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Theoretical and experimental spectroscopic analysis by FTIR in the effect of the silanes on the chemical modification of the surface of rice husk.

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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 7.0 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.
***Keywords*:** Silane, Hyper Chem, Rice Husk, Cellulose.

I. 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. The natural fibers, waste of the agro-industry are being used as filler in polymeric matrices to obtain composites with special properties[1,2,3,4,5]. The rice husk, being a by-product of the rice industry, has not had a suitable final disposition to get a value- added product. A considerable production of this cellulose fiber combined with its physicochemical properties do that could be used as filler[6,7,8]. The challenge of the most works, where other types of cellulose fibers are used, consists in solving the problem of compatibility between the fiber and matrix generating the need to carry out a surface chemical modification in the fiber. At 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. In the literature there are no reports of theoretical and experimental studies to study the coupling effect of the silanes on cellulose as modifying agents. It is important to include theoretical studies to corroborate the experimental part[9].

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 Hyper-Chem Release 7.0 were reported.

II. EXPERIMENTAL

2.1 Materials

3-(trimethoxysilyl) propyl methacrylate 97% and Trichlorovinylsilane 97% (density 1.27g/cm^3) both were obtained from Aldrich., Dichlorodimethylsilane 99% (density 1.064 g/cm^3) was obtained from Dow Corning., reagent grade acetone of Aldrich., Nitrogen 99% INFRA., rice husk was obtained from rice company san José, Jojutla, Mor., Morelos variety A70, anhydrous ethanol 99%, J.T. Baker., and distilled water (Químicos farmacéuticos e Industriales S.A.de C.V.).

2.2 Equipment

Equipment Infrared Spectrum Analysis Model Spectrum Two, Perkin Elmer. Sieves of mesh numbers 20 FIIC brand, SA de C.V. whit mechanical vibrator. Drying oven, SHEL LAB brand, model No. VA1. Grill with magnetic stirrer model Nuova, Thermolyne brand and Simulator molecular Hyperchem Release 7.0 .

2.3 Modification of Rice Husk with silanes(TMS, DDS and TVS).

In a flask are added 750 mL of acetone, 100 g of rice husks and 5 g of silane. The system is refluxed at constant temperature and nitrogen atmosphere for 2 h. The system is allowed to cool and then filtered with filter paper to separate the husk. The husk is washed with CH_2 Cl to remove unreacted silane. It is filtered again and dried in a vacuum oven at 50 °C[10].

2.4. Characterization FTIR.

2.4.1 Characterization Experimental FTIR.

FTIR spectra of the silanes, rice husks modified and unmodified were obtained using the ATR technique in TWO SPECTRUM spectrophotometer in the range of 900-1300 cm^{-1} in transmittance mode, number of scans: 16 and Resolution: 4 cm^{-1}.

2.4.2 Theoretical FTIR characterization

Theoretical FTIR characterization of silanes and modified rice husk were obtained using Theoretical characterization FTIR of silanes and modified rice husk were obtained using the software hyper-chem release 7.0 building a three-dimensional model estimating the energy of the system. For this analysis a quantum mechanical method (semi-empirical method) is used. FTIR spectrum is calculated by the method PMS (Vibrational Spectrum).

III. RESULTS AND DISCUSSION

Tables 1, 2 and 3 show the results of the vibrational theoretical analysis (FTIR Hyper Chem 7.0) of the silanes used in the chemical modification. The main stretch and bending vibrations modes for the functional groups in the silanes are listed.

Experimental results show changes in signals of the region 900-1300 cm^{-1} is due to changes chemical bond between the silane and the fiber (see Figure 1). DDS spectra and TMS treated fibers exhibit more clearly an absorption peak attributable to vibration C-O-Si stretching, confirming the chemical modification of the fiber.

We can see the allocations for the different absorption peaks corresponding to the bonds of the silanes with different vibration modes.

The chemical bonding between the cellulose fiber and the silane is observed 1152 and 1154 cm^{-1} corresponding to (C-O-Si symmetric stretch). Both signals are observed in the results of the experimental analysis. These peaks are more intense when the DDS and TMS are used.

Tables 4, 5 and 6, the structures of two monomeric units of cellulose and one of silane present. Theoretical analysis software using the Hyper Chem demonstrates the presence of functional groups in the silanes as methacrylic, allyl or vinyl groups based on the silane used.

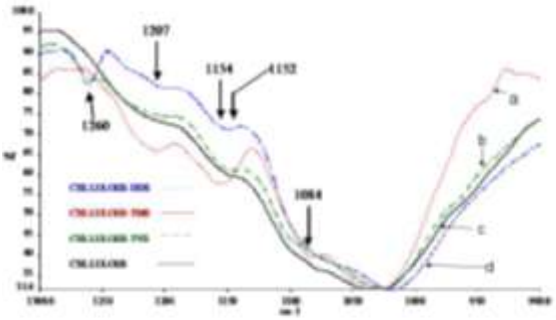


FIGURE 1.- FTIR experimental analysis of silanizated rice husk fiber after and their absorption peaks. , CELLULOSE-TMS (a), CELLULOSE-TVS (b), CELULLOSE (c) and CELLULOSE-DDS (d).

TABLE 1.- FTIR theoretical analysis results of TMS (3-(trimethoxysilyl) propyl methacrylate) and its assignments in the region 700-1900 cm^{-1}Treatments of rice husk.

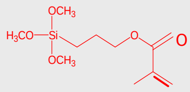
(3-(trimethoxysilyl) propyl methacrylate) SILANE TMS :	
Theoretical results by Hyper-Chem 7.0,	Vibrational mode
838.99	$Si-CH_2$ (asymmetric stretch)
1076.54	C-O-C (symmetric stretch)
1207.02	$Si-O-CH_3$ (Si-O bending)
1641.23	C=C (stretch)
1866.92	C=O (C=O asymmetric stretch)

TABLE 2.- FTIR theoretical analysis results for DDS (dichlorodimethylsilane) and its assignments in the region 700-1900 cm-1

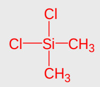
(dichlorodimethylsilane) SILANE DDS :	
Theoretical results by Hyper-Chem 7.0,	Vibrational mode
653.13	Si-Cl (Si-Cl stretch)
662.76	C-Si-C (asymmetric stretch)
803.78	$Si-CH_3$ (Si-C bending)
845.58	$CH_3-Si-CH_3$ (C-Si-C asymmetric bending)
1265.37	$Si-CH_3$ (C-H stretch)

TABLE 3.- FTIR theoretical analysis results for TVS (trichlorovinylsilane) and its assignments in the region 350-1900 cm-1

(trichlorovinylsilane) SILANE TVS : Cl–Si(Cl)(Cl)–C(H)=CH2	
Theoretical results by Hyper-Chem 7.0.	Vibrational mode
360.92	$Si-Cl_3$ (Si-Cl stretch)
414.44	Si-Cl (Si-Cl bending)
530.29	C=C-Si (C-Si asymmetric stretch)
637.65	C=C-Si (C-Si symmetric stretch)
665.14	Si-Cl (Si-Cl bending)
1618.56	C=C (C=C stretch)

TABLE 4.- Theorical and experimental analysis results for cellulose-TMS in the region 700-1900 cm-1 and the molecular structure.

CELLULOSE-TMS

CELLULOSE + 3-(trimethoxysilyl) propyl methacrylate (TMS)

Theoretical results by Hyper-Chem 7.0, cm^{-1}	Experimental results, cm^{-1}	Vibrational mode
637.65	641	C=O [illegible]
798.23	799	Si-C-H (bend C-H)
1082.21	1084	C-O-C (stretch C-O-C)
1150.87	1152	C-O-Si (stretch C-O-Si)
1186.44	1190	$Si-O-CH_3$ (stretch Si-O)
1207.40	1207	$Si-O-CH_3$ (bend Si-O)
1640.02	[illegible]	C=C (stretch)

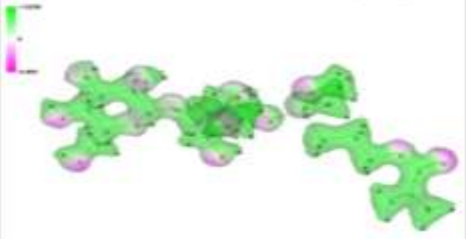


TABLE 5.- Theorical and experimental analysis results for cellulose-DDS in the region 700-1900 cm-1 and the molecular structure.

CELLULOSE-DDS

CELLULOSE + dichlorodimethylsilane (DDS)

Theoretical results by Hyper-Chem 7.0, cm^{-1}	Experimental results, cm^{-1}	Vibrational mode
[illegible]	653	Si-Cl (stretch)
798.03	[illegible]	Si-C-H (bend C-H)
805.22	805	Si-C (stretch)
1150.87	1152	C-O-Si (stretch)
1277.49	1280	Si-C-H (bend C-H)

TABLE 6.- Theorical and experimental analysis results for cellulose-TVS in the region 700-1900 cm-1 and the molecular structure.

CELLULOSE-TVS

CELLULOSE + trichlorovinylsilane (TVS)

Theoretical results by Hyper-Chem 7.0, cm^{-1}	Experimental results, cm^{-1}	Vibrational mode
653.75	-	C=C-Si (stretch C-Si)
668.67	672	Si-Cl (stretch)
823.29	825	Si-O-C (stretch)
1008.11	1015	$Si-CH=CH_2$ (bend =C-H)
1150.87	1154	C-O-Si (stretch)
1621.78	1626	C=C (stretch)

IV. CONCLUSIONS

The theoretical results obtained by Hyper Chem Release 7.0 were compared with those obtained experimentally confirming the chemical modification of the fiber. This study demonstrated the chemical modification rice hull fiber after silanization which gives specific function fiber in the resulting functional groups properties. This will determine the polymer matrix to use for the preparation of composite materials. The Software Hyper Chem 7.0 is an important tool in chemical research, was acquired by the Technological Institute of Zacatepec for the department of graduate and research.

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