

COMPOSITES FROM KERATIN BIOFIBERS. STUDY OF COMPATIBILITY USING POLYOLEPHINIC MATRICES.

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Keywords: Chicken feathers, Renewable Resources, Mechanical Properties, FTIR.

Abstract

The study deals with the analysis and characterization of chicken feathers (CFs) based thermoplastic composites. The performance of the composite has been characterized in terms of mechanical properties which have been related to the fibre-matrix compatibility of the composite components analyzed by FTIR and SEM. The results have shown that the addition of short CFs as a filler to the PP thermoplastic matrix did not significantly improve the mechanical properties. A slightly increase of the stiffness has been observed when using small quantities of CFs (5-10% v/v) that provides to the composites a more brittle behaviour. Analogous behaviour has been observed for HDPE/CFs composites. FTIR spectroscopy and SEM micrographs analyses show limited compatibility between the composite components (CFs and polyolephinic matrices).

1 Introduction

Chicken feathers (CFs) are an interesting biogenic material, constituted of keratin and other minority components [1]. Nowadays about 800,000 tons of CFs waste are produced annually in Europe [2] which are processed as a waste according to the requirements established in the European Directive [3]. This regulation permits only few uses for CFs including incineration, composting and hydrolysis for pet food production processes. These treatments transform CFs waste into materials of low added value so that the search for alternative processing method and applications which could valorise renewable CFs waste as a second raw material would be very interesting. In this regard, one potential solution is to process the CFs waste to obtain an useful technical material that could potentially be used to manufacture composites, taking advantage of their unique properties such as low density, biodegradability and good thermal and acoustic properties [4, 5, 6].

Pretreated keratin fibres (KF) obtained from chicken feathers (CFs) have been used to manufacture composites materials with improved mechanical, thermal and acoustic properties [7, 8]. The properties and development of these materials are influenced by the compatibility between the composite components since the fibre-matrix interaction can significantly influence the final macroscopic properties of the composite product. In this regard, the use of CFs could be an advantage since better interaction with polymeric matrices can be achieved [4] due to the combined hydrophilic and hydrophobic character of CFs resulted from their chemical nature [1].

In this study properties of composites based on CFs and thermoplastic matrices of HDPE and PP are studied and characterized. Macroscopic results are related to the microstructure of the fibre-matrix interface and the possibilities of establishing interactions between matrix and reinforcement has been studied.

2 Experimental

2.1. Materials

High-density polyethylene (HDPE) with a melt flow index of 1.35 g/min and density of 960 kg/m³ and Polypropylene with a melt flow index of 1.15 g/min and density of 913 kg/m³ were used. CFs were collected from a waste management Spanish company.

2.2 Preparation of composite materials

CFs were first washed in a bath at 25°C containing 6,75 g/l of a cationic antibacterial surfactant (Tetranyl BC-80, Kao Corporation S.A., Spain) with a 40/1 (v/w) liquor ratio for 60 minutes to clean and sanitize the fibres. After that, the CFs fibres were rinsed with deionised water and dried in an air oven at 60 °C for 48 h. Deionised water was used in all procedures.

With the aim to homogenize particle size, cleaned CFs were chopped with a grinder machine (Moulinex 1000 W, France) until each particle size was 20mm or less.

CFs were air-dried at 105°C for 4 hours and kept under dry atmosphere (dessicator) before composite fabrication.

Composite specimens were obtained by mixing the previously ground and dried CFs with HDPE and PP matrices. Seven compositions have been studied: 5, 10, 15, 20, 25, 30 and 35 % fibre volume fraction (v/v), and controls of neat HDPE and PP were used as references. The components were mixed using a Brabender mixer type W 50 EHT PL (Brabender® GmbH & Co. KG, Germany) heated at 170 °C and 155 °C for PP and HDPE, respectively. The HDPE and PP matrices were melted for a minute and then, the fibres were added and mixed for another 5 min. The blend was then consolidated at 100 kN and 185°C (PP) and 155(for HDPE based composites) for 5 min in a Collin Mod. P 200E (Dr. Collin GmbH, Germany) hot plates press forming square plates, measuring 150 x 150 x 3 mm³. The cooling process was carried out under pressure using cool water until room temperature.

Test samples were properly shaped according to the ASTM 412 specifications to carried out tensile test measurements.

2.3. Mechanical testing

Tensile tests were carried out in a Instron 3366 (Instron, UK) universal machine following the specifications of the ASTM-D-638-84. Speed of the test was set at 20 mm/min and temperature and relative humidity were 23 ± 2 °C and 50 ± 5%, respectively. From load versus displacement test curves, Young's modulus, tensile strength, elongation at break and toughness were calculated using Bluehill version 2 software. Four replicate specimens were analysed, and average and standard deviation were calculated.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) microphotographs of surfaces of composites samples were taken to qualitatively examine the fracture surface of the broken samples to study the fibre/matrix compatibility. The photographs were taken in a JEOL 5610 (JEOL, USA) scanning electron microscope at the accelerating voltage of 10 kV. Previously the samples were coated with a 15 nm layer of gold-palladium in order to increase their conductivity.

2.5. FTIR analysis

Fourier transform infrared (FTIR) spectra were obtained by means of a Nicolet Avatar spectrometer with CsI optics. Samples of the powdered composite were ground and dispersed in a matrix of KBr (9 mg finely divided composite in 300 mg KBr), followed by compression

at 167 MPa to consolidate the formation of the pellet. FTIR spectra were collected in the range of 4000 – 650 cm⁻¹ with 40 scans and a resolution of 4 cm⁻¹.

3 Results and discussion

3.1 Mechanical properties

Tensile strength values (figure 1) show a moderate decrease in both composite materials (mainly in PP/CFs). In all compositions, HDPE matrix produces slightly poorer tensile strength values than the PP matrix.

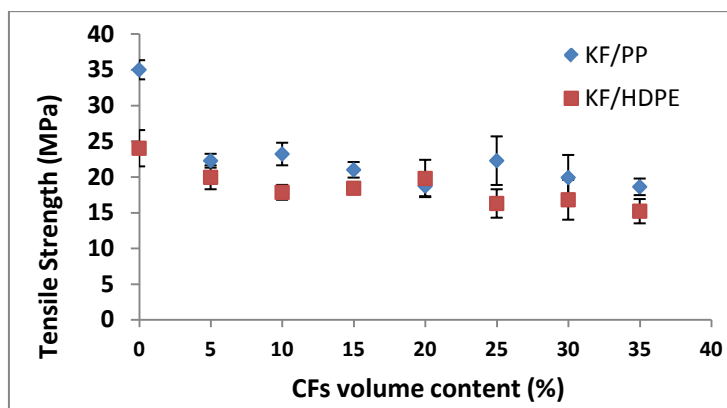


Figure 1.-Tensile Strength values as a function of CFs content.

The evaluation of the results of tensile strength as a function of the content of CFs, did not show significant difference in the behaviour of composites with a content comprised between 5-35 % v/v. The main decrease (up to 42%) is observed when adding only a 5% of CFs in case of the PP matrix. The decrease using the HDPE matrix reinforced with 5% of CFs is smaller, about 16%.

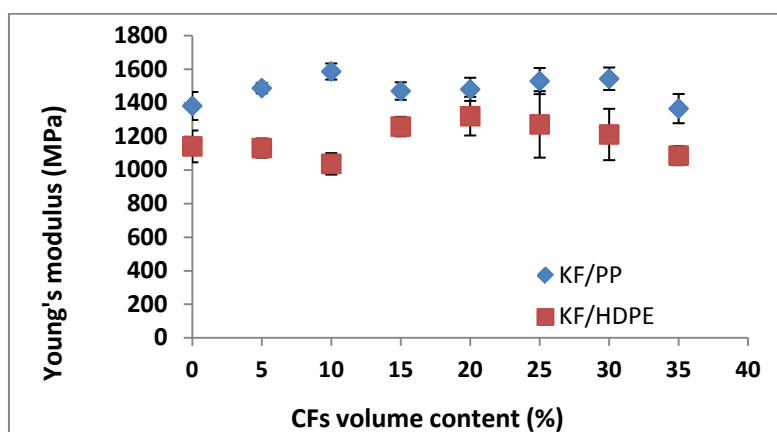


Figure 2.- Young's Modulus values as a function of CFs content

Figure 2 shows the evolution of Young's Modulus as a function of CFs content. In this case, all compositions of the CFs/PP composite show a higher value compared to neat PP matrix, being stiffness generally improved. Values obtained for the CFs/HDPE composite material are lower. The highest modulus values are achieved at 10% of CFs in case of PP matrix and at 20% for HDPE.

Toughness and elongation at break values are shown in figure 3 and 4. Both mechanical properties experience a drastic decrease with the presence of the CFs.

The values of toughness (figure 3) show an important drop when incorporating only a 5% of CFs (from 134 J to 2 J in CFs/PP and 118 J to 1.5 J in HDPE/CFs).

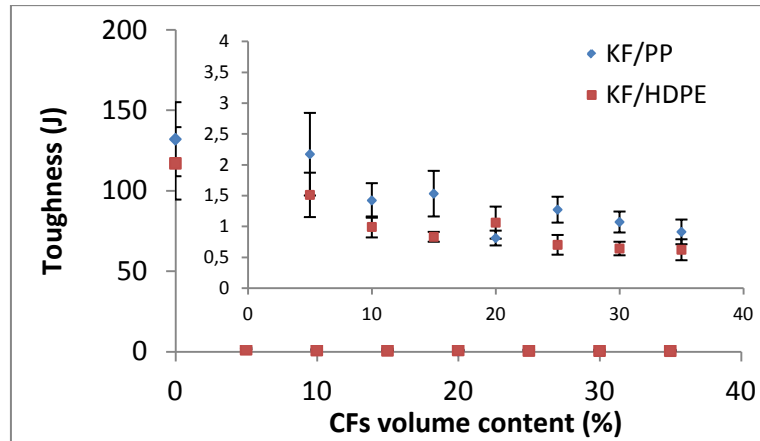


Figure 3. Toughness values as a function of CFs content.

Elongation at break also depends strongly of the addition of CFs fibres (figure 4). This property decreases significantly when incorporating a 5% of CFs (from 470% to 9% in PP/CFs and from 620% to 7.5% in HDPE/CFs). From 10 to 35% of CFs content the elongation at break values remain approximately constant.

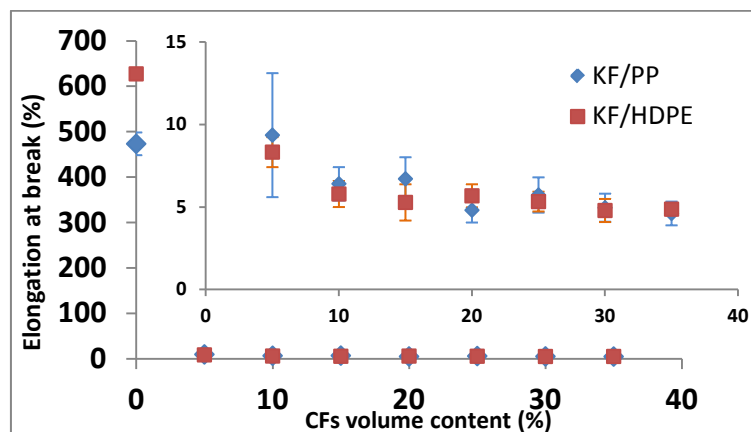


Figure 4. Elongation at break values as a function of CFs content.

In summary, the Young's Modulus of the polyolephinic composites is higher than neat PP for all the CFs contents. In case of the HDPE matrix is higher when compositions are higher than 10%. Toughness and Elongation at break are always lower than neat polyolephins when including CFs. The fact of including CFs, in concentrations high enough to collapse and agglomerate the composite and that have poor interfacial adhesion to the matrix produce a decrease of the mechanical properties in general.

In all cases the decrease of tensile strength, elongation and break and toughness are related to the lack of interfacial adhesion between the fibre-matrix components due to the different chemical nature of both components (more hydrophilic nature of CFs compared to the highly hydrophobic nature of the matrices). It was noticed that some properties as tensile strength are

more affected by the presence of CFs in case of PP than HDPE. As shown in figure 1, the decrease of tensile strength from the initial value for neat polymers produced by the inclusion of only a 5% of KF may be related to differences in the interfacial adhesion or as a consequence of the changes in the crystalline structures of the matrix that are disturbed by the presence of the CFs component. In this sense, HDPE seems to accommodate more easily the CFs than PP. On the other hand the higher values obtained in PP/CFs composites compared to HDPE/CFs are probably related to the differences in the behaviour of the matrix.

3.2 Scanning electronic microscopy of CFs thermoplastic composites

Two microphotographies depicting the fracture surface of the materials are shown at figure 5.

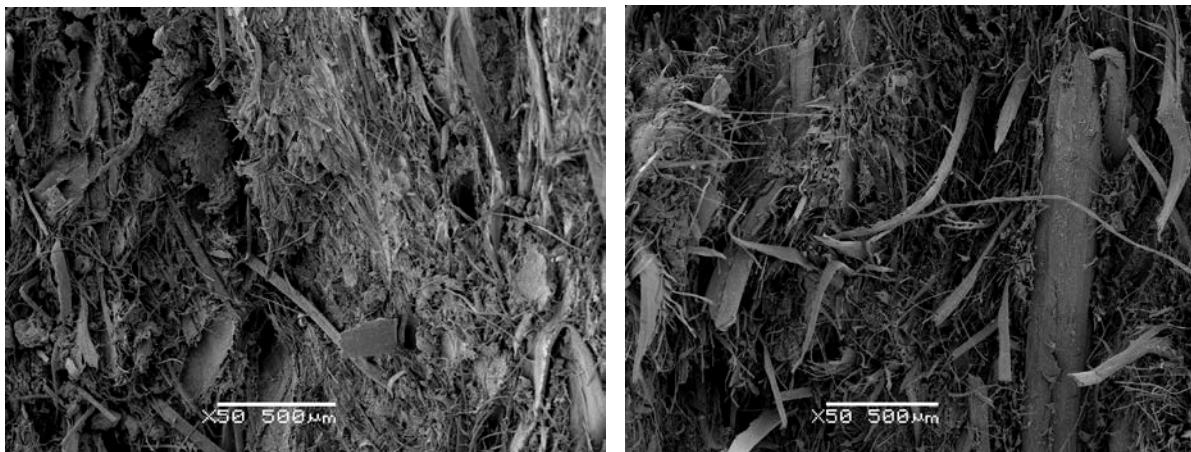


Figure 5. (a) PP/CFs and (b) HDPE/CFs composite fracture's surface.

The figure 5.a shows a sample containing PP/CFs with the presence of a great amount of heterogeneous fibres with different shapes and sizes that introduce a lot of cracks and pores. The fibres seem to be resting on the PP matrix, without being properly attached to it. On the other hand, the matrix has been strained and deformed plastically. Microphotography labelled as Figure 5.b show similar characteristics to the Figure 5.a, but in this case the matrix used is HDPE and the particle size of CFs fibres embedded in that particular area seem to be higher than in the previous case. In both cases the interaction between components of the composite is not good and there are many cavities around the CFs.

3.3 FTIR spectroscopic characterization

The spectroscopic study has been carried out by comparing the FTIR spectrum of a sample of both PP/CFs and HDPE/CFs composites with the FTIR spectrum obtained by the theoretical weighed addition of the 20% of CFs and 80% of PP and HDPE matrices. Differences observed between the experimental and the theoretical spectra are due to the changes of the vibration modes of the groups belonging to matrix and CFs polymer chains which are involved in interactions that produce a change in the frequency of vibration.

Table 1 shows the most significant representative absorption bands of the PP and CFs and their corresponding assignments. The groups related to these bands are amide I (1645 cm^{-1}), amide II (1537 cm^{-1}), methylene (1460 cm^{-1}), and methyl (1378 cm^{-1}). There are also three bands related to the configuration isomerism and conformational order characteristics of PP (812 , 901 , and 976 cm^{-1}) [9,10].

Wavenumber (cm ⁻¹)	Assignment	Component
1645	Amide I (C=O i NH)	CFs
1537	Amide II (C=O i NH)	CFs
1460	-CH ₂ -	PP
1378	-CH ₃	PP
1358	-CH ₃	Composite (PP)
1260	-CH ₂ -	Composite (PP)
1100	-CH ₂ -	Composite (CFs)
976 901 812	Iso-PP	PP

Table 1. FTIR absorption bands characteristic of PP and CFs.

Figure 6 compares the spectra of PP/CFs composites containing 20% of CFs and the spectra of their individual components: the pure polypropylene matrix and pure CFs fibres. Arrows shown in the figure point out the IR absorption bands involved in the interaction between both components. Simulated spectra of composites were obtained by the ponderated spectral addition of each component of the composite and are representative of a blend completely free of interactions.

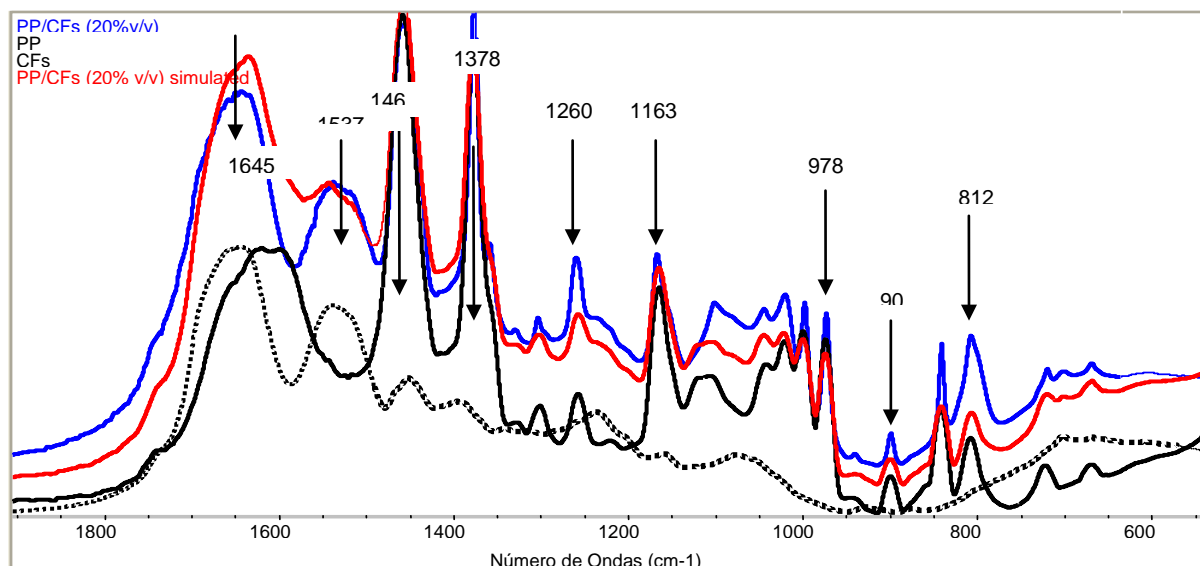


Figure 6.- Spectra of different samples: Composite PP/CFs (20% v/v), PP pure matrix, CFs filler and simulated PP/CFs (20% v/v).

Comparing both FTIR spectra, real and theoretical addition or simulated, some differences in the shape and intensity of the bands were observed. These differences between the theoretical addition and the real blend are representative of the reciprocal influence of one of the components on the other that produces changes in the vibration of the molecules [11].

In figure 7 (magnification of Figure 6) three special FTIR absorption bands are observed: 1358, 1260 and 1100 cm⁻¹. These bands belong neither to the CFs nor to the PP or simulated spectrum and only appear in the original PP/CFs(20% v/v) composite. As explained above, these bands are representative of the change in the environment of the dipoles of one component produced by the presence of the other. The spectral bands at 1358 cm⁻¹ and 1260 cm⁻¹ are due to structural changes, mainly conformational, generated by the interaction of the

two composite components and affecting at the $-CH_3$ and $-CH_2-$ groups of PP. The spectral band at 1100 cm^{-1} corresponds also to $-CH_2-$ interaction.

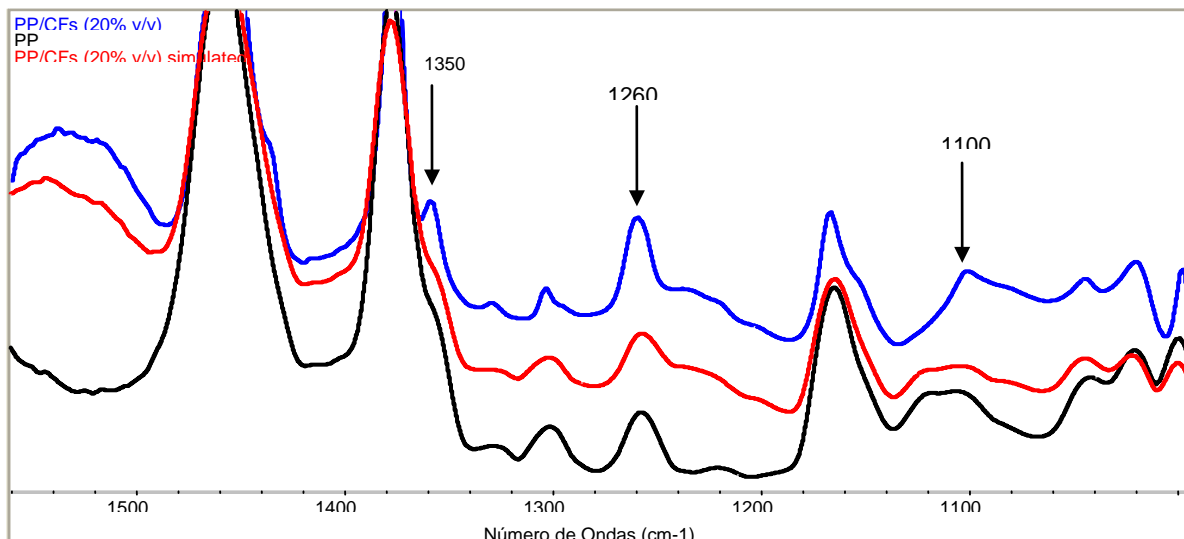


Figure 7. Comparative spectra of PP/CFs (20% v/v) composite, PP/CFs (20% v/v) simulated composite and PP pure matrix.

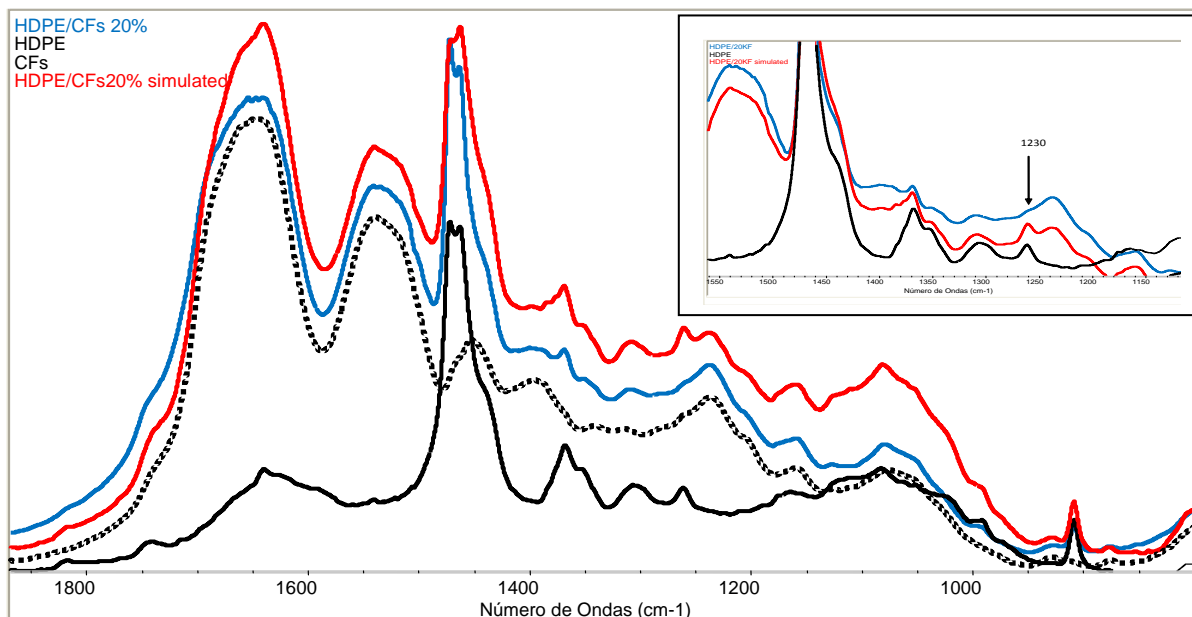


Figure 8. FTIR spectra of HDPE/CFs (20% v/v) simulated composite, HDPE/CFs (20% v/v) composite, CFs filler and HDPE pure matrix.

The vibrational perturbations that appear in these bands indicate that interactions of small order take place between both components. These small order interactions are the maximum compatibilization possibility according to the chemical structure of the components.

Figure 8 shows the spectra corresponding to HDPE composite containing 20% of CFs (HDPE/CFs-20%v/v). The difference between the original and the simulated FTIR spectrum is very small. Only the band at 1230 cm^{-1} , which is assigned to conformational vibrations of backbone in HDPE appears significantly changed, disappearing in the original composite. This means that the vibration of backbone have a change due to the presence of CFs in its

environment. Despite this matrix modification the interactions between HDPE and CFs are quite irrelevant and this circumstance corroborated the observed mechanical behavior of the composites discussed in section 3.1.

4 Conclusions

Composites including CFs with a matrix either of PP or HDPE may represent a viable solution to the valorisation of these residua.

Young's modulus of the composites was improved when adding CFs to the composites. Maximum values are obtained at 5% (PP) and 10% (HDPE). Tensile strength show a little decrease when adding CFs but still remains in acceptable limits. PP pure matrix show higher values of these properties. Moreover, elongation and toughness are drastically decreased.

The mechanical behaviour is related to a lack of interfacial adhesion between matrix and reinforcement. SEM studies show that fibres are pulled out quite clean without signs of adhesion. FTIR spectroscopy corroborates these results. Comparing the spectra of the composites to the theoretical spectra in absence of interfacial interaction, only slight changes are noted. This is an indicative of presence of only weak interaction between the polyolephinic matrices (PP and HDPE) and the pre-treated CFs.

5 Acknowledgments

FEDER and Spanish Ministry of Science and Innovation funding (MAT 2010-17057) are gratefully acknowledged.

6 References

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