Chapter 6

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Abstract

Through the application of computational chemistry was determined a possible structure of the Chitosan/PVP/Mimosa tenuiflora using methods semi empirical (PM3 and AM1, respectively). It was observed the presence of hydrogen bonds to form a three-dimensional network. The results of both methods are very similar.

Keywords: Chitosan, PVP, Mimosa Tenuiflora, AM1, PM3, Simulation

6.1 Simulation Results

6.1.1 Optimization Geometry

Figure 6.1 shows the geometry of optimization of Chitosan/PVP/Mimosa tenuiflora obtained through the application of the PM3 and AM1 semi-empirical methods, where the DG has negative values (Table 6.1) by causing the spontaneity of reaction. Furthermore, the formation of hydrogen bonds between the OH group (bond 37-38) of the *Mimosa tenuiflora* and hydrogen (bond 75-94) the PVP is observed, resulting in a three-dimensional network. It should be noted that DG values are similar between both methods.

Table 6.1 *Gibbs energy free for Chitosan/PVP/Mimosa tenuiflora structure.*

Method	ΔG (Kcal/mol)
AM1	- 6847
PM3	- 6992

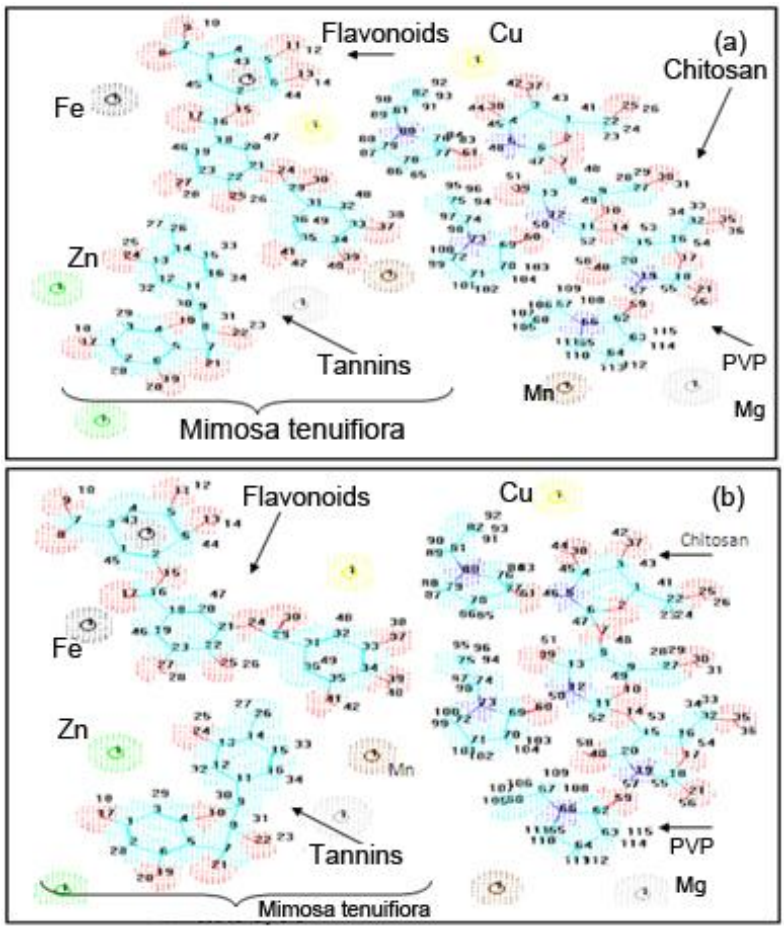

Figure 6.1 *Geometry optimization (ΔG) of Chitosan/PVP/Mimosa tenuiflora, where (a) PM3 and (b) AM1 semi-empiric method.*

6.1.2 FTIR Analyses

As both high molecular weight blend components contain proton donor OH (Flavonoids) groups and proton acceptor (PVP, Tannins C=O), they may appear

to be miscible, due to the hydrogen bond formation [1]. Thus, the FTIR spectra of film blends, in the carbonyl stretching region of PVP at 1675-1670 cm^{-1}, and the hydroxyl stretching bands of chitosan near 3605–3584 cm^{-1} FTIR results obtained using PM3 and AM1 semi-empiric methods applied in Chitosan/PVP/*Mimosa tenuiflora* are presented in Table 6.2 The OH stretching (flavonoids) is assigned in the region of 6715-6300 cm^{-1}, between 6004-5987 corresponding to CH and OH stretching of chitosan [2]. The sign between 4469-4460 cm^{-1} clearly indicates strong intermolecular interactions between chitosan/PVP/*Mimosa tenuiflora*.

Table 6.2 *FTIR results of Chitosan/PVP/Mimosa tenuiflora (flavonoids and tannins) attributed to PM3 and AM1 semi-empiric method.*

ASSIGNMENT	**PM3 (FREQUENCIES CM^{-1})**	**AM1 (FREQUENCIES CM^{-1})**
OH stretching (Flavonoids)	6725-6581	6715 - 6398
CH and OH stretching (Chitosan)	6004	5987
CH (Chitosan) CH (CH_2-CH_2) (PVP)	5836	5784
CH asymmetric stretching (CH_2-OH) (Chitosan)	5412	5420
CH asymmetric stretching (PVP)	5203	5163
CH (Chitosan and PVP rings)	4827	4769
OH and CH (Chitosan, Flavonoids and Tannins)	4469	4460
C-H (Chitosan ring)	4101	4021
C=C (Flavonoids and tannins)	3716	3632
O-H (Chitosan)	3605	3584
C=C (Flavonoids)	3584	3522
C-C (PVP ring)	3309	3269
C=O (PVP)	3065	3058
C=O (Flavonoids)	2876	2858
CH=CH (Tannins)	2593	2551
C-C (PVP and Chitosan)	2441	2397
C-C (PVP ring)	2109	2038
C=O (PVP)	1675	1670
C-C, C-N, C-O (PVP and Chitosan)	1674	1604
C-O, C-C (Flavonoids)	1349	1316
CH (Tannins)	1007	1000
C-C and C-O out of plane (Chitosan)	451	444

6.1.3 Electrostatic Potential

Figure 6.2 shows the electrostatic potential of Chitosan/PVP/*Mimosa tenuiflora* obtained through the application of the PM3 and AM1 semi-empirical methods. Shows that the values vary from 4.212-0.082 and 4.891-0.084 respectively, these results prove the formation of hydrogen bonds between NH (chitosan) with C=O (PVP) and OH of flavonoids with the CH_2-CH_2 of the PVP obtained as well the formation of three-dimensional network. There is a region of the flavonoid structure presents a green color characteristic of a nucleophilic region, It should be noted that it is staining also occurs in the CH of the PVP bond.

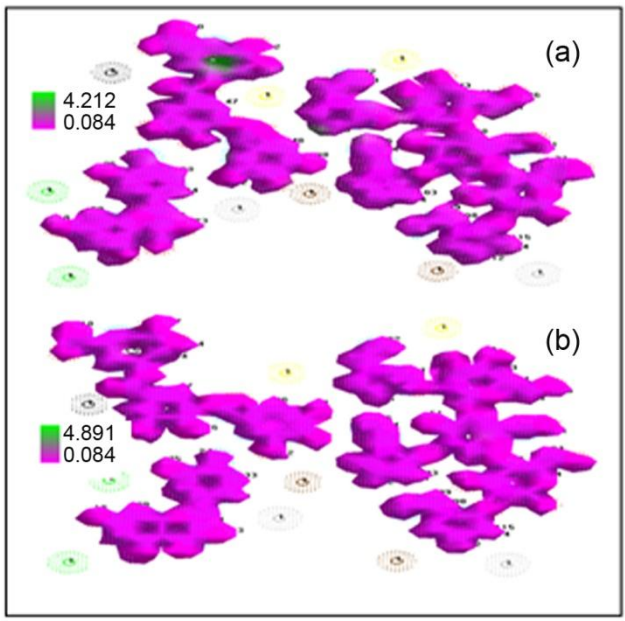

Figure 6.2 *Electrostatic potential of Chitosan/PVP/Mimosa tenuiflora (flavonoids and tannins) using (a) PM3 and (b) AM1 method.*

6.1.4 Molecular Orbitals

Tables 6.3 and 6.4 show values of the molecular orbitals (HOMO and LUMO) obtained through the application of the semi-empirical methods (PM3 and AM1, respectively). Shown that orbital HOMO compared their respective LUMO in each method is verified the spontaneity of reaction as well as the formation of hydrogen bonds for the three-dimensional network that is shown in Figure 6.3.

Table 6.3 *HOMO and LUMO orbitals for Chitosan/PVP/Mimosa tenuiflora (tannins and flavonoids) using PM3 semi-empiric method.*

ORBITAL	HOMO		LUMO	
	ENERGY (eV)	SYMMETRY (Å)	ENERGY (eV)	SYMMETRY (Å)
50	-13.26	23	-1.00	173
20	-12.99	26	-11.57	354
10	-12.94	154	-12.75	344
5	-12.93	158	-12.79	339
-5	-12.80	338	-12.93	159
-10	-12.76	343	-12.94	155
-20	-11.61	353	-12.98	25
-50	-1.00	173	-13.26	22

Table 6.4 *HOMO and LUMO orbitals for Chitosan/PVP/Mimosa tenuiflora (tannins and flavonoids) using AM1 semi-empiric method.*

ORBITAL	HOMO		LUMO	
	ENERGY (eV)	SYMMETRY (Å)	ENERGY (eV)	SYMMETRY (Å)
50	-13.20	21	-1.01	174
20	-12.91	23	-11.60	351
10	-12.92	152	-12.73	342
5	-12.95	159	-12.82	339
-5	-12.83	340	-12.95	159
-10	-12.77	344	-12.92	152
-20	-11.60	351	-12.90	22
-50	-1.01	174	-13.20	21

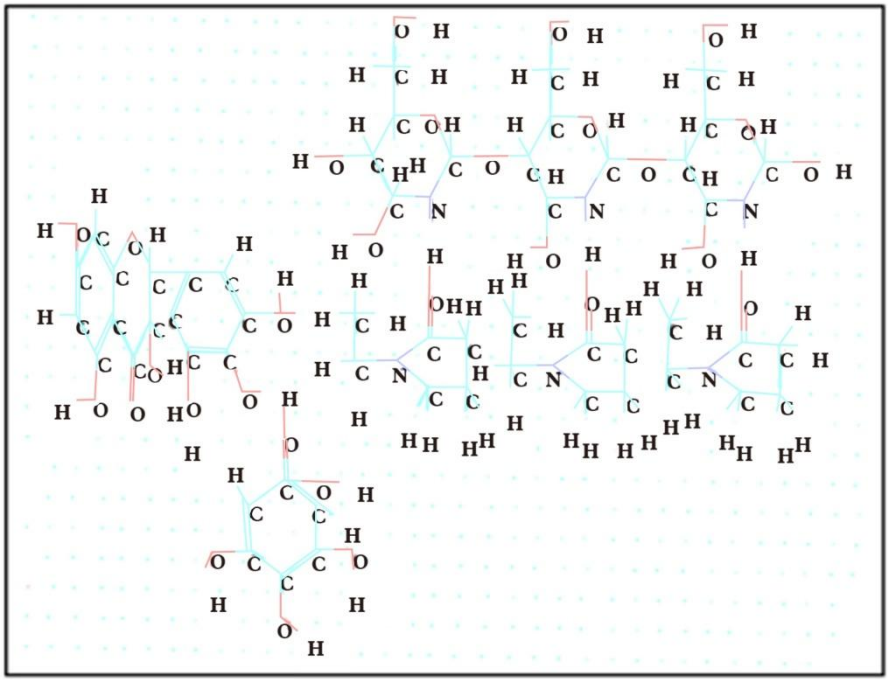

Figure 6.3 *Three-dimensional network of Chitosan/PVP/Mimosa tenuiflora.*

6.1.5 Conclusions

Gibbs free energy determined the spontaneity of reaction through the application of both semi-empirical methods. Also the main signals of FTIR were obtained. With the molecular orbital and electrostatic potentials determined the formation of hydrogen bonds which were tested with the obtaining of the nucleophilic areas in the structure. These results are very similar in both methods.

References

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