

Spectroscopy Analysis of Chemical Modification of Cellulose Fibers

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Abstract. The development of new fibrous composites with specific properties has attracted a big interest in the development of new technologies. One of the biggest problems in this area is the improvement of the fiber/matrix interface to increase the mechanical properties in the final composite. In this work, surface chemical modifications of the rice husk (by-product of the rice industry) were carried out to achieve a better compatibility with diverse polymeric matrices. These modifications include the use of three different silanes: 3-(trimethoxysilyl) propyl methacrylate (TMS), dichlorodimethylsilane (DDS) and trichlorovinylsilane (TVS). The natural fibers and their changes after each treatment were studied experimentally by Fourier Transformed Infrared Spectroscopy (FTIR). This experimental spectroscopic information was compared with a theoretical analysis of molecular vibrations using the Hyperchem Release 7 software as molecular modeling tool. The result of this comparison confirmed the chemical modification. It was concluded that the chemical modification was carried out and after an experimental spectroscopic analysis (FTIR) the molecular vibrations data were agree with those calculated by theoretical analysis being verified in this way the chemical modification of the rice-husk fiber surface. The successes of the synthesis of the cellulose with different silanes were confirmed with NMR.

Keywords: Cellulose, rice husk, fibers.

Resumen. El desarrollo de nuevos compuestos fibrosos con propiedades específicas ha atraído un interés grande en el desarrollo de nuevas tecnologías. Uno de los problemas más grandes en esta área es la mejora de la interface fibra/matriz para incrementar las propiedades mecánicas en el compuesto final. En este trabajo, la modificación química de la superficie de la cáscara del arroz (derivado de la industria del arroz) se llevó a cabo para lograr una mejor compatibilidad con matrices de diferentes polímeros. Estas modificaciones incluyen, el uso de tres diferentes silanos: 3-(trimetoxisilil) propil metacrilato (TMS), diclorodimetilsilano (DDS) así como, triclorovinilsilano (TVS). Las fibras naturales y los cambios después de cada tratamiento fueron estudiados experimentalmente mediante, Espectroscopia de Infrarrojo por Transformadas de Fourier (FTIR). Esta información experimental espectroscópica fue comparada con un análisis teórico de las vibraciones moleculares que se emplearon a través del software Hyperchem Release 7, herramienta de modelación molecular. El resultado de esta comparación confirmó la modificación química efectuada. Los datos de las vibraciones moleculares coincidieron con aquellos calculados por análisis teórico, los cuales comprobaron la modificación química de la superficie de fibra de arroz-cáscara. La síntesis de la celulosa con los silanos fueron confirmados por RMN.

Palabras clave: Celulosa, cascarilla de arroz, fibra.

Introduction

The science and engineering of new materials are revolutionizing constantly the quality of life of the human being. Most of the industry by-products have generated a problem for the society [1]. The natural fibers, waste of the agro-industry are being used as filler in polymeric matrices to obtain composites with special properties [2]. A special interest has grown in composites based on thermoplastic matrixes reinforced with raw lignocellulosic materials such as wood fillers, wheat straw, almond husk, or ash rice husk. These fillers introduce some advantages compared to traditional inorganic fillers, including their renewable nature, low density, nonabrasive properties, reasonable strength, and stiffness. The raw lignocellulosic materials are mainly made up of a complex network of three polymers: cellulose, hemicellulose, and lignin. Table 1 shows the percentage of each polymer in different organic fillers and the percentage of natural moisture. The percentage of silica in the rice husk is included. Cellulose is a lineal polysaccharide-type polymer with high molecular weight. In contrast, hemicellulose is a branching polysaccharide composed mainly of pentosanes and hexosanes, which contain a large number of hydroxyl groups. Because of its branching formation and complex chemical structure, its contribution to the polar behavior

of the filler is higher than cellulose. Finally, lignin is an aromatic polymer with a high content of branched molecules, which are polar hydroxyl groups that are responsible for the hydrophilic nature of the lignocellulosic materials and nonpolar hydrocarbon and benzene rings [3].

Previously, most researchers have used wood flour, rice husk and empty fruit bunch as reinforcement in the various polymers such as polyethylene, polyvinyl chloride and polypropylene [4-5]. In spite of all the advantages mentioned about

Table 1. Dry chemical composition of different organic fillers and fibers.

Organic filler	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Silica (%)	Natural moisture (%)
Pine (softwood)	44	27	28	—	25
Yellow birch (hardwood)	47	31	21	—	25
Jute	73.2	13.6	13.4	—	10
Wheat straw	48.8	35.4	17.1	—	18
Rice husk	45	19	19.5	15	14

natural fiber, there are also drawbacks in using natural fiber as reinforcement in thermoplastics.

The main drawbacks are the difficulties of achieving good dispersion and strong interfacial adhesion between the hydrophilic fiber and the hydrophobic polymer [6]. Poor adhesion leads to composites with rather poor durability and toughness [7-14]. This is the main reason of using silane technology in crosslinking polyethylene-rice straw composites [6]. Rice husk is a by-product in the process of obtaining rice grain. It contains nearly 20% silica in hydrated amorphous form [15]. One application is to use rice husk as a reinforcing agent for thermoplastics, and is attracting much attention because of the potential for enormous gains in certain important properties of these products. It has been shown that the use of rice husk in natural rubber/linear low-density polyethylene composite results in an increase in tensile modulus and hardness. These properties were further enhanced with the use of a coupling agent, which improved the interfacial adhesion between rice husk and thermoplastic matrix [16]. In fact, in the context of cellulose fibers reinforced composites, similar chemical processes are applied to cellulose macromolecules, but their impact is limited to the macromolecular layers constituting the fiber surface. In fact in order to have high-performance reinforcing elements, the fiber integrity should be preserved. Instead, the surface properties are modified bearing the matrix in mind, in order to yield the best interface between the two phases (the matrix and the reinforcing fibers) [17]. NMR spectroscopy is the most powerful method for characterizing the detailed structure and molecular motion of the respective constituent units. In particular, chain conformation, orientation, and intermolecular interactions such as hydrogen bonding can be well analyzed for the respective carbons [18]. ^{29}Si solid-state NMR probes the local structure of a silicon atom and does not rely on long-range order in the samples and is therefore a powerful technique to characterize amorphous silica. Crystalline samples are characterized by well-defined bond angles which are reflected in narrow NMR resonances, whereas amorphous samples are characterized by distributions in bond angles in general leading to broad Gaussian line shapes.

Although the use of ^{29}Si solid-state NMR in the study of rice husk is widespread [15] Present analytical techniques as FTIR are used to study this effect and an option to justify the obtained results is using theoretical calculations by means of the computational chemistry tools. Consequently, in this work the modification of the rice husk cellulose fiber was conducted, as well as the evaluation of the chemical changes by FTIR and its theoretical analysis using Hyperchem Release 7 was reported [19-20].

Results and discussion

Determination of Gibbs free energy

The set of thermodynamic data obtained is listed in Table 2. These values clearly show that the interaction of cellulose with

Table 2. Reaction thermodynamic dates of different silanes

Reaction	Gibbs Free Energy	Entropy
TMS – Cellulose	–235 Kcal/mol	1.97 J/°K
DDS – Cellulose	–265 Kcal/mol	2.21 J/°K
TVS – Cellulose	–236 Kcal/mol	2.04 J/°K

the surface of different silanes indicate a spontaneous reaction, as expressed by the negative Gibbs free energy, whose values did not differ significantly for these surfaces. For this parameter there is a favorable contribution from the exothermic enthalpic values [21].

FTIR analysis

Tables 3, 4 and 5 show the results of the vibrational theoretical analysis (FTIR Hyperchem) of the silanes used in the chemical modification. The main stretch and bending vibrations modes for the functional groups in the silanes are listed [22-26].

The peaks corresponding to the molecular vibrations of the rice husk and the silane are shown in Figure 1. As can be seen (Figure 2) the region 900 to 1300 cm^{-1} was studied, where it was expected to find the peaks that could demonstrate a chemical linkage between the silanes and the fiber. The cellulose hydroxyl groups in the fiber are relatively unreactive,

Table 3. FTIR theoretical analysis results for TMS (3-(trimethoxysilyl) propyl methacrylate and its assignments in the region 700-1900 cm^{-1} .

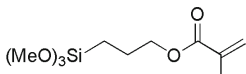
SILANE TMS:		
		
Theoretical results by Hyperchem 7.0 cm^{-1}	Vibrational mode	
838	Si-CH ₂	(Asymmetric stretch)
1076	C-O-C	(Symmetric stretch)
1207	Si-O-CH ₃	(Si-O bending)
1641	C=C	(Stretch)
1866	C=O	(Asymmetric stretch)

Table 4. FTIR theoretical analysis results for DDS (dichloro dimethylsilane) and its assignments in the region 700-1900 cm^{-1} .

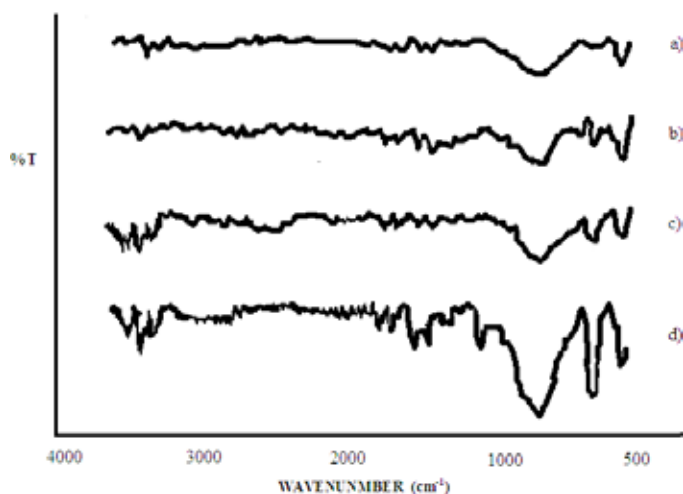
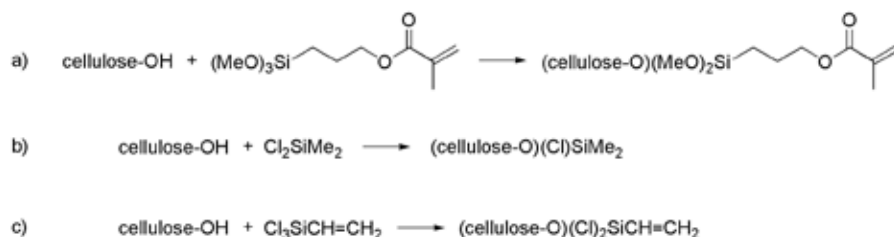
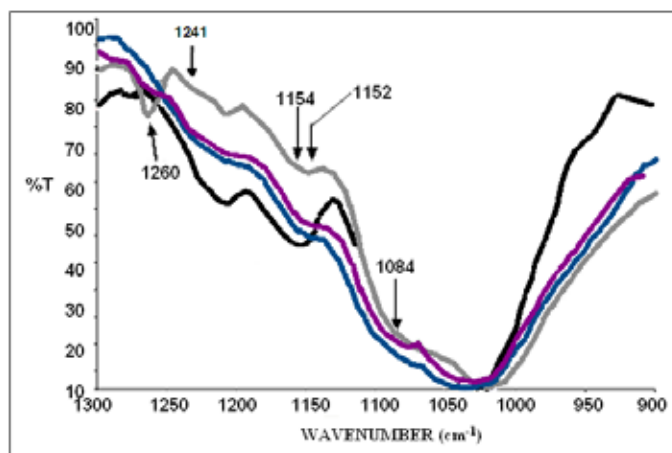
SILANE DDS: (Cl) ₂ SiMe ₂		
Theoretical results by Hyperchem 7.0 cm^{-1}	Vibrational mode	
653	Si-Cl	(Stretch)
662	C-Si-C	(Asymmetric stretch)
803	Si-CH ₃	(Si-C bending)
845	CH ₃ -Si-C H ₃	(C-Si-C Asymmetric bending)
1265	SiCH ₃	(Stretch)

Table 5. FTIR theoretical analysis results for TVS (Trichlorovinylsilane) and its assignments in the region 700-1900 cm^{-1} .

SILANE TVS:	$\text{Cl}_3\text{SiCH}=\text{CH}_2$
Theoretical results by Hyperchem 7.0 cm^{-1}	Vibrational mode
360	Si-Cl ₃ (Si-Cl Stretch)
414	Si-Cl (Si-Cl bending)
530	C=C-Si (Si-C asymmetric stretch)
638	Si-Cl (Stretch)
1618	C=C (Stretch)

since they form strong hydrogen bonds. Alkali treatment may destroy the hydrogen bonding in cellulosic hydroxyl groups, thereby making them more reactive. The possible reaction between the silanes (TMS, DDS and TVS, respectively) and cellulose is illustrated in Figure 3. The chemical linkage with the silanes and the fiber was by the formation of a chain of covalent chemical bonds [27]. The absorption band of rice husk treated with DDS and TMS were characterized, at 1100 cm^{-1} was assigned to various types of C-O-Si stretching vibration, which corroborates the chemical modification of fiber [28-32].

The major difference between the different spectrums was the strong increase in the carbonyl stretching vibration

**Fig. 1.** Silanization reactions of the cellulose fiber, where a) Nature cellulose, b) Cellulose-TMS, c) Cellulose-DDS d) Cellulose-TVS**Fig. 3.** Silanization reactions of the cellulose fiber (rice husk). a) Cellulose-TMS, b) Cellulose-DDS, c) Cellulose-TVS.**Fig. 2.** FTIR experimental analysis of silanized rice husk fiber after and their absorption peaks. Cellulose-DDS, cellulose-TMS, cellulose-TVS, cellulose

(mC=O) at 1750 cm^{-1} after modification. In addition, the intensity of the band at 1241 cm^{-1} also increased and was associated to the C-O stretching vibration (mC-O) of the acetate function. The intensity of the band at 604 cm^{-1} (see Figure 1) also increased due to vibration of the methyl groups. In addition, the intensities of absorption bands at 2942, 1376 and 900 cm^{-1} were assigned to the vibrations of the methyl groups (of acetyl group) also increased [33]. The strong absorption bands at 1162 and 1059 cm^{-1} was attributed to the Si-O-Si stretching vibrations (mSi-O-Si) and at 1463 cm^{-1} , to C-H deformations of the methoxy groups (dSiOC-H) [33-34].

Tables 6, 7 and 8 show the assignments for the different absorption peaks corresponding to the bonds of the cellulose and the three different silanes, also peaks at 1152 and 1154 cm^{-1} can be observed which indicate the chemical linkage between the rice husk cellulose fibers and the silanes (C-O-Si symmetric stretch) [2]. Figure 1 shows, the carbonyl stretching band -C=O at 1731 cm^{-1} did not change and had no relevance to the adhesion process. At about 1635 cm^{-1} there was a characteristic, broad band due to C=C stretching (methacrylate and vinyl groups). Generally, the silane film thickness is not dependent on contact time, but on the silane concentration [27]. Tables 6-8, the structures of two monomeric units of cellulose and one of silane are presented. The bond angle, energies and distances are calculated by Hyperchem software as well as the data of the molecular vibrations. All silanized reveal absorption peaks at around 766 cm^{-1} which could be attributed by Si-C stretch-

Table 6. FTIR theoretical and experimental analysis results of cellulose-TMS in the region 700-1900 cm^{-1} and the molecular structure.

Cellulose + (3-(trimethoxysilyl) propyl methacrylate (TMS)		
Theoretical results by Hyperchem 7.0 (cm^{-1})	Experimental results (cm^{-1})	Vibrational mode
637	641	C=O (sobretone strech)
793	795	Si-CH (bend C-H)
1082	1084	C-O-C (Strech C-O-C)
1150	1152	C-O-Si (Strech C-O-Si)
1188	1190	Si-O-CH ₃ (Strech Si-O)
1207	1207	Si-O-CH ₃ (Bend Si-O)
1640	1610	C=C (Strech)
1731	1740	C=O (Strech)

Table 7. FTIR theoretical and experimental analysis results of cellulose-DDS in the region 700-1900 cm^{-1} and the molecular structure.

Cellulose + Dychloro dimethylsilane (DDS)		
Theoretical results by Hyperchem 7.0 (cm^{-1})	Experimental results (cm^{-1})	Vibrational mode
653	652	Si-Cl (Strech)
798	795	Si-C-H (bend C-H)
805	803	Si-C (Strech)
1150	1152	C-O-Si (Strech)
1277	1280	Si-C-H (Bend C-H)

Table 8. FTIR theoretical and experimental analysis results of cellulose-TVS in the region 700-1900 cm^{-1} and the molecular structure.

Cellulose + Trichlorovinylsilane (TVS)		
Theoretical results by Hyperchem 7.0 (cm^{-1})	Experimental results (cm^{-1})	Vibrational mode
633	—	C=C-Si (Strech C-Si)
668	672	Si-Cl (Strech)
823	825	Si-O-C (Strech)
1008	1015	Si-CH=CH ₂ (Bend =C-H)
1150	1154	C-O-Si (Strech)
1621	1625	C=C (Strech)

ing bond. Another new peak appears at 1720 cm^{-1} may come from carbonyl group. Again, there are very weak peaks found at 860 and 980 cm^{-1} which could be assigned to Si-OH. This fact confirms that OH group of silanol reacts with cellulose or undergoes condensation reaction [35].

NMR Analysis

Figure 4, 5 and 6 show the chemical shifts of the theoretical analysis (NMR Hyperchem) of the silanes on the surface

chemical modification of cellulose fibers. The signals between 54–57 ppm are assigned to the lignin methoxy groups and the methyl band of acetyl groups, respectively. The aromatic groups of lignin appear at 150 ppm as a wide band. The signal at 77 and 65 ppm seems to indicate the amorphous carbons of cellulose, respectively, have reacted. The signal of the acetyl groups at 171 ppm (carbonyl) and 21 ppm (methyl) confirm that a cleavage of the grafted acetyl groups occurred.

Three additional chemical shifts emerged at 7, 35 and 52 ppm. The signal at 52 ppm was easily attributed to the carbon of the methoxy group. The two signals at 7 and 35 ppm were not clearly identified at this stage of the study but could be the result of a number of chemical rearrangements due to high temperature employed [33]. ^{29}Si -NMR spectra show the presence of hydroxyl groups at 92 ppm and isolated or vicinal hydroxyl groups at 100 ppm. Against the above support Ogenko et al have proposed that the peak at 92 ppm may be attributed to the changes in the coordination of surface silicon atom and electronic interaction between the silanols [36].

Conclusions

The theoretical results obtained by Hyperchem Release 7 were compared with those obtained experimentally, corroborating them and verifying them. This study showed that there was chemical modification in rice husk fiber after silanization, which give specific properties to the fiber depending on the resulting functional groups. This will determine the polymeric matrix to use for preparing composites. The collected data demonstrate spontaneity for the complexation reaction, as reflected by negative Gibbs free energies, which result from favorable negative enthalpies and positive entropies.

Experimental sections

Materials. 3-(trimethoxysilyl) propyl methacrylate (TMS) (Molecular weight 248.35, purity 98%, Sigma-Aldrich), dichlorodimethylsilane (DDS) (Molecular weight 129.06, purity 99%, Aldrich) and trichlorovinylsilane (TVS) (Molecular weight 161.49, purity 97%, Sigma-Aldrich)

Methods. *Alkali treatment.* The rice husk was soaked in a 0.5N NaOH solution at room temperature maintaining a ratio of (500 mL alkali solution /50g rice husk), rice husk was kept immersed in the alkali solution for 2 h. The fibers were then washed several times with fresh water to remove any NaOH sticking to the fiber surface, neutralized with dilute hydrochloric acid and finally washed again with distilled water. Final pH maintained was 7. The fibers were then dried at 70 °C for 24 h.

Silane treatment. The surface chemical modification of the cellulose fibers using silanes as agents allows using it as filler

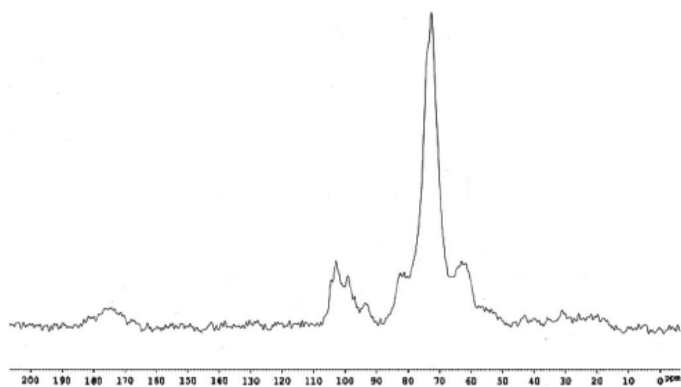


Fig. 4. ^{13}C -NMR of the effect TMS on rice husk.

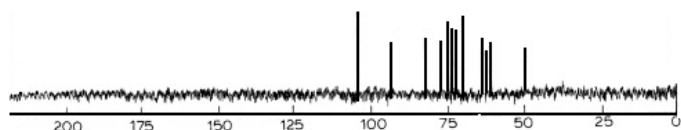


Fig. 5. ^{13}C -NMR of the effect DDS on rice husk.

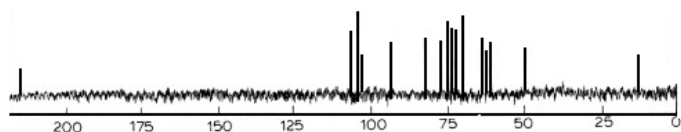


Fig. 6. ^{13}C -NMR of the effect TVS on rice husk.

in polymeric matrices. Depending on the type of silanes and substituents, the compatibility with polymeric matrices would be enhanced [20, 37].

The silanization reactions of the rice husk fiber using 3-(trimethoxysilyl) propyl methacrylate (TMS), dichlorodimethylsilane (DDS) and trichlorovinylsilane (TVS) are shown in Figures 3 (a, b and c), respectively. The chlorosilanes (TMS, DDS or TVS) were added to anhydrous ethanol to yield a 2% solution. The silane solution was stirred for 30 min at room temperature. Then rice husk was immersed and stirred in the silane solution for 30 minutes in a proportion of 9g/50mL and finally filtered and cured for 9 min at 180 °C.

Computational methods. All the calculations were carried out on a Pentium IV 3.0 GHz machine on windows 2003 environment using the computer software Hyperchem version 7.0. The ^{29}Si NMR of the ligands was calculated by applying TNDO/2 (Typed Neglect of Differential Overlap) semi-empirical method (with convergence limit 0.01 and maximum iterations 50).

Characterization. FTIR analysis. The FTIR spectra of various samples in KBr pellets were obtained using a Perkin Elmer-FTIR instrument with a resolution of 4 cm^{-1} . The average of 16 scans was used to obtain each spectrum. NMR (^{13}C and ^{29}Si). The ^{29}Si MAS NMR spectra were recorded on a Varian Unity INOVA 400 MHz spectrometer, at a spinning rate of 5.5 kHz, a pulse length of 3 s and a recycle delay of 12 s. The ^{29}Si chemical shifts were reported relative to external TMS. The estimated values of the chemical shift corresponding to differ-

ent environments of the SiO_4 unit were obtained by Gaussian signal deconvolution [38].

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