SUPPORTING INFORMATION

To Sec. II. SIMULATION MODELS, PROCEDURE AND METHOD

B: Procedure and Method

Partial atomic charges

Table 1. Partial atomic charges calculated in the present study and taken from [45].

Atom	Charge	Charge [45]	Atom	Charge	Charge [45]	Atom	Charge	Charge [45]
C1	0.33	0.35	C3	-0.11	0.15	C5	-0.21	0.10
H1	0.12	0.10	H3	0.15	0.10	O5	-0.36	-0.40
O1	-0.32	-0.65	O3	-0.52	-0.65	H5	0.14	0.10
H(OH)1	–	0.40	H(OH)3	0.42	0.40	H5’	0.14	0.105
C2	0.14	0.15	C4	0.05	0.15	C6	0.08	0.05
H2	0.15	0.10	H4	0.13	0.10	H6	0.14	0.10
H(OH)2	0.36	0.40	H(OH)4	–	0.40	H(OH)6	0.38	0.40
O2	-0.52	-0.65	O4	-0.32	-0.65	O6	-0.62	-0.65

HX refers to the respective carbon-bound hydrogen, and H(OH)X refers to the hydroxyl hydrogen atom.
The ring oxygen is designated by 05.

Comparison of the conformational characteristics obtained in the present study and by other authors

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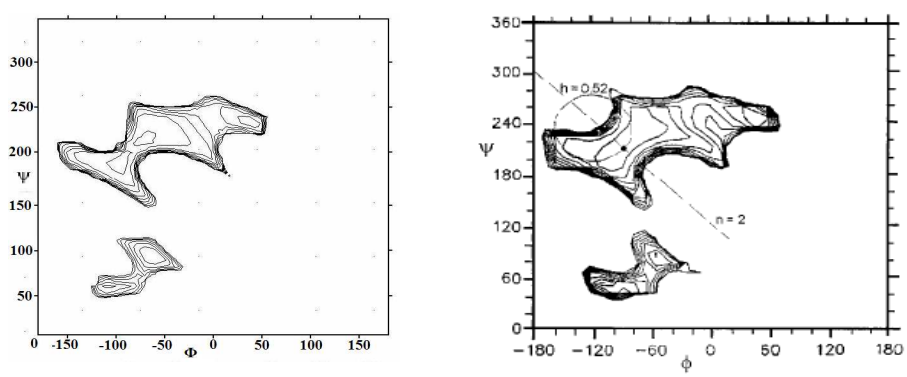


a b

Fig.1. Conformational energy maps calculated for cellobiose (a) in the present study and (b) in [48]. Iso-energy contours are shown at 4.18 kJ/mol intervals relative to the global minimum.

We have found that the calculated conformational map is very similar to the map produced by using the MM3 force-field [48]. This force field, as shown recently [49], gives the results very close to those obtained by the newer force fields, such as GROMOS and GLYCAM06. In

addition, a comparison of the calculated energy surface with the surfaces from [50] obtained at the HF/6-31G(d) and HF/6-311+G(d) levels showed that all the surfaces have well separated local minima in the same regions of torsion angles and the differences in the minima positions are in the energy range not exceeding 4.18 kJ/mol.

There are two well separated local minima in the central region (Fig. 1 a) of the potential surface calculated in this study with a barrier greater than 4.18 kJ/mol corresponding approximately to the 2-fold screw-axis. One of the minima (lowest) corresponds to the conformation with torsion angles φ=-96˚ and ψ=202˚ (or -158˚) and the other minimum is at φ =-71˚ and ψ =224˚(or -136˚) (φ — O5-C1-O4-C4' and ψ— C1-O4-C4'-C5'). The torsion angles corresponding to the lowest energy minimum are very close to the experimental data obtained for a cellulose crystal in [51]: φ_1,φ_2 = -99˚, -89˚ and ψ_1,ψ_2 = -142˚, -147˚, and also to the results of DFT calculations of the Iβ crystal structure [52]: φ_1,φ_2 = -95˚, -95˚ and ψ_1,ψ_2 =-144˚, -143˚. Subindexes 1 and 2 are for two (corner and central) cellulose chains.

Optimized structure of the oligomer chain

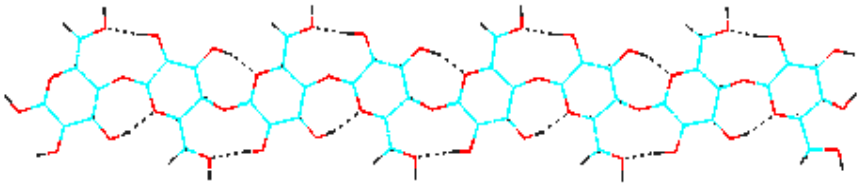


Fig. 2. Optimized structure of the oligomer molecule of cellulose.

The structure of the optimized oligomer chains was well hydrogen bonded.

To Sec. III. RESULTS

B. HAP-BC

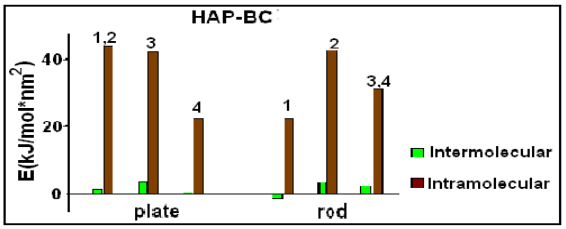


Fig. 3. Histogram of the intermolecular and intramolecular contributions to the deformation energy of the BC layer in the HAP-BC interfacial structure.

C. Whitlockite-BC

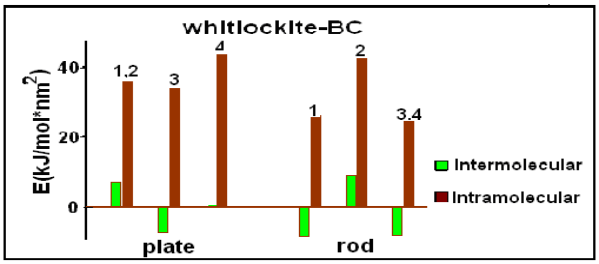
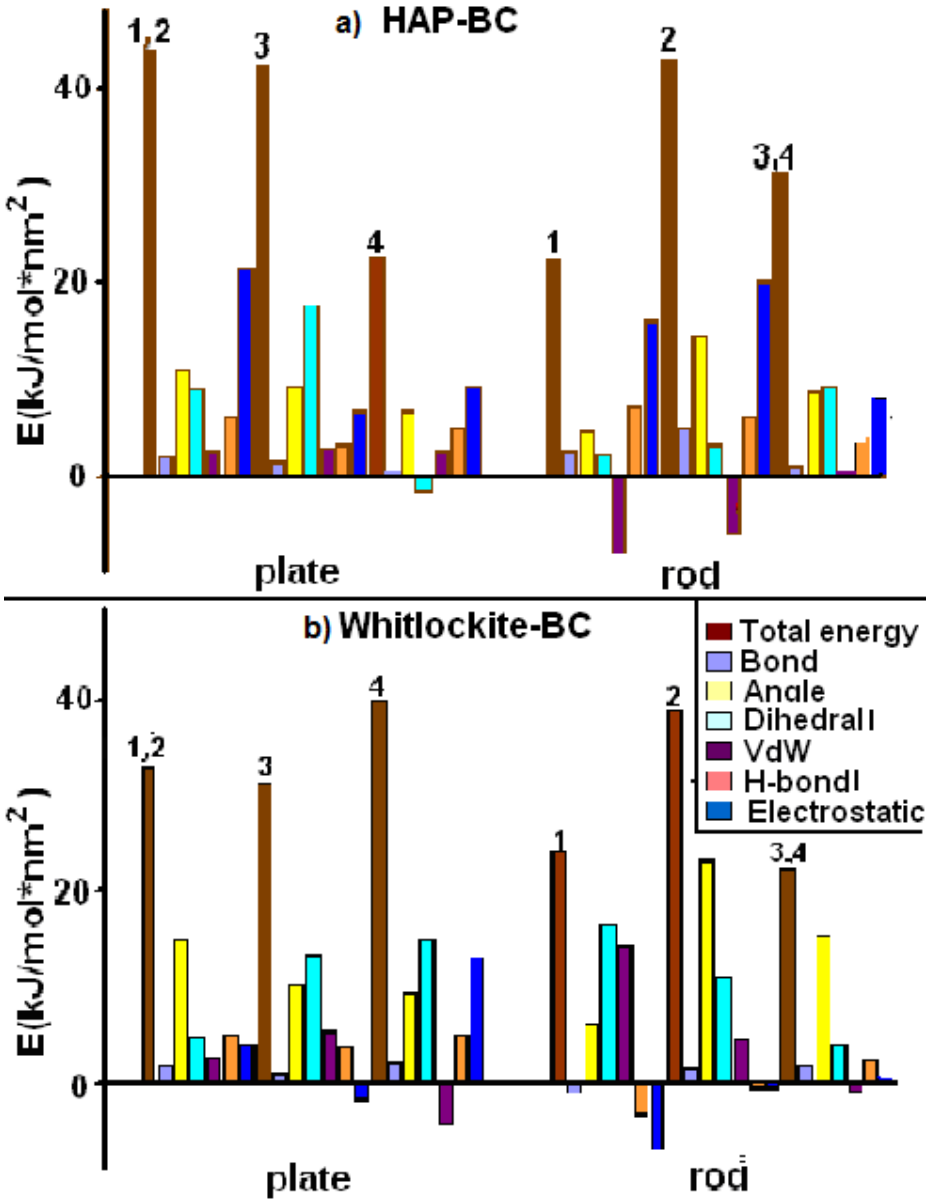


Fig. 4. Histogram of the intermolecular and intramolecular contributions to thedeformation energy of the BC layer in the whitlockite-BC interfacial structure.

A. Structural changes in cellulose molecules



a) b)

Fig. 5. Histograms of the intramolecular deformation energy of the BC layer and different contributions: a) for the HAP-BC structures and b) for the whilockite-BC structures.

Deformations of valence angles in cellulose molecules

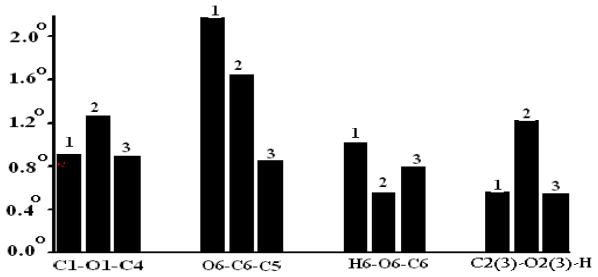


Fig. 6. Deviations of the valence angles from their initial values where C1-O1-C4 is the valence angle of the glycosidic oxygen, O6-C6-C5 and H6-O6-C6 are the valence angles of the primary hydroxyl groups, and C2(3)-O2(3)-H is the valence angle of the secondary hydroxyl groups. The results are presented for (1)-plate-shaped HAP-BC, (2)-rod-shaped HAP-BC and (3)-rod-shaped whitlockite-BC.