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Atomistic simulations of the structure and thermodynamic properties of poly(1,2-vinyl-butadiene) surfaces

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Abstract

Computer simulations play an important role in the design of new polymers and in the prediction of the properties of existing polymers. Atomistic modeling of amorphous poly(1,2-vinyl butadiene) using molecular mechanics and molecular dynamics simulations was carried out in three-dimensionally periodic and effective two-dimensionally periodic condensed phases. Sets of sample structures of two different periodicity (box edge lengths of 23.982 and 30.042 Å) were generated in order to explore the structural and energetic aspects as a function of the simulation cell size. The calculated surface energy for poly(1,2-vinyl-butadiene) compares very well with the experimental value reported in literature. The equilibrium structure of the films shows an interior region of mass density reasonably close to the value in the bulk state and an outer surface layer of approximately 20 Å across which the density falls rapidly but smoothly to zero at the outer limit of the free surface. The overall characteristics of the atomistic simulation approach is found to be similar to those presented in previous investigations for flexible polymers. In order to create the surface from the bulk state, energetic changes as a result of changes in the states of torsions and bond angles are favored, and these are opposite to the changes in the energies originating from non-bonded interactions. The dominant molecular energetic contribution to the formation of the surface is from dispersion forces (van der Waals).

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Keywords: Poly(1,2-vinyl-butadiene); Thin films; Surfaces

1. Introduction

The experimental design and synthesis of new polymers for a particular application is a time consuming and expensive procedure. The properties of polymeric materials at the molecular level can be predicted to a reasonable degree of success, at the present time, using computer based molecular simulations. Atomistic modeling can give useful insights when applied to polymeric systems in their condensed phases without loss of the details of their chemical structure. Simulations of amorphous polymers are typically performed by several established methodologies, whereby atoms are subjected to Monte Carlo simulations (MC), energy minimizations (EM) and molecular dynamics (MD). Such simulation methods can be used to obtain equilibrium conformations of polymer chains which bring the polymers sufficiently close to their thermodynamically realistic states, depending on how the simulations are performed and the nature of the overall simulation strategy. The quality of the force field that is employed in such atomistic simulations is an important factor in determining the ability of the simulations to predict the particular properties of experimental interest.

Due to widespread practical applications, the occurrence of polymer surfaces is important in several areas of polymer science and technology such as coatings, adhesives and paints [1,2]. Computer based simulations offer a neat, powerful and inexpensive way for the prediction of structural and thermodynamic properties of polymer surfaces. First, lattice MC simulations of a polymer melt-vacuum interface (free polymer surface) were performed by Madden [3] using a film adsorbed on a solid surface. Subsequently other studies have used lattice MC [4,5], off-lattice MC [6–8], and lattice-fluid models [9,10] in the literature, with most of these studies looking at surfaces made of polyethylene-like chains either in their glassy state or in the form of an amorphous melt. More recently, high coordination lattice MC simulations reported by Mattice and coworkers have become popular, due to their speed of

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implementation to large systems, where the methods have been employed to successfully simulate the structure and thermodynamics of polyethylene [11] and polystyrene [12] free surfaces with reverse mapping to provide full atomistic description.

Simulations of atomistic chains are attractive as opposed to coarse-grained approaches at this time, as currently available coarse-graining procedures are not general in their formalisms and have yet to be tested for a wide range of polymers and a variety of different polymer properties. Fully atomistic simulations, either using MC or MD techniques have been in use for a considerable time in the past. Atomistic level descriptions offer the advantage of (a) a correct chemical representation of the polymer structure, (b) potential of accurately predicting structure and thermodynamic properties of condensed phases and (c) the applicability to polymers that have more complicated chemical structure than polyethylene or bead-spring chains, with the validated force-field parameters derived from experiments or ab initio quantum mechanical calculations. Such simulations have been employed in the past for the calculation of surface properties of some semi-crystalline polymers such as polyethylene [13], atactic polypropylene [14], poly(1,4-*cis*-butadiene) [15], poly(1,4-*trans*-butadiene) [16], atactic linear hydrocarbons like ethylene–propylene random copolymers [17], and of styrene–butadiene (SB) and styrene–butadiene–acrylonitrile (SBA) random copolymers containing butadiene segments having all three types of stereochemical units [18]. In all of these studies, the predicted surface energies of the polymers compared favorably with experimental data, except for the study on the ethylene–propylene copolymers [17] where atomistically calculated surface energies could not be directly compared to experimentally derived Flory mixing parameter χ for the blends among these copolymers. We therefore extend the atomistic approach here to calculate the surface energy and atomistic structure of poly(1,2-vinyl-butadiene) so that we can test the results of the simulations with available experimental data on the surface energy from the literature.

Commercially, atactic poly(1,2-vinyl-butadiene) is extensively used in rubber and tire industry, while syndiotactic poly(1,2-vinyl-butadiene) is used for the manufacture of footwear soles, tubes and hoses. Earlier studies on four microstructures formed by poly(1,4-*cis*-butadiene), poly(1,4-*trans*-butadiene), poly(1,2-vinyl-butadiene), and a random copolymer of these stereochemical structures (55% *trans*, 35% *cis*, and 10% vinyl) were analyzed for their single chain properties and the bulk amorphous structural properties [19–22]. Here, we chose poly(1,2-vinyl-butadiene), hereafter denoted as 1,2-PBD, to study the molecular factors that lead to its amorphous surface properties. Our investigation also aimed at determining the effect of simulation box size on the surface properties. The structural aspects of the surfaces and the thermodynamic properties such as surface energy in our present study is compared with results of previous simulation reports on other polymers. The comparison of simulated surface energy with experimental data is favorable and this is discussed in the later section of this paper.

2. Simulation methodology and computational details

The overall methodology is described in a simplistic manner in Fig. 1. The Doublepar force field [19–22], which is a modification of the Dreiding force field, that has proven to be successful previously for modeling of polybutadienes [19–22], was used in our study. The potential parameters specific to polybutadienes are taken from the original work of De Rosa et al. [23]. In the case of 1,2-PBD chains in vacuum, in their 3D condensed bulk state and in the 2D thin film state, the non-bonded van der Waals were calculated between atom pairs within a distance of 12 Å by an interaction termination using a spline function between 9 and 12 Å. The overall potential energy (i.e., the decomposition of force-field terms), is given by

$$E = E_{\mathrm{stretch}} + E_{\mathrm{bend}} + E_{\mathrm{torsions}} + E_{\mathrm{oop}} + E_{\mathrm{vdW}} \tag{1}$$

The terms in the force-field function in Eq. (1) include energy deviations for the bond lengths (stretch) and the bond angles (bend), the torsional potentials (torsions), the energy deviations due to the out-of-plane inversions (oop) of the double bond, and the non-bonded van der Waals (vdW) potential interactions. The *Accelrys* Cerius^2 molecular modeling software [24] was used for running the simulations on a Silicon Graphics Octane Workstation.

2.1. Amorphous cells

2.1.1. Generation of initial samples

Chains were generated with 45 and 89 monomer units of 1,2-butadiene. The chains generated were isotactic in their stereochemical structure. Cubic bulk cells with edge lengths 23.982 and 30.042 Å to give a set of small and a set of large cells, respectively, were obtained at 300 K by packing three 1,2-PBD chains into a box with periodic boundary conditions according to the method of Theodorou and Suter [25]. The bulk structures were generated using the procedure essentially similar to those in earlier reports on polybutadienes [20–22]. However, one difference in our approach here, compared to those from previous studies, rests on the use of relatively larger dimensions for the periodic box. The edge length of the periodic box was decided based on the experimental bulk density of polybutadiene (0.89 g/cm^3) and the molecular weight that we set for the chains. For cutting off the interatomic pairwise non-bond interactions a spline function fit between 9 and 12 Å was used for smaller cells and between 12 and 15 Å was used for the larger cells. Using RIS Monte Carlo, 100 initial samples for the smaller dimension cells and 50 initial samples of larger dimension cells were generated

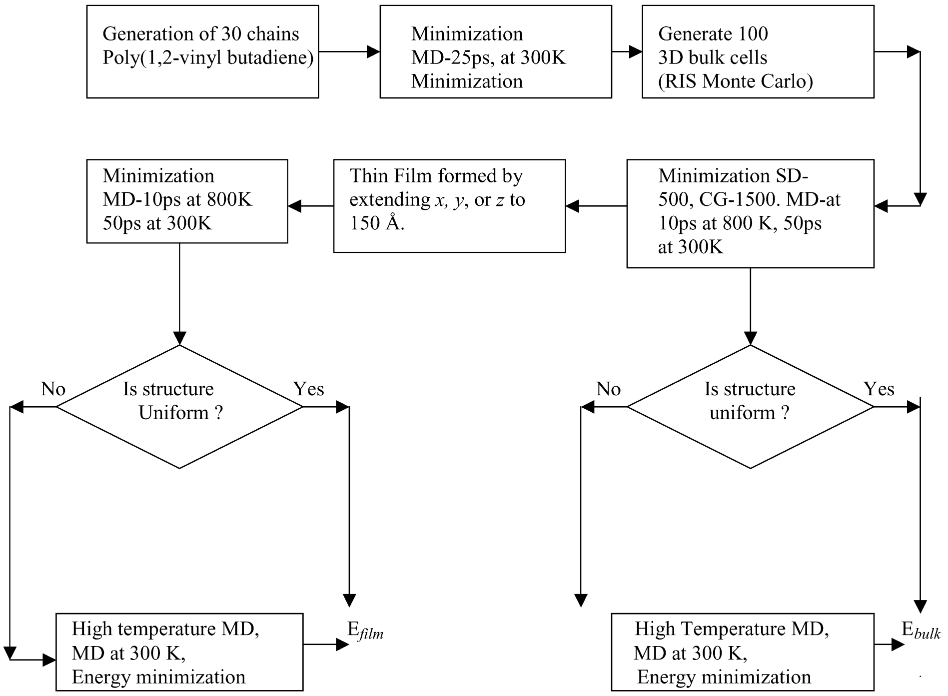


Fig. 1. Flow chart of the modeling procedure in order to derive equilibrium structures of amorphous nanoscale thin films of poly(1,2-vinyl butadiene).

with maximum allowable van der Waals overlap radii fraction set to an optimum value of 0.5. Using a value of 0.3 for this overlap parameter lead to poor packing and a value of 0.6 resulted in significantly higher potential energies. The number of atoms per cell was 1374 and 2694, corresponding to 24 and 30 Å cubic cell edge lengths, for the smaller and larger cells, respectively.

2.1.2. Molecular dynamics relaxation simulations

The NVT ensemble molecular dynamics simulation was employed to relax the bulk cells. The shape of the amorphous cells was kept constant (cubic) by not allowing the lengths and angles of the cell edges to vary. The velocity Verlet algorithm, one of the most widely used method for the time integration of the equations of motion, was employed with the advantage of being able to have the positions and velocities of atoms at the same time, without compromise on computational accuracy [26]. The temperature of the system was maintained with respect to the target simulation temperature as provided by an external temperature bath by using the stochastic collisions method of Anderson [27], which is known to generate rigorous ensemble. The overall result is a canonical ensemble simulation with an almost constant system temperature (as calculated from the kinetic energy at any time during the integration), but with small fluctuations which were less than 3% with respect to the specified temperature (during the 300 K runs). This provides a series of microcanonical simulations by maintaining constant energy between each stochastic collision. This method results in good equilibration of polymer bulk structures and sufficies for our present purpose. Acceptable equilibration of potential and kinetic energies by way of relatively small fluctuations ($<3\%$) were achieved.

The bulk samples were relaxed through an alternating series of constant NVT dynamics and energy minimization stages. Energy minimization was terminated successfully when the sum of energy gradients of all energy interactions was less than 0.05 kcal mol^{-1} Å^{-1} (i.e., total root mean-square atom force was less than 0.05 kcal mol^{-1} Å^{-1}). For most part, the molecular dynamics simulations were carried out at 300 K. For all of the initial independently generated structures, short dynamics at 700 and 800 K for 10 ps were required to shake the cell out of unfavorable local minima that had high energies. Subsequent to this high temperature stage, a molecular dynamics simulation at 300 K for 50 ps was performed. This was followed by energy minimization using Conjugate Gradient method. The cells that had low and acceptable potential energies were shortlisted and used as the 'collection of suitable samples' for further relaxation simulations and the rest of the initial samples were discarded. Also, additionally we applied the criterion that cells having a homogeneous structure, in terms of meeting the correct features of the radial distribution functions expected for 1,2-PBD [20], should be chosen to generate the thin films having two-dimensional periodicity (2D).

The relaxation molecular dynamics simulations at 300 K was performed on the shortlisted samples, for approximately 100–200 ps, depending on the time required to achieve fluctuations in the potential and kinetic energies less than 3% of the mean value which did not deviate running along integration time. The dynamics was done essentially using alternating stages of high temperature and room temperature dynamics, and finally subsequent to the alternating stages a sufficiently long molecular dynamics simulation (typically 100 ps) was performed at the end in order to obtain the final relaxed samples. Again, a final stage of energy minimization using conjugate gradient technique resulted in relatively low potential energies. This final sample for each different (independent) starting sample, was obtained after several hundred steps of energy minimization using the conjugate gradient method. In few of the cases, only 100 ps molecular dynamics run at 300 K was enough for sufficient energetic and structural relaxation of the starting structure without need for additional stages at high temperatures. The final energy- minimized samples were saved in order to give the set of independently relaxed structures for all property calculations. The details are provided in Table 1.

The end-to-end distances for the chains in the bulk state were approximately equal to 41.0 and 57.7 Å for small and large cells, respectively, for our relaxed bulk samples. These chain dimensions (reduced in terms of $\langle R^2 \rangle / M$) were close to the values under the theta conditions [28]. However, one must note that despite these numbers that naturally resulted from our simulations, the values are of the end-to-end distance and the radius-of-gyration were in most of the cases greater than one half the cell dimension. Therefore, these values do not reflect the actual state of the chains with respect to these particular geometric properties. This aspect is an outcome of the sizes of the atomistic periodic cells that we have used for the present study.

2.2. Thin films (free surfaces)

The thin film generation and relaxation was performed according to the method described previously [15,17,18] which has been found to be quite successful for amorphous, flexible polymers. We briefly describe the method here. Initial samples of amorphous thin films of 1,2-PBD were created by extending (in a single move all at once) the Z dimension of the 3D bulk periodic cell to 150 Å. This cell extension results in a rod-like cell having no effective non-bonded interactions between the images in the Z direction (the distance between images in the Z direction was kept at 150 Å). The Z direction specifies the direction perpendicular to the plane of the surface of the thin film. This cell extension resulted in two free surfaces per thin film.

These initial configurations of the chains (initial samples) as a result of the cell extension process, were subjected to alternating stages of high temperature (700 or 800 K, choice of the temperature is ad hoc) and room temperature (300 K) molecular dynamics simulations in the NVT ensemble (here constant volume refers to the cell volume and not the effective volume occupied by the atoms in the periodic box). The molecular dynamics procedure employed for relaxing the thin film samples was similar to the method we described earlier for the 3D bulk samples. No additional thermodynamic constraints on the atoms or the cell was employed, other than those posed by the molecular dynamics method we described in the previous section on the 3D bulk cell relaxation. The surface layers were eventually formed by this relaxation procedure and the final molecular dynamics stage was run at 300 K. Sufficient relaxation of the structure and acceptable fluctuations were observed for the potential and kinetic energies in order to ascertain whether samples were acceptable for the purpose of estimating the surface properties. High temperature MD stages were applied at certain times during the overall relaxation procedure, in order to bring the polymer films to their structural and thermodynamic realistic states by removal of unrealistic free volumes and packing inefficiencies generated by the initial stage of the cell extension. The last snapshot of the cell during the molecular dynamics simulation was subsequently energy-minimized. This final cell (sample) which was used for the property estimation,

Table 1
Total molecular dynamics (MD) run time for the amorphous structures of 3D (bulk) and 2D (film with free surfaces) periodicity towards equilibration

Sample	Bulk		MD trajectory length used for calculating RDF[a] (ps)	Film	
	Total MD at 700–800 K (ps)	Total MD at 300 K (ps)		Total MD at 700–800 K (ps)	Total MD at 300 K (ps)
Small cells[b]					
1	30	475	50	13	275
2	40	250	100	25	350
3	50	325	88	10	150
4	50	150	50	20	225
5	45	500	100	30	325
6	25	350	375	10	200
Large cells[c]					
1	40	310	65	15	200
2	70	480	50	30	200

[a] Radial distribution functions for carbon atoms.

[b] Periodic 3D cell dimensions $x = 23.98$ Å, $y = 23.98$ Å, $z = 23.98$ Å.

[c] Periodic 3D cell dimensions $x = 30.02$ Å, $y = 30.02$ Å, $z = 30.02$ Å.

was derived from each starting film (from its respective bulk cell that was used for the extension procedure to generate the film). The surface properties, such as atom mass density variations and bond orientation order parameter across the thickness of the thin film and the surface energy were then calculated for each cell and average values of these properties were estimated over all samples. The details of the thin film simulations are provided in Table 1. Fig. 2 shows two sample structures of relaxed amorphous state of 1,2-PBD thin films.

3. Results and discussion

3.1. Atomistic structure and cohesive energy density of 3D bulk

The radial distribution functions for the various atom pairs, not presented here, are in agreement with results previously reported by Mattice and coworkers [20]. The potential energy decompositions for the relaxed bulk structures are given in Table 2. The cohesive energy E_{coh} is defined as the increase in internal energy per mole of substance if all intermolecular forces are eliminated. E_{coh} can thus be estimated as the ensemble average of the difference

$$E_{coh} = E_{isolated} - E_{bulk} \tag{2}$$

The Hildebrand solubility parameter δ is then defined as

$$\delta = (E_{coh}/V)^{1/2} \tag{3}$$

where V is the volume per mole of monomer units.

The values of E_{coh} and δ from our simulations for 1,2-PBD are given in Table 3. The mean solubility parameter δ for all the cells taken into account is calculated to be equal to 7 cal$^{1/2}$/cm$^{3/2}$ which is exactly the same as that obtained in the previous work by Mattice and coworkers on their independently generated structures [20]. The experimental value of solubility parameter that is reported for polybutadiene (stereochemical composition not presented) is 8.1–8.6 cal$^{1/2}$/cm$^{3/2}$ [29]. Our result for the solubility parameter of 1,2PBD is in perfect agreement with the value of 7.2 (cal/cm^3)$^{1/2}$ obtained by Lee [30] which was based on the correlation between δ and critical surface tension by the use of Small's constants.

3.2. Atomistic structure and surface energy of 1,2PBD films

Figs. 3 and 4 show the average mass density profiles and backbone C–C bond orientation order parameters for films created by the smaller periodic cells as well as the larger periodic cells. We first discuss the density variations across the film thickness. The density profiles are shown as a function of the distance from the center of mass of the film. The density of the film at its center of mass, is obtained as 0.8 g/cm^3 and this value is somewhat lower than the bulk density of 0.89 g/cm^3. Even though we do not perfectly recover the bulk density at the center of the film, since we do not employ the NPT molecular dynamics simulations, the surface properties such as density variations across the surface layer as well as the surface energy show correct trend and comparison with experimental value. The surface layer over which the density varies is found to be approximately 20 Å in thickness for the set of smaller and larger cells. One can therefore consider the surface layer thickness across which the mass density changes from the bulk value to a value of zero, is roughly 20 Å in case of 1,2PBD. The cell sizes as shown by our simulations do not have any impact on the surface layer thickness. Similar values of quantification of the surface layer have been obtained from previous studies, but their values are slightly smaller by using atomistic simulations on other polymers [15,18].

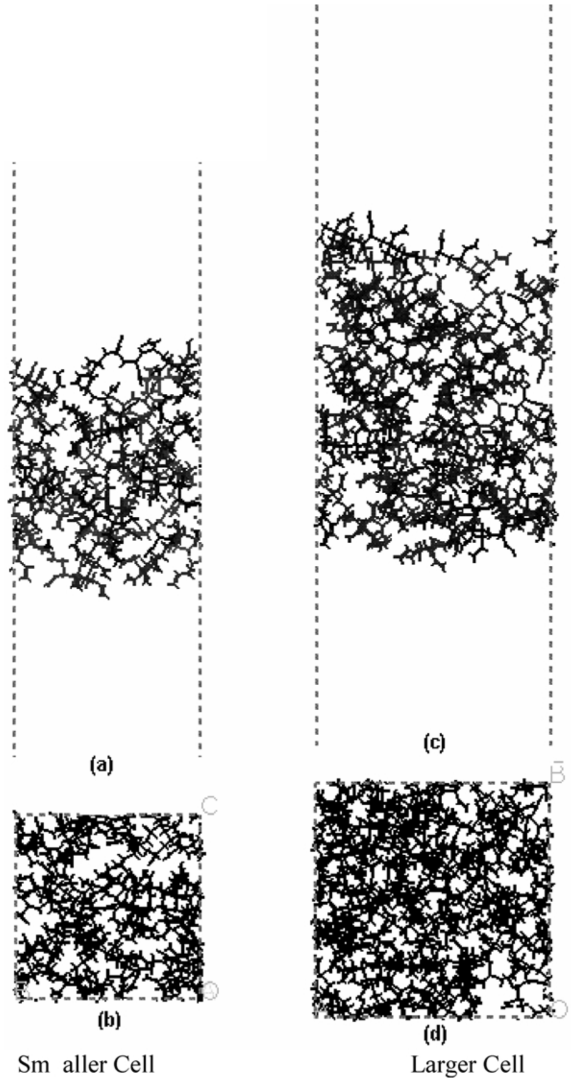


Fig. 2. (a) View in the direction of the surface plane of the film for smaller dimension cell. (b) View along the direction perpendicular to the surface of the film for smaller dimension cell. (c) View in the direction of the surface plane of film for larger dimension cell. (d) View along the direction perpendicular to the surface of the film for larger dimension cell.

Table 2
Total potential energy decomposition for 3D periodic bulk structures

Sample	Total (kcal/mol)	Bond stretching (kcal/mol)	Angle bending (kcal/mol)	Torsions (kcal/mol)	Inversions (kcal/mol)	vdW (non-bonded) (kcal/mol)
Smaller cells ($x = 23.98$ Å, $y = 23.98$ Å, $z = 23.98$ Å)						
1	1031	180.8	584.2	377.4	0.6	− 111.6
2	958	174.8	544.8	341.5	0.8	− 103.9
3	981	165.9	558.8	378.3	0.5	− 122.1
4	881	170.3	531.8	309.6	0.5	− 131.6
5	1004	167.6	584.3	377.7	0.6	− 126.3
6	1025	173.3	596.1	375.9	0.8	− 120.7
Mean	980 ± 55.9	172.1 ± 5.4	566.7 ± 25.5	360.1 ± 28.6	0.6 ± 0.1	− 119.4 ± 10.1
Larger cells ($x = 30.02$ Å, $y = 30.02$ Å, $z = 30.02$ Å)						
1	2105	341.8	1136	781.5	1.4	− 155.1
2	1946	332.1	1067	768.4	1.4	− 222.6
Mean	2025 ± 112.6	337 ± 7	1101 ± 49	774.9 ± 9.3	1.4 ± 0.0	− 188.9 ± 47.7

The C–C bond orientation order parameter, averaged over backbone bonds along the chains about the plane (x, y) of the film, at each distance across the film thickness is shown in Fig. 4. Only the backbone bonds were used in order to calculate the order parameter. The angle made by each bond with respect to the direction perpendicular to the plane of the surface (Z direction of the periodic cell) was used in order to calculate the orientation function according to the Hermann's orientation function method. The thickness of the thin film sample was divided into bins of 2 Å width along the Z direction and the average orientation angle was calculated in each bin by taking the average of the angle made by each bond that fell in the particular bin. The extension procedure employed to create the surface layers is such that a non-zero orientation function in the lateral dimensions (x and y) along the plane of the film are not facilitated, unless a preferred non-zero orientation in these directions prevails for the parent 3D bulk cell from which the film is created. The well-relaxed and structurally realistic 3D bulk cells all had zero orientation function (random bond orientations) in all three directions (dimensions). We therefore do not need to use additional orientation functions in the x and y directions, in order to determine the orientation order parameter in the Z direction, which otherwise would be needed in situations such as biaxial orientation processes for creation of thin films. For the samples based on smaller cell dimensions, the bond order (orientation) shows that the backbone bonds are orientated in a random manner with respect to the Z direction, in the interior region of the thin film away from the surface layer. For these cells with the smaller periodic dimension value, there is a slight tendency for in-plane orientation at the start of the surface layer from the direction of the bulk phase, but an orientation of the bonds to be somewhat perpendicular to the plane of the film is observed in going towards the outer limits of the free surface. This could be possible due to the limited statistics on the bond orientations contributing to the orientation function or a specific feature for this particular stereochemical polybutadiene. Previous studies have seen a distinct preference towards negative values of the orientation order parameter for the backbone bonds in the surface layers [14,15,18].

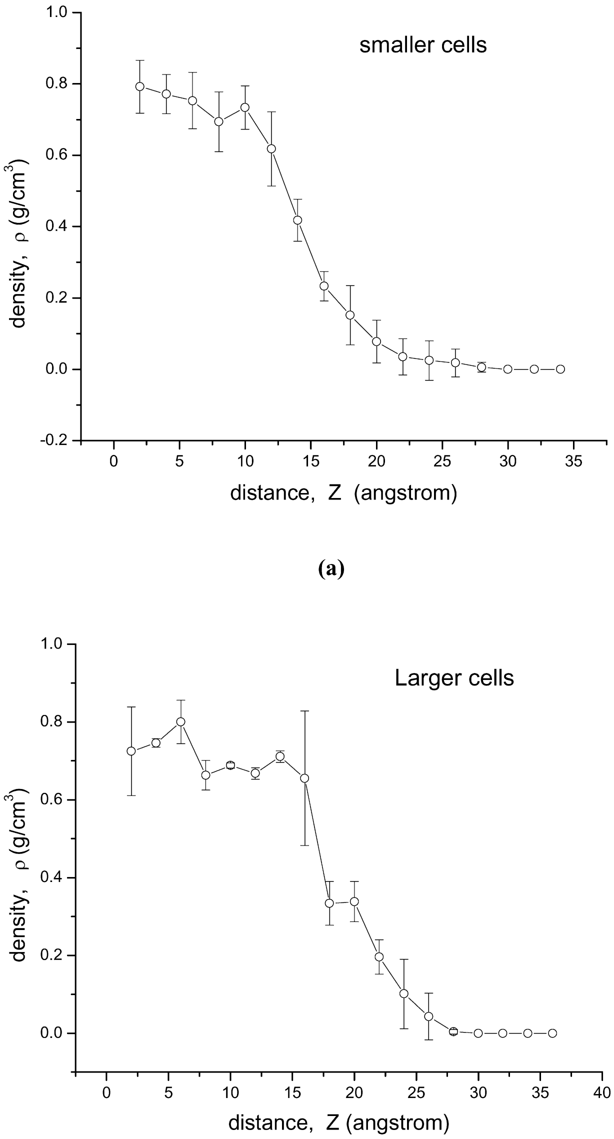
Table 3
Cohesive energy density (E_{coh}) and solubility parameter (δ) for vinyl PBD

Sample	$E_{\mathrm{coh}} \times 10^{-3}$ (cal/mol)	δ (cal$^{1/2}$/cm$^{3/2}$)
Smaller cells ($x = 23.98$ Å, $y = 23.98$ Å, $z = 23.98$ Å)		
1	395.6	6.90
2	405.2	6.98
3	431.3	7.21
4	406.8	7.00
5	408.6	7.01
6	430.6	7.20
Mean	413.0 ± 14.6	7.0 ± 0.1
Larger cells ($x = 30.02$ Å, $y = 30.02$ Å, $z = 30.02$ Å)		
1	743.0	6.75
2	775.9	6.89
Mean	759.4 ± 23.2	6.8 ± 0.1

Table 4 provides the energetic contribution of each of the bonded and non-bonded components of total potential energy for the fully relaxed samples of the thin films (surface structures). The surface energy is calculated from the difference in potential energy between the thin film (E_{film}) and its corresponding parent 3D bulk amorphous cell (E_{bulk}) from which the film is created. The surface energy was calculated using the relation

$$\gamma = \frac{E_{\mathrm{film}} - E_{\mathrm{bulk}}}{2A} \tag{4}$$

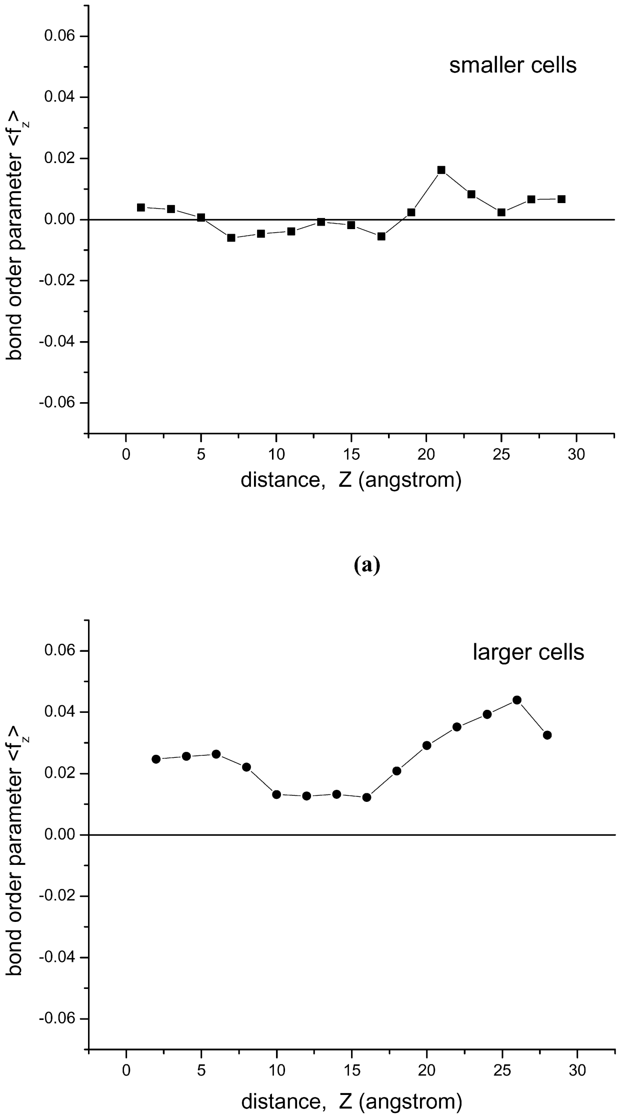
where E_{bulk} is the energy of the amorphous bulk, E_{film}, energy of the thin film and A is the area per free surface of the film having two free surfaces. The most dominant contribution to the formation of the free surface of the film comes from the van der Waals dispersion energy as can be seen from Table 5 wherein the energy differences, for each type of molecular contributor from the force-field terms, is



(a)

(b)

Fig. 3. Mass density profile for poly(1,2-vinyl butadiene) structures across the films as a function of the distance from the film center of mass. (a) The profile is averaged over six independently generated structures ($x = 23.982$ Å, $y = 23.982$ Å). (b) The profile is averaged over two independently generated structures ($x = 30.02$ Å, $y = 30.02$ Å).



(a)

(b)

Fig. 4. Distance profile of backbone C–C bond orientation order parameter across the thickness of the films as a function of distance from the center of mass of the films. (a) Profile for the set of two structures having smaller *XY* cell dimensions. (b) Profile for the set of six structures having smaller *XY* cell dimensions.

presented. The dispersion energies are significantly positive for the films in comparison to the isotropic bulk state, which means that a significant level energetic penalty has to be met in order to create the surface. Table 6 lists the surface energy for the samples along with the contributions coming from the bonded and non-bonded energetic interactions. Also significant, but via an opposing effect, are the energy contributions (difference between bulk and thin film samples) arising from changes in the bond torsions and bond angles in going from the bulk state to the surface state.

The surface energy value of 22.2 ± 3.5 erg/cm^2 for the set of six smaller cells, 25.6 ± 3.7 erg/cm^2 for the set of two larger dimension cells, and 23.0 ± 3.6 erg/cm^2 as obtained when averaged over the smaller and larger cells put together (without making disparity in the cell dimensions), shows that the simulation results presented here are able to predict successfully the experimentally derived surface energy of 1,2-PBD which is 25 erg/cm^2 [30]. The comparison between simulated and experimental values of the surface energy is good and the experimental value falls within the positive standard deviation imposed on the mean calculated value. The simulated value slightly underpredicts the experimental value and this has also been observed in previous

Table 4
Total potential energy decomposition (in kcal/mol) for thin film samples (each having two free surfaces) of poly(1,2-vinyl butadiene)

Sample	Total (kcal/mol)	Bond stretching (kcal/mol)	Angle bending (kcal/mol)	Torsions (kcal/mol)	Inversions oop (kcal/mol)	VdW non-bonded (kcal/mol)
Smaller cells ($x = 23.98$ Å, $y = 23.98$ Å)						
1	1069	177.5	555.4	319.8	0.6	15.4
2	995	176.7	492.2	288.1	0.5	37.2
3	1018	172.3	558.7	279.3	0.4	7.4
4	934	171.2	506.8	252.3	0.4	3.4
5	1047	172.6	566.3	324.2	0.5	−16.1
6	1067	176.8	562.0	302.7	0.5	28.0
Mean	1022 ± 51.7	174.5 ± 2.8	540.2 ± 32.1	294.4 ± 27.0	0.5 ± 0.1	12.5 ± 18.8
Larger cells ($x = 30.02$ Å, $y = 30.02$ Å)						
1	2189	351.9	1110.4	640.4	1.0	85.6
2	2015	344.5	1041.2	603.1	0.9	25.2
Mean	2102 ± 123.3	348.2 ± 5.2	1076 ± 48.9	621.7 ± 26.4	0.9 ± 0.1	55.4 ± 42.7

Table 5
Molecular contributions to the potential energy difference between thin film and bulk structures

Sample	Potential energy (kcal/mol)	Bond stretch (kcal/mol)	Angle bend (kcal/mol)	Torsions (kcal/mol)	Inversions (kcal/mol)	vdW non-bonded (kcal/mol)
Smaller cells ($x = 23.98$ Å, $y = 23.98$ Å)						
1	37.2	−3.3	−28.8	−57.7	0.0	127.0
2	36.7	1.9	−52.6	−53.4	−0.3	141.1
3	36.7	6.4	−0.1	−99.0	−0.2	129.5
4	53.5	0.9	−25.0	−57.3	−0.1	134.9
5	43.6	4.9	−17.9	−53.5	−0.1	110.2
6	44.6	3.5	−34.2	−73.1	−0.3	148.7
Mean	42.0 ± 6.6	2.4 ± 3.4	−26.4 ± 17.4	−65.7 ± 17.9	−0.2 ± 0.1	131.9 ± 13.2
Larger cells ($x = 30.02$ Å, $y = 30.02$ Å)						
1	83.9	10.1	−25.5	−141.0	−0.4	240.7
2	68.7	12.4	−25.7	−165.3	−0.4	247.7
Mean	76.3 ± 10.8	11.2 ± 1.6	−25.6 ± 0.2	−153.1 ± 17.1	−0.4 ± 0.04	244.2 ± 4.9

Table 6
Molecular contributions to the surface energy

Sample	Total potential energy difference (erg/cm^2)	Bond stretching (erg/cm^2)	Angle bending (erg/cm^2)	Torsions (erg/cm^2)	Inversions out-of-plane (erg/cm^2)	vdW non-nonded (erg/cm^2)
Smaller cells ($x = 23.98$ Å, $y = 23.98$ Å)						
1	19.6	−1.7	−15.3	−30.5	0.0	67.1
2	19.4	1.0	−27.8	−28.2	−0.1	74.5
3	19.4	3.4	−0.0	−52.3	−0.1	68.4
4	28.3	0.5	−13.2	−30.3	−0.0	71.3
5	23.0	2.6	−9.5	−28.2	−0.0	58.1
6	23.5	1.9	−18.0	−38.6	−0.2	78.3
Mean	22.2 ± 3.5	1.3 ± 1.8	−14.0 ± 9.2	−34.7 ± 9.5	−0.1 ± 0.07	69.6 ± 7.0
Larger cells ($x = 30.02$ Å, $y = 30.02$ Å)						
1	28.3	3.4	−8.57	−47.5	−0.1	81.1
2	23.0	4.2	−8.63	−55.7	−0.1	83.4
Mean	25.6 ± 3.7	3.8 ± 0.5	−8.6 ± 0.0	−51.6 ± 5.8	−0.1 ± 0.02	82.2 ± 1.6
Mean (over all samples)	23.0 ± 3.6	1.9 ± 1.9	−12.6 ± 8.2	−38.9 ± 11.4	−0.1 ± 0.07	72.7 ± 8.3

simulations on SB and SBA copolymers [18]. But the level of agreement between simulated and experimental values is slightly better than those provided by the previous studies on other polymers such as atactic polypropylene [14] and SB copolymer [18].

The standard deviation in the calculated surface energy is reflective of the relatively fewer number of samples that were used in the calculation and this is not a drawback of atomistic simulation approach in itself. We also find that it is not easy to generate a large number of independent initial structures which can give good thin films with accurate surface energies and we were able to chose eight best structures out of more than 150 generated initial structures through an initial series of molecular dynamics and energy minimizations. The final structures were those which initially gave reasonably uniform and well packed surfaces upon extension of the periodicity of the respective bulk cell. The approach here, is shown to be successful in order to predict the surface energies of amorphous flexible polymers with full atomistic details so as to also recover the structural properties such as density profiles of the surfaces. We did not perform entropy simulations in our present study. Notwithstanding minor entropic contributions relative to the far more dominant enthalpic contributions to the surface tension, we compare calculated surface energy from atomistic simulations with the experimental surface tension that is reported. This has given good agreement.

Alternatively, the surface energy can also be calculated from the solubility parameter values using the following empirical equation as provided in the reference of Zisman [2] among other papers in the literature

$$\gamma = 0.75E_{\mathrm{coh}}^{2/3} \tag{5}$$

The surface energy values of 1,2-PBD calculated using Eq. (5), with the cohesive energy density obtained from our bulk cell simulations, are 27.1 erg/cm^2 for small cells and 30.2 erg/cm^2 for large cells. These values are in good agreement with the values obtained from Eq. (4) based on our atomistic simulations for the smaller dimension cells, but not for the larger dimension cells for which these values are also farther apart from the experimental value of 25 erg/cm^2 [30,31]. The values obtained using Eqs. (4) and (5) can therefore be ascertained to be comparable with the experimental value of 25 erg/cm^2 provided in the literature [30] from contact angle measurements (Zisman critical surface tension of wetting).

4. Summary and conclusions

Atomistic simulations employing molecular mechanics and molecular dynamics have been used to generate bulk and thin film structures of poly(1,2-vinyl-butadiene). The calculated bulk properties are in agreement with experimental values. The surface properties such as density variations across the thickness of the thin film bearing two free surfaces per film and the surface energy, show the correct behavior and compare well with experimental data. Two sets of samples having smaller and larger cell dimensions for the periodicity of bulk and surface structures were used in deriving the properties. Both sets of structures show predictive capability. This study extends previous studies employing similar procedures, to the case of poly(1,2-vinyl-butadiene) here, which is a polymer of significant fundamental and practical relevance. The ability of the simulation methodology to extract the structural and energetic information on the amorphous polymer phase in the bulk as well as at the free surface, shows promise for such techniques especially when applied to reasonably flexible polymers.

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