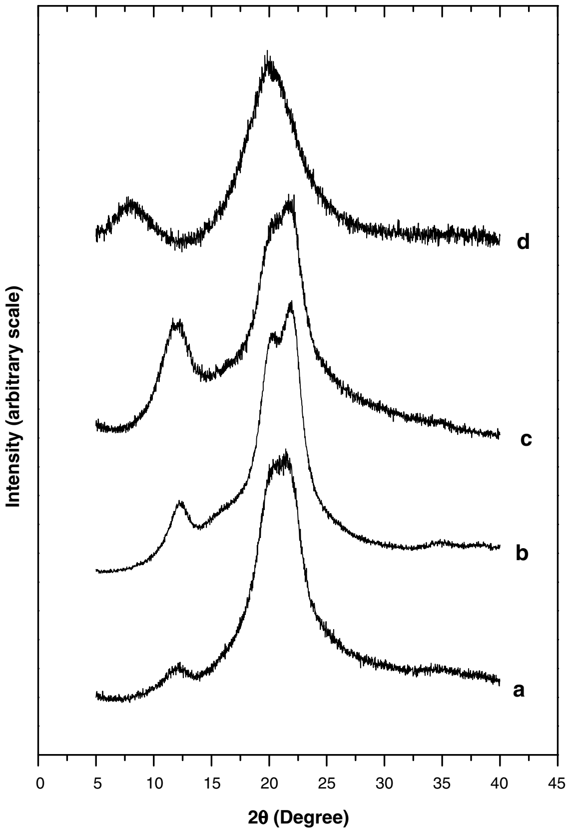

Fig. 2. X-ray diffraction patterns of cellulose samples (a) RY, (b) RYPO1, (c) RYPO3, and (d) RYPO5.

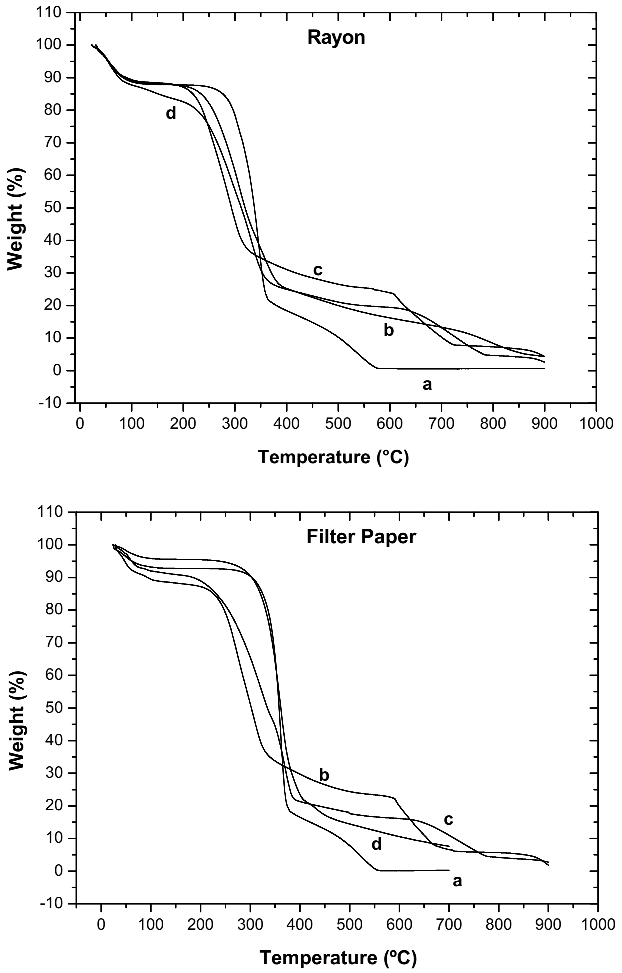

Fig. 3. TGA curves of (a) unmodified RY and FP cellulose samples, and modified samples (b) RYPO1 and FPPO1, (c) RYPO3 and FPPO3, and (d) RYPO5 and FPPO5.

Table 3 gives the relevant thermal behavior of all the samples expressed as the temperature at which they lost 2% of their weight, apart from the first weight loss, observed between room temperature and 130 °C, which was attributed to evaporation of residual moisture. Whereas up to a [PO]/[cellulose OH] ratio of 3 the oxy-

Table 3
Temperature corresponding to 2% weight loss in the degradation of the different cellulose samples, before and after oxypropylation, as detected by TGA.

Samples	Temperature at 2% weight loss (°C)			
	Unmodified	PO1	PO3	PO5
AV	316	204	200	169
FP	297	211	200	271
KR	276	183	125	256
RY	268	208	141	225

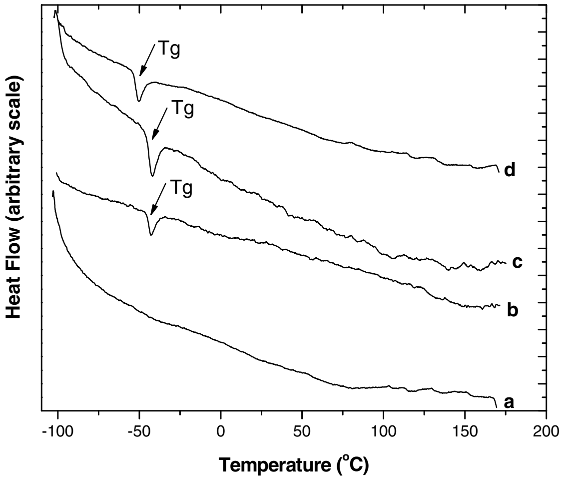

Fig. 4. DSC curves of cellulose samples (a) FP, (b) FPPO1, (c) FPPO3, and (d) FPPO5.

Table 4
Surface energy components (mJ m^{-2}) of the cellulose samples before and after oxypropylation, calculated by contact angle measurements.

Sample	γ_S^p	γ_S^d	γ_S
AV	31.3	28.1	59.4
AVPO1	33.1	27.4	60.5
AVPO3	25.0	30.8	55.8
AVPO5	4.5	48.1	52.6
FP	29.6	26.2	55.8
FPPO1	28.2	27.9	56.1
FPPO3	23.3	31.3	54.6
FPPO5	4.4	46.5	50.9
KR	20.4	33.6	54.0
KRPO1	20.2	30.6	50.8
KRPO3	9.5	39.7	49.2
KRPO5	5.7	46.6	52.3
RY	24.1	30.8	54.9
RYPO1	26.9	26.1	53.0
RYPO3	17.8	32.8	50.6
RYPO5	4.4	46.5	50.9

propylated materials displayed a progressively lower degradation temperature (Fig. 3), associated with the grafted macromolecules, at a ratio of 5, the behavior became erratic, with the exception of the AV samples which followed a continuous trend. The reasons for the irregular features are unclear and require further study.

Fig. 4 shows the DSC curves for the Filter Paper samples before (FP) and after (FPPO1, FPPO3 and FPPO5) oxypropylation. As expected, the pristine cellulose did not display any glass transition, whereas for the corresponding oxypropylated samples a Tgs between −55 and −45 °C were recorded, essentially independent of the [PO]/[cellulose OH] ratio. This behavior was already observed with different polysaccharides grafted with PPO chains (de Menezes et al., 2007; Gandini et al., 2005; Schoenenberger, Le Nest, & Gandini, 1995; Velazquez-Morales, Le Nest, & Gandini, 1998) and has been interpreted as reflecting the glass transition of the appended polyether chains, without any substantial contribution from the polysaccharide trunk macromolecules.

Table 4 gives the surface energy (γ_S) components calculated from the corresponding contact angles formed by the droplets of the two testing liquids deposited at the surface of the different cellulose samples (pellets of AV, KR, FP and RY) and of their respective oxypropylated films. The dispersive component, γ_S^d, did not change in any univocal direction for samples prepared with [PO]/[cellulose OH] ratios up to 3, but increased considerably when this ratio reached 5. The different morphology of these materials, associated with an excessive fiber modification

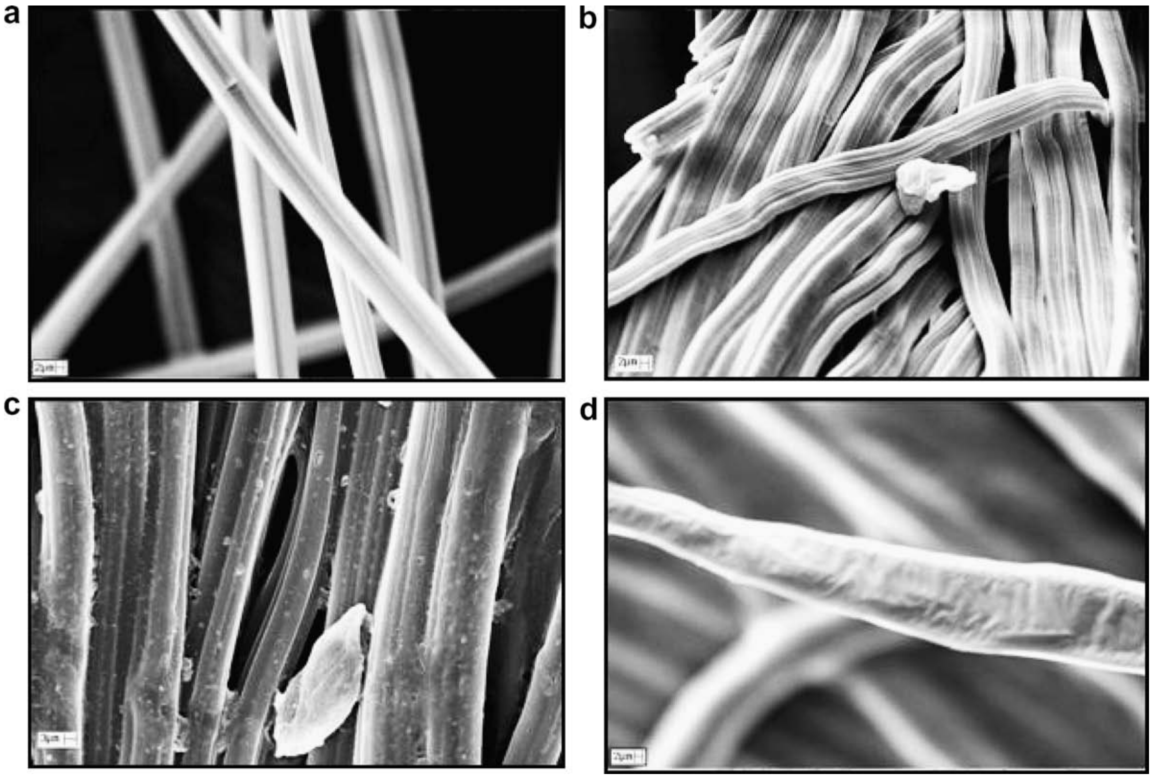

Fig. 5. SEM micrographs of cellulose samples (a) RY, (b) RYPO1, (c) RYPO3, and (d) RYPO5 (magnification 3000×).

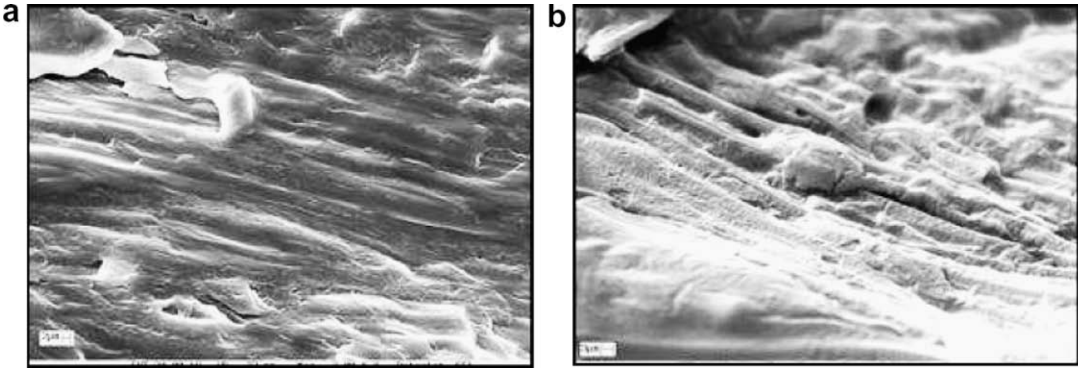

Fig. 6. SEM micrographs of the hot-pressed samples (a) RYPO3 and (b) RYPO5 (magnification 3000×).

could have generated a correspondingly different surface roughness affecting the contact angle measurements. This point requires further investigation. The polar counterpart, $\gamma_S{}^P$, decreased with the extent of oxypropylation, particularly with the higher [PO]/[cellulose OH] ratios. This trend is in tune with the lower polar character of PPO, as compared with that of cellulose. The increase in hydrophobic character represents a positive feature in terms of the lower aptitude of these composites to absorb atmospheric moisture.

All the samples were inspected by SEM, the pristine substrate in their fibrous form and the oxypropylated counterparts both as they were recovered after the *n*-hexane extraction and after being hot-pressed for 3 min at 135 °C. Fig. 5 shows the thermoplastic sleeve generated around the modified RY cellulose fibers before hot pressing, compared with the "naked" morphology of the starting material. As the [PO]/[cellulose OH] ratio increased, this thermoplastic shell became progressively more blatant. Fig. 6 shows the micrographs of the RYPO3 and RYPO5 hot-pressed samples, which displayed the material continuity associated with the flow-joined sleeves and the presence within this matrix of the unmodified inner core of the fibers. These features were more prominent with the higher [PO]/[cellulose OH] ratio.

Finally, the question of the preferential sites of oxypropylation deserves some comments. Two factors are relevant here, viz. on the one hand the well-known preferential reactivity of the primary hydroxyl groups of cellulose and, on the other hand, the fact that the amorphous microphases (cellulose II) of this substrate are obviously more prone to be modified than their crystalline counterparts (cellulose I), as clearly shown by the X-ray patterns and the corresponding variations in the CI values.

4. Conclusions

Self-reinforced composites in which the oxypropylated outer sleeve of cellulose fibers generate the matrix upon hot pressing, leaving their inner core to act as reinforcing elements, were shown to be readily prepared using a variety of substrates. The interest of this process resides not only in the novel exploitation of renewable resources, but also in its green connotation, since it does not require the use of solvents nor the application of any processing operation, given the fact that the final product is ready for further exploitation as it is removed from the reactor. Work is in progress to assess the mechanical properties of these novel materials.

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