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Density Functional Theory; a New Route for Structural and Thermodynamic Parameters Calculations

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Abstract

Structural and thermodynamic parameters of the studied virgin polymeric matrices poly ε-caprolactone (PCL), Chitosan (Chi) and their polymer blend were investigated using theoretical density functional theory (DFT). Thermodynamic functions were calculated based on vibrational frequencies and optimized geometrical coordinates in the temperature range 25-1000 °K which cannot be amended easily. Calculated free energy was found to be convex in terms of extensive variable and concave in terms of intensive ones.

Keywords: Density functional theory (DFT); Thermodynamic parameters; Free energy; Entropy; Specific heat.

1. Introduction

Physical and thermodynamic parameters of solids are attributable to their structural arrangement and also to the internal energy of their complexes. Experimental measurement of such structural parameters are limited due to the expenses and facilities that can give results with accurate precision. Polymer blends are composed of two or more organic polymer matrices. Due to the unsatisfactory thermal, mechanical and electric properties, there is a need to functionalize them in an attempt to improve their properties to extend their potential applications [1, 2]. Chitosan (Chi) is obtained from chitin, the second most abundant polysaccharide in nature, which is found in the exoskeletons of crustaceans such as crab and shrimp [3]. Chitin comprises of a linear chain of Nacetyl D-glucosamine molecules. Deacetylaton of chitin to various degrees (typically 60- 95%) in hot concentrated alkali removes the acetyl groups and forms chitosan. Therefore, chitosan may be considered as a copolymer of D-glucosamine and N-acetyl Dglycosamine residues where the relative ratio of D-glucosamine to N-acetyl-Dglucosamine represents the degree of deacetylation of chitosan. The chemical structure of chitosan has been investigated by Fourier Transform Infrared Spectroscopy (FTIR) in which functional groups of a molecule absorb infrared radiation at specific wavenumbers. FTIR of chitosan shows the amine and hydroxyl functional groups which show overlapping peaks in 3300-3500 cm-1 [3-5]. The degradation rate is dependent on several factors including MW, DD, local pH, temperature, structural stability and homogeneity of source [6-8].Poly(ε-caprolactone) (PCL) is one of the most flexible and easy to process polymers, but also one of the slowest degrading ones [9]. This could be achieved by mixing chitosan and PCL for their unique contribution to the necessary biomechanical properties. However, chemical reactions such as copolymerization or crosslinking between chitosan and PCL may compromise their individual properties. Therefore, an ideal option is to make the polymeric components co-exist by mixing them physically. Physical mixing can be done by dissolution in a common solvent. However, there is a lack of common solvent for chitosan and PCL as they are hydrophilic and hydrophobic by nature, respectively. Chitosan and PCL mixtures present a model system for studying composites of two semi-crystalline polymers that differ in charge distribution, as chitosan is cationic in nature and PCL is uncharged.Blending two polymers is an approach to develop new biomaterials exhibiting combinations of properties that could not be obtained by individual polymers and to develop a new composite biomaterial that can be fabricated into thin films with alterable mechanical [10], biological and degradation properties for the regeneration of a variety of soft tissues [11]. The hypothesis of this work is that chitosan and PCL are versatile polymers with mutually complementary biomechanical properties and combining them would result in a unique biomaterial that can be fabricated into three-dimensional constructs with tunable physicochemical and biomechanical properties for a wide range of tissue engineering applications. As a modern technique of physics, Computational molecular modeling has greatly accelerated success in the determination of structural parameters, vibrational frequencies, and also thermodynamic properties of complexes. It is started in the last several decades and improvements in the computing power help physicist to predict thermodynamics of polymeric systems which is difficult to be measured experimentally. Determination of the thermodynamic quantities from experiments is always constrained by the particular technique used, and it may difficult to compare quantities derived from different techniques.

2. Materials and Methods

Selected polymeric material including poly ε-caprolactone (PCL), Chitosan (Chi) and their semi-natural polymer blend with a huge number of applications were studied theoretically for their atomic arrangement, interaction and their thermodynamic parameters. The efficient density functional theory (DFT) was applied to determine the structural parameters and thermodynamic parameters.

Studied thermodynamic functions of selected materials were calculated on the base of optimized geometrical coordinates for temperature interval between 25−1000 K. DFT/B3LYP method was applied for the calculations of the equilibrium geometrical and thermodynamic parameters of chitosan, PCL and their blend.

3. Formalism of thermodynamics quantities

For a free energy F, the condition of stability must be slightly amended, as it was generated from the energy using a Legendre transform. For an extensive variable X, the stability condition is identical to that of the energy,

$$\frac{\partial^2 F}{\partial X^2} \geq o, \qquad (1)$$

and the free energy is convex in X. However, for intensive variables x, the free energy is concave in x:

$$\frac{\partial^2 F}{\partial x^2} \leq o \qquad (2)$$

The first derivatives of the free energies have been previously given a physical meaning. The second derivatives also have physical meaning for certain free energies, and in these contexts they are known as "susceptibilities". Two important susceptibilities are the heat capacity Cp, which is an extensive measure of the heat flow necessary to change temperature,

$$C \equiv \frac{\delta Q}{dT} = T\,\frac{dS}{dT}\ , \qquad (3)$$

and the bulk modulus K, an intensive measure of the change in pressure upon expansion/contraction of the system,

$$K \equiv -V\frac{dP}{dV} \quad . \qquad (4)$$

Both equations (3,4) assume a particular process is being carried out, the former that temperature is changing and the later that volume is changing, but knowledge of the other constrained variable are necessary to convert these into proper thermodynamic quantities. It is usually assumed that particle number is fixed, so the heat capacity may be evaluated at fixed pressure Cp or fixed volume CV , and the bulk modulus may be evaluated at fixed temperature KT or fixed entropy KS. Each quantity suggests a natural ensemble,

$$K_T = V \left.\frac{\partial^2 A}{\partial V^2}\right| T,\{N_i\} \quad (5)$$

$$K_S = V \left.\frac{\partial^2 U}{\partial V^2}\right| S,\{N_i\} \quad (6)$$

$$C_V = -T \left.\frac{\partial^2 A}{\partial T^2}\right| V,\{N_i\} \quad (7)$$

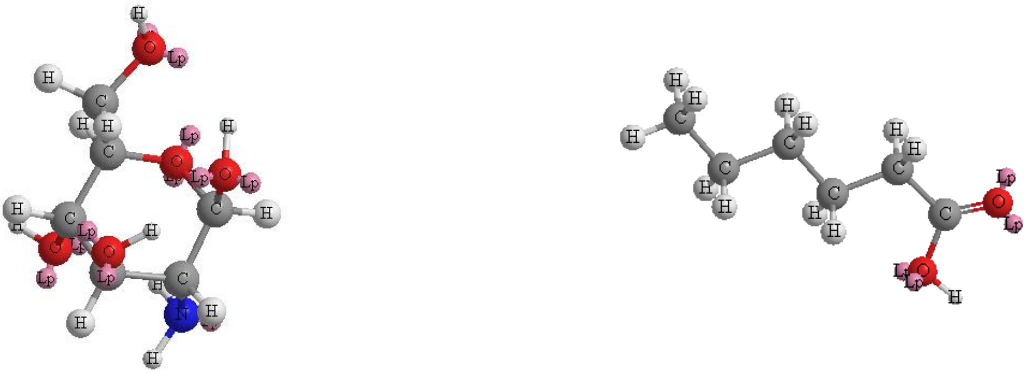
$$C_P = -T \left.\frac{\partial^2 G}{\partial T^2}\right| P,\{N_i\} \quad . (8)$$

The stability requires all four of these quantities to be positive, and the specific heat and bulk modulus must always be non-negative.

4. Results and Discussion

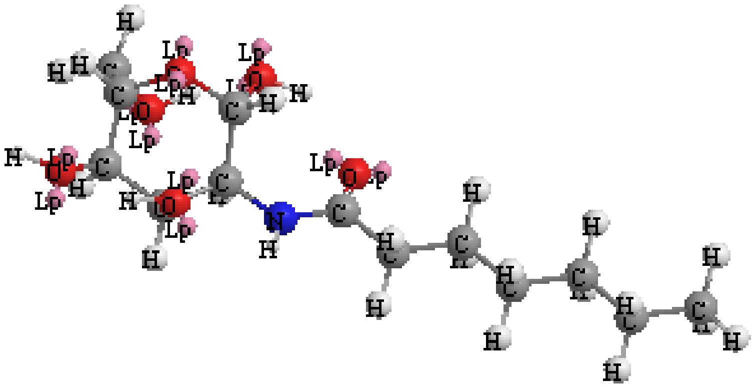
DFT route can be used to perform calculations without fitted parameters, so, it is a power tool to examine the polymeric materials. It predicts the structures stability in the infinite time and volume. DFT route also can provide energy optimization of the three dimensional network of solid material unit structure.

Optimized three dimensional polymeric network of the studied solid material Chi, PCL and their suggested interaction counterpart can be shown in Figure (1, a-c). Calculated values of molar heat capacity C_p, Gibbs reduced free energy Φ, entropy S and enthalpy increment H(T) – H(0) corresponding to this optimized structures are listed in Tables (1-3) for Chitosan, PCL, and their blend respectively.



(a) Optimized structure of Chitosan

(b) Optimized structure of PCL



(c) Optimized structure of PCL/Chi blend

Figure 1 Optimized structure of studied polymeric materials

Table (1): The thermodynamics properties of chitosan.

T(K)	**Cp** (J.mol^{-1}K^{-1})	**S** (J.mol^{-1}.K^{-1})	**ϕ** (J.mol^{-1}.K^{-1})	**H(T)-H(O)** (kJ.mol^{-1})
25	21.743	71.701	354.108	355.901
50	38.125	92.024	352.056	356.657
75	51.906	110.132	349.526	357.786
100	64.917	126.858	346.561	359.247
125	77.504	142.703	343.19	361.028
150	89.715	157.918	339.431	363.119
175	101.661	172.647	335.298	365.511
200	113.47	186.994	330.802	368.201
225	125.222	201.038	325.951	371.184
250	136.932	214.838	320.752	374.461
275	148.557	228.435	315.211	378.03
298.15	159.182	240.867	309.778	381.593
300	160.023	241.854	309.332	381.888
325	171.246	255.108	303.119	386.029
350	182.146	268.2	296.578	390.448
375	192.659	281.127	289.711	395.134
400	202.736	293.885	282.523	400.077
425	212.35	306.467	275.018	405.266
450	221.487	318.866	267.201	410.69
475	230.147	331.075	259.076	416.337
500	238.341	343.09	250.649	422.194
525	246.085	354.908	241.923	428.25
550	253.402	366.527	232.905	434.495
575	260.314	377.945	223.599	440.917
600	266.848	389.163	214.009	447.507
625	273.029	400.183	204.142	454.256

650	278.88	411.006	194.002	461.156
675	284.427	421.636	183.594	468.198
700	289.689	432.076	172.922	475.375
725	294.689	442.329	161.991	482.68
750	299.444	452.401	150.807	490.107
775	303.97	462.294	139.373	497.65
800	308.285	472.013	127.694	505.304
825	312.401	481.563	115.774	513.063
850	316.332	490.948	103.617	520.923
875	320.09	500.172	91.227	528.878
900	323.684	509.24	78.609	536.926
925	327.124	518.156	65.767	545.061
950	330.42	526.924	52.703	553.281
975	333.579	535.548	39.422	561.581
1000	336.608	544.032	25.927	569.958

Table (2): The thermodynamics properties of PCL.

T(K)	Cp (J.mol^{-1}K^{-1})	S (J.mol^{-1}.K^{-1})	ϕ (J.mol^{-1}.K^{-1})	H(T)-H(O) (kJ.mol^{-1})
25	8.72	49.831	108.212	109.458
50	11.211	56.627	106.875	109.707
75	13.667	61.642	105.395	110.018
100	15.928	65.889	103.799	110.388
125	18.032	69.671	102.104	110.813
150	20.079	73.14	100.318	111.289
175	22.151	76.39	98.449	111.817
200	24.3	79.487	96.5	112.398
225	26.551	82.478	94.476	113.033
250	28.906	85.396	92.377	113.726
275	31.35	88.265	90.206	114.479
298.15	33.669	90.892	88.132	115.232
300	33.856	91.1	87.964	115.294
325	36.393	93.91	85.651	116.172
350	38.931	96.7	83.269	117.114
375	41.442	99.472	80.816	118.118
400	43.904	102.226	78.295	119.185
425	46.302	104.96	75.705	120.313
450	48.623	107.672	73.047	121.5
475	50.861	110.361	70.322	122.744
500	53.012	113.025	67.53	124.042
525	55.075	115.662	64.671	125.393
550	57.052	118.27	61.747	126.795
575	58.946	120.848	58.758	128.245
600	60.758	123.396	55.704	129.742
625	62.494	125.911	52.588	131.283
650	64.156	128.395	49.409	132.866

675	65.75	130.846	46.169	134.49
700	67.277	133.265	42.867	136.153
725	68.743	135.652	39.506	137.853
750	70.15	138.006	36.085	139.59
775	71.501	140.329	32.606	141.36
800	72.8	142.619	29.069	143.164
825	74.048	144.879	25.475	145
850	75.249	147.107	21.825	146.866
875	76.404	149.305	18.12	148.762
900	77.516	151.473	14.36	150.686
925	78.586	153.612	10.546	152.637
950	79.616	155.721	6.68	154.615
975	80.609	157.802	2.76	156.618
1000	81.565	159.855	-1.21	158.645

Table (3): The thermodynamics properties of blend.

T(K)	Cp (J.mol^{-1}K^{-1})	S (J.mol^{-1}.K^{-1})	ϕ (J.mol^{-1}.K^{-1})	H(T)-H(O) (kJ.mol^{-1})
25	11.868	59.944	241.754	243.253
50	18.904	70.274	240.122	243.636
75	26.001	79.297	238.251	244.198
100	32.487	87.681	236.162	244.931
125	38.386	95.574	233.871	245.817
150	43.891	103.063	231.387	246.847
175	49.223	110.23	228.72	248.011
200	54.564	117.151	225.878	249.308
225	60.025	123.891	222.864	250.74
250	65.648	130.505	219.684	252.31
275	71.422	137.032	216.34	254.023
298.15	76.863	143.021	213.098	255.74
300	77.301	143.498	212.833	255.882
325	83.221	149.919	209.165	257.889
350	89.119	156.302	205.337	260.043
375	94.934	162.65	201.35	262.344
400	100.618	168.959	197.205	264.789
425	106.135	175.225	192.903	267.374
450	111.46	181.444	188.444	270.094
475	116.577	187.608	183.831	272.945
500	121.479	193.713	179.064	275.921
525	126.167	199.755	174.146	279.017
550	130.643	205.728	169.077	282.228
575	134.914	211.63	163.86	285.547
600	138.99	217.459	158.496	288.972
625	142.881	223.212	152.988	292.495
650	146.595	228.889	147.336	296.114

675	150.144	234.489	141.544	299.824
700	153.536	240.011	135.613	303.62
725	156.783	245.456	129.544	307.499
750	159.891	250.824	123.34	311.458
775	162.87	256.115	117.004	315.493
800	165.726	261.332	110.535	319.601
825	168.467	266.473	103.938	323.778
850	171.098	271.542	97.212	328.023
875	173.627	276.538	90.361	332.332
900	176.057	281.464	83.386	336.704
925	178.394	286.32	76.289	341.134
950	180.642	291.107	69.071	345.622
975	182.805	295.828	61.734	350.166
1000	184.888	300.482	54.28	354.762

Figure (2) reveals relation between temperature and entropy of chitosan, PCL and their blend in the temperature range 25-1000 K. Such range of temperature cannot be reachable or obtainable in any experimental device.

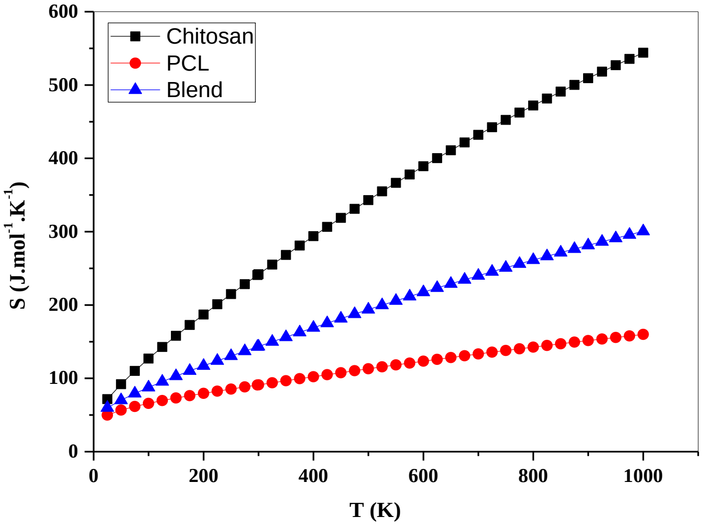


Figure (2) temperature versus entropy of the studied samples

It was noticed from this figure that Chitosan has the largest entropy while the PCL has the lowest and the blend have intermediate values between both partners. The entropy for all of them increased by increasing the temperature in the range from 25-1000 K. It is evident that mixing Chi and PCL the configuration of both of them changed to a new configuration.

Figure (3) shows the relation between both temperature and calculated specific heat capacity of the studied materials. It was observed that the heat capacity of studied polymeric materials was gradually increase in the temperature range from 25-1000 K, the rate of increase was found to be different for each partner. It is noted that Chi has the highest rate of increase over PCL while the blend shows an intermediate values between both polymers in full temperature range indicating some type of interaction and complexation between both Chi and PCL.

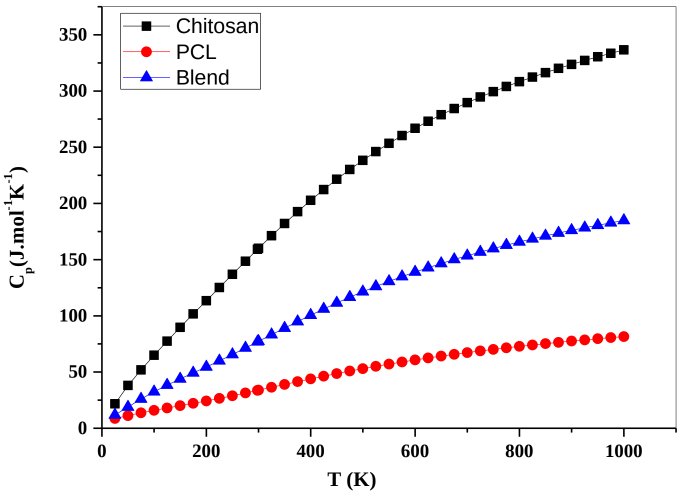


Figure (3) temperature versus heat capacity of the studied samples

Figure (4) shows the relation between temperature and free energy of studied samples. The free energies decreases with increasing temperature for all studied samples and the most probable reason for this behavior may attributed to mixing effect.

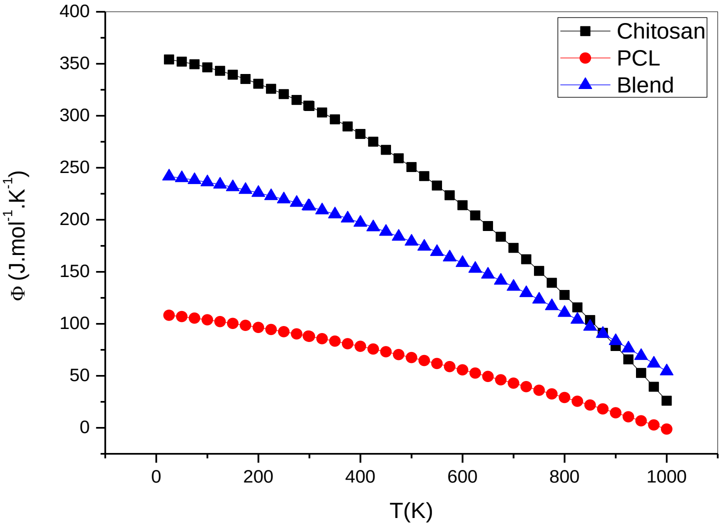


Figure (4) temperature versus free energy of the studied samples

Figure (5) represent the relation between the temperature and the enthalpy of studied samples.

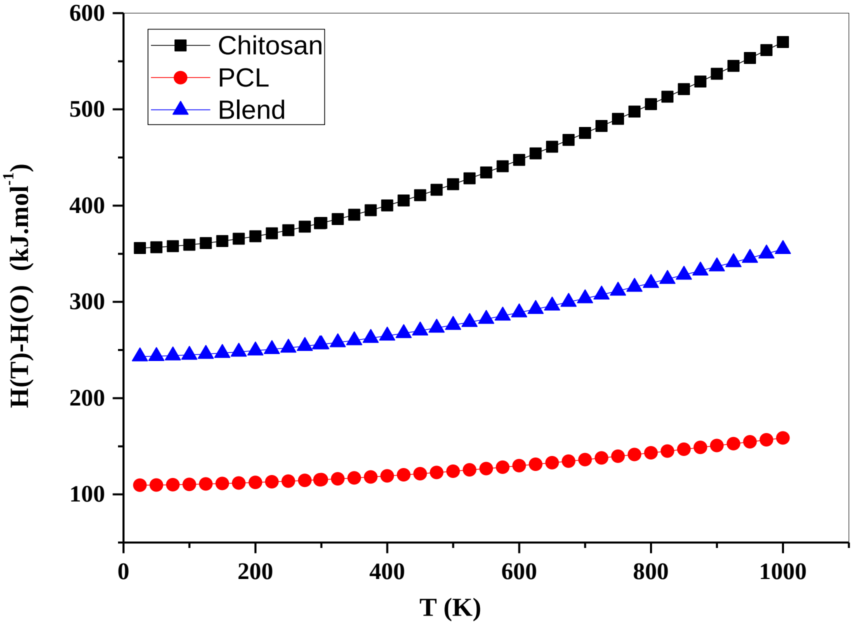


Figure (5) temperature versus enthalpy of the studied samples

Energy optimization of the selected samples shows a three dimensional arrangement of the constituting atoms per unit cell which results in absorption behavior correlated to the frequency previously studied [12, 13] and compared and supported with published data of similar system [14, 15]. Such compatibility open gate for the comparison of other related data which can be obtained by the same route including thermodynamic parameters such as specific heat, entropy, free energy and enthalpy even in a non-reachable temperatures. Obtained thermodynamic parameters shows some type of interaction and complexation indicated by the intermediate values for semi-natural blend of all parameters over the whole studied temperatures (25-1000 K) with a comparable values at marked room temperature (289.15 K) in all graphs and tables. In addition, the absence of negative or imaginary frequencies in calculated data point out and support the structural arrangement of both virgin polymers and also in their suggested complexes poly blend. In the contrary of figures (2, 3 and 4) which show convex behavior according to equation (2), the enthalpy shows a concave behavior eq. (1).

Conclusions

Calculated vibrational spectra proved the equilibrium of suggested structures especially in the absence of imaginary frequencies. Present study indicates that the use of DFT can predict the thermodynamic parameters at temperatures not reached through any experimental methods. Obtained data of polymer blend lay between that of both polymeric constituents indicating interaction and complexation of polymer blend at all temperatures. The plot of the entropy and heat capacity as a function of temperature show a convex behavior while the enthalpy show a concave behavior supported by the given equations.

Conflicts of Interest

No conflict of interest.

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