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Molecular simulation of diblock copolymers; morphology and mechanical properties

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Abstract

Molecular modeling and computer simulations were used to construct, visualize, control and predict nanostructures with specific morphologies, self-assembling regions and mechanical properties associated to poly(styrene)–poly(isoprene) and poly(styrene)–poly(methyl methacrylate) diblock copolymers. Molecular structures of each diblock copolymer were constructed and used to obtain a Gaussian chain constituted of beads. Segment–segment interactions representing the chemical nature of the systems were obtained by means of numerical simulations. The numerical simulations for the two diblock systems predict structures with classic morphologies like bcc, hex, lamellar or gyroids and also other partial structure like islands and labyrinths. Young, bulk and shear modulus were also predicted from the structure and composition of the copolymer generating these morphologies. The excellent agreement between numerical and available experimental results opens a new strategy to modify existing diblock copolymer synthetic chemical processes to obtain products with specific morphologies.

Keywords: Morphology; Simulation; Gaussian chain

1. Introduction

Nowadays, polymeric materials science focuses on the synthesis of new materials with specific structures with dimensions between 1 and 100 nm. These mesoscopic scale materials are expected to have improved physical and chemical properties over the existing ones. Block copolymers comprise a particularly interesting class of materials constituted by two or more blocks of different polymer chains where each block presents sequences of 50–1000 repetitive units, linked by covalent bonds. When the blocks are miscible, these materials are homogeneous and exhibit disordered domains with properties intermediate with respect to the constituent blocks. In contrast, local segregation is observed whenever the blocks are incompatible; this is the case of ordered phases. This segregation leads to a process known as microphase separation generating materials with highly desirable properties impossible to achieve with classical blends [1–3]. Due to their ability to self-assemble in a variety of ordered phases, block copolymers present an important number of superstructures with dimensions ranging from a few nanometers to several micrometers. The transition from the disordered to the ordered state on these materials leads to periodic structures with specific morphologies which are controlled by several factors such as composition, block copolymer architecture and the segregation between different blocks governed by temperature and polymerization degree. At the mesoscopic scale, block copolymers are composed of microdomains with a particular phase dispersed in the other. Thus mechanical and physical properties of the resulting materials are strongly affected by the sample morphology [4]. Therefore, one may think that block copolymers will play an important role on the future of new polymeric materials. They can be employed to produce

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a wide range of microstructured materials such as nanoporous materials, membranes, nanoparticles and drug carriers, in a controlled way. Applications in materials science, molecular biology, electronics and pharmacy are being currently investigated [5]. At present, in addition to the ionic copolymerization techniques, new polymerization techniques are employed [6–9] which allow handling even hundreds of monomers, a capability not shown by existing processes, thus opening a way for new polymeric materials.

Molecular simulations offer a particularly useful way to explore the morphology and other physical properties of these materials and to make predictions that may be of interest in improving existing synthetic processes. Recent advances in molecular dynamics methodology [10] together with the high performance of modern computers have made possible to routinely study the microscopic details of chemical processes in condensed phase. These are advances in molecular simulations which permit to study systems in the mesoscopic domain [11–13] and, in particular, make possible to describe very large polymeric systems. In this work, the nanostructures and mechanical properties that generate the poly(styrene)–poly(isoprene) and poly (styrene)–poly(methylmethacrylate) diblock copolymers are studied by means of state-of-the-art of numerical simulations and molecular modeling techniques.

In the field of nanomaterials, and particularly in polymeric materials, self-assembling processes are phenomena with an enormous potential in practical applications. This self-assembling processes are a consequence of the chemical incompatibility between different constituting blocks, are governed by dissipative intermolecular (long-range) and attractive intermolecular forces (short-range), and are a fundamental requisite to generate superstructures. The long-range repulsive interactions occur between different chemical regions, whereas the short-range attractive interactions keep the blocks bind avoiding the macrophase separation in the system. The competition between attractive and repulsive forces in the block systems leads to segregation on the microphase domains and, therefore, to the formation of a structured material with characteristic dimensions in the 10–100 nm range. In the self-organization internal processes two competing effects govern the thermodynamics of the formation of nanostructures of bock copolymers melts. At high temperatures, the chains of these materials are homogeneously mixed (disordered system) and the mixing entropy governs the random process. When the temperature decreases, the tendency of the blocks to segregate is favored by the demixing enthalpic process [14,15]. The demixing enthalpy is related with the Flory–Huggins segmental interaction parameter (χ) and, together with the degree of polymerization (N) (configurational and translational entropy), represents the magnitude of segregation between the different blocks into microdomains (microphase separation). The order–disorder transition in these materials drives the formation of periodic structures of ordered phases with specific morphologies. Experimentally it is known that the behavior of microphase separation is controlled by the following parameters: (i) Degree of polymerization; (ii) architecture (diblock, triblock, block star) and composition; (iii) segment–segment interaction parameter (χ).

In the present work, mesoscale models were used to represent the diblock copolymers molecules. Considering the self-assembling ability of these materials in the bulk, this is a logical assumption. In these models, the molecular architecture and the segment–segment interaction parameter drive the chemistry of the system. The present models are developed for the representation of macromolecular systems like polymers, but these can be easily used for other complex systems displaying the self-assemble phenomenon.

2. Methodology

The structures of poly(styrene)–poly(isoprene) (PS–PI) and poly(styrene)–poly(methylmethacrylate) (PS–PMMA) diblock copolymers were built using a polymers builder. Each diblock molecule contains 100 repetitive units in the main chain and the lineal architecture is the characteristic for each system. The molecular weights for each studied system presented an interval of 7160–10040 for the PS–PI and of 10040 at 10360 for the PS–PMMA. The conformational properties of molecular systems were calculated using the RIS Metropolis Monte Carlo software (RMMC) from Accelrys Inc. and the COMPASS (Condensed-phase optimized molecular potentials for atomistic simulation studies) force field [16,17]. The polymeric chains are represented by a group of spherical beads or particles connected by harmonic springs (Gaussian Model) [18], where each bead represents a section of the chain of the block copolymer. The quantitative estimates of the bead–bead interaction for the systems were calculated from the segment–segment interactions using the statistical thermodynamic model of the polymer solutions Flory–Huggins theory. In this theory the miscibility behavior is governed by the mixing Gibbs free energy and can be obtained from Eq. (1);

$$\Delta G = \frac{\phi_1}{X_1}\ln\phi_1 + \frac{\phi_2}{X_2}\phi_2 + \chi\phi_1\phi_2 \qquad (1)$$

where ΔG, mixing free Gibbs energy per mole, ϕ_1 and ϕ_2, volume fraction for components 1 and 2, respectively, X_1 and X_2, degree of polymerization (chain length) for components 1 and 2, respectively; and χ, Flory–Huggins interaction parameter defined as:

$$\chi = \frac{Z\Delta E_{12}}{RT} \qquad (2)$$

where Z is the coordination number of the model lattice and E_{12} is the differential energy of interaction of an unlike pair, Eq. (3):

$$\Delta E_{12} = \frac{1}{2}(E_{12} + E_{21}) - \frac{1}{2}(E_{11} + E_{22}) \tag{3}$$

In this model, each repeating unit is defined as occupying a single lattice site.

To calculate the mixing Gibbs free energy and the interaction parameter Z and ΔE_{12} are calculated by means of molecular simulation techniques using the Flory–Huggins modified model by Feng and Blanco [19]. In this extension of the Flory–Huggins model, the molecules are not arranged on a regular lattice, as in the original Flory–Huggins theory, but they are arranged off-lattice. The coordination number Z is explicitly calculated for each of the possible molecular pairs using Monte Carlo molecular simulations. This numerical procedure involves generating clusters in which nearest neighbors are packed around the central molecule until no extra volume is left for additional packing. Average calculated Z values are employed in the temperature dependence expression of the interaction parameter. The mixing Gibbs free energy dependence on the temperature, $\Delta G(T)$, is obtained from the configurationally interaction energies and coordination numbers as follows:

$$\Delta G(T) = \frac{[Z_{12}E_{12}(T) + Z_{21}E_{21}(T) - Z_{11}E_{11}(T) + Z_{22}E_{22}(T)]}{2} \tag{4}$$

The corresponding temperature dependent interaction parameters, $\chi(T)$, are also calculated as a function of temperature from $\Delta G(T)$ and Z as in Eq. (5).

$$\chi(T) = \frac{\Delta G(T)}{RT} = \frac{(Z_{12}E_{12} + Z_{21}E_{21} - Z_{11}E_{11} + Z_{22}E_{22})}{2RT} \tag{5}$$

To predict the phase structure (morphology) of diblock copolymers a method known as dissipative particle dynamics (DPD) has been employed. This method, as conceived by Hoogerbrugge and Koelman [20], represents an improvement over conventional molecular dynamics MD especially well suited to describe the hydrodynamics behavior of complex systems constituted by particles with a computational efficiency similar to that obtained using the canonical ensemble. Español and Warren [21] identified the link between the DPD algorithm and an underlying stochastic differential equation for particle motion, thereby establishing DPD as a valid method for the simulation of the dynamics of mesoscopic particles. Groot et al. [22–24] have recently related the DPD method to the solutions of the Flory–Huggins theory thus allowing one to study large molecular weight systems under efficient operation conditions. Further, they have demonstrated that this approach is consistent with the mean field theory.

In the simulation, the dynamic evolution of all particles representing small regions of the diblock copolymer chain is governed by the Newton's equation of motion. The dynamic behavior of the system is followed by integration of the equations of motion using a modified version of the Verlet algorithm. In the simulation, each particle is defined by its position r_i and momentum p_i, which are calculated at each time step. Each particle is subject to soft interactions with its neighbors via three forces within a given cutoff radius r_c. These are: a conservative force F_{ij}^{C}, which is lineal with respect to the particle–particle separation, a dissipative force F_{ij}^{D} which is proportional to the relative speed of the two particles, and a random force F_{ij}^{R} between the particle and its neighbors. For particles separated by a distance larger than r_c, the interaction forces are neglected. Therefore, the total force acting on a given particle is as Eq. (6)

$$F_i = \sum_{i \neq j} \left[-a_{ij}(1 - |r_{ij}|\hat{r}_{ij}) \frac{\text{if}|r_{ij}| < 1}{0\ \text{if}|r_{ij}| > 1} - \gamma\omega^{D}(r_{ij})(v_{ij}\hat{r}_{ij})\hat{r}_{ij} + \sigma\omega^{R}(r_{ij})\xi_{ij}\hat{r}_{ij} \right] \tag{6}$$

The coefficients of the random and the dissipative forces are ω, ξ and γ, respectively, and the variances of the random forces is σ. Mathematical details of these forces and of the algorithm are given in Kong et al. [25], and Groot et al. [24].

The mechanical properties of PS–PMMA and PS–PI materials are assumed to exhibit a small-strain behavior (i.e., small deformations) and were calculated as a function of the chemical composition and molecular structure of each diblock copolymer system, using the relationships developed by Seitz et al. [26]:

$$B(T) \approx 8.2333E_{\mathrm{coh}} \left[\frac{5V(0K)^4}{V(T)^5} - \frac{3V(0K)^2}{V(T)^3} \right] \tag{7}$$

$$\nu(T) \approx 0.513 - 3.054 \times 10^{-6} \sqrt{\frac{V_\mathrm{w}}{l_\mathrm{m}}} \tag{8}$$

$$E = 2(1 + \nu)G = 3(1 - 2\nu)B \tag{9}$$

where ν is the Poisson's ratio, l_m denotes the length of a copolymer repeat unit in this fully extended conformation, V is the molar volume, V_w is the van der Waals volume, E_{coh} is the Fedors-type cohesive energy and E, B, G are the Young, Bulk and shear modulus, respectively. Eq. (7) is based on a potential function model that considers the effect in a polymer of a deformation on the non bonded interchain interaction whereas Eq. (8) is completely empirical.

3. Results and discussion

For a proper simulation of the block copolymers and for the specific case of the PS–PMMA and PS–PI systems in bulk the degree of polymerization, architecture and composition and finally, the segment–segment interaction parameter are of fundamental importance. The role of these variables was analyzed leading to representative models for the prediction of mechanical properties. The PS–PMMA and PS–PI diblock copolymer chains with a lineal architecture were analyzed by molecular simulations to obtain their conformational properties. All single and double bonds in the diblock chain are allowed to rotate during the simulation except those involving bonds of the rings of the poly(styrene) fragment. The molecular chains of each diblock copolymer was represented by a standard Gaussian Model constituted by beads of type; $[\text{block A}]_m-[\text{block B}]_n$. The number of beads in each Gaussian Model was determined using the degree of polymerization and characteristic ratio (C_n) of the block copolymer. Each model is composed of N beads, each bead represents a large number of repetitive units (segment) of the molecular chain of which an f fraction forms the (PS) block and the rest forms the (PI or PMMA) block. Different segments are assumed to have equal volume; this is a necessary assumption in order to conform the Flory–Huggins theory and for the dissipative particle dynamics model [22,27]. The election of the appropriate parameters for the representation of diblock copolymers is an important aspect that must be kept in mind for the subsequent molecular simulations. From a practical numerical point of view, it is desirable to use few beads in the diblock copolymer description. Hence, the PS–PI diblock copolymer is represented by a model constituted by 10 beads whereas PS–PMMA copolymer by a model of 12 beads as is exemplified in the Fig. 1.

Because of the mesoscopic scale of the present problem, all atomistic details are ignored in the statistics representation (Gaussians Models) of the diblock systems. The chemistry of each copolymer is governed by bead–bead interactions and by the molecular architecture. The bead–bead interactions between different segments $[\text{block A}]_m$ and $[\text{block B}]_n$ is given by the magnitude of repulsion between different repetitive units. For each diblock system, this repulsive interaction was determined from the thermodynamic behavior of polymer/polymer binary mixtures by combining the Flory Huggins theory and molecular simulations. Prior mesoscopic simulations, the polymeric fragments of poly(styrene), poly(*cis*-1,4 isoprene) and poly(methyl methacrylate) were constructed from molecular models and their structure optimized with the COMPASS force field. Typically 100,000 pair configurations and 500 clusters, where the statistical error is small, were examined to calculate the interaction energy and coordination number of each binary system. The resulting temperature dependent interaction parameters $\chi(T)$ of each polymer/polymer fragment are shown in Fig. 2. The parameters of interaction obtained by simulation are comparable with the obtained from experimental data (solubility parameters) [28,29] using the Flory–Huggins relation [30]. For example: At temperature of 300 K for the PS–PI and PS–PMMA systems we obtain from the simulation the following values $\chi=0.3855$, $\chi=0.2632$, where experimental values are $\chi=0.3812$, $\chi=0.2517$, respectively.

The PS, PI and PMMA fragments are incompatible in different degrees and the phase separation occurs with temperature lowering. A small incompatibility between different polymeric fragments is amplified in giant molecules as the block copolymer builds up; this fact has been exploited in the subsequent simulations. The a_{ij} parameter of the conservative force (Eq. (6)) referred to as bead–bead repulsion parameter or simply as DPD interaction parameter depends on the underlying atomistic interactions of segments polymeric.

3.1. Mesoscopic simulation: PS–PI and PS–PMMA systems

The mesoscopic simulations were carried out in a DPD simulations cell of $20r_\text{c}\times20r_\text{c}\times20r_\text{c}$ containing a total of 24,000 beads and a density $\rho=3$. All simulations were made at temperature KBT = 1, this allows a reasonable and efficient relaxation for each diblock system, where the disturbance noise is diminished to the maximum. The number of beads representative for each diblock model were

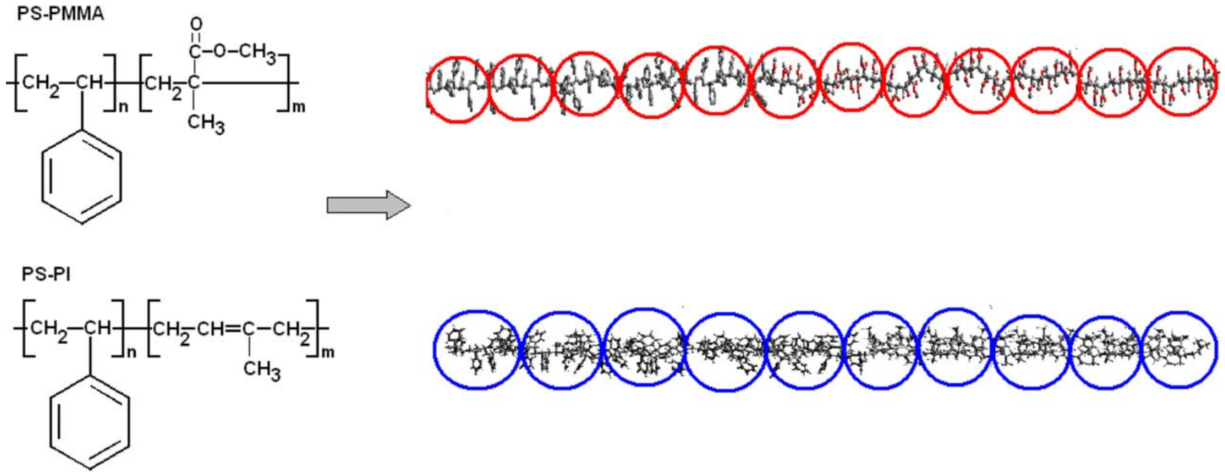

Fig. 1. Statistical representation of PS–PMMA and PS–PI diblock copolymer systems obtained by molecular simulation.

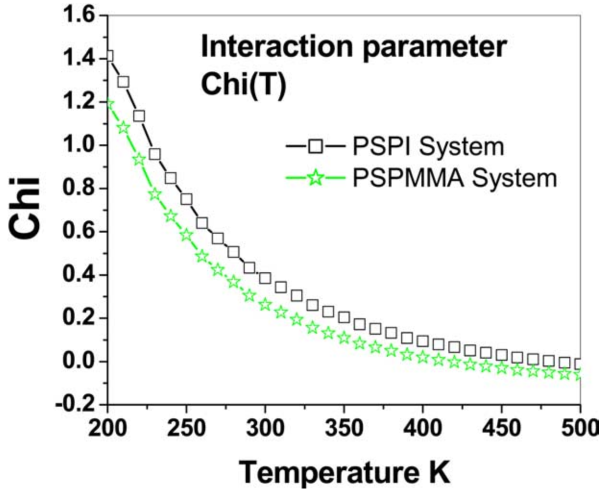

Fig. 2. Interaction parameters for the PS–PI and PS–PMMA systems.

assumed to be constant and the composition intervals analyzed were 0.1–0.9 (volume fraction).

All simulations start from a random disordered state (homogenous), hence, the final structures can be considered as dependent of the composition and initial architecture of the diblock copolymer. The description of each diblock model generates a coarse-grained system sufficiently large to determine the separation of the microphase and the formation of structures with defined morphologies. Figs. 3 and 4 shown the surfaces of density of different microdomains obtained from simulations on the PS–PI and PS–PMMA systems. The morphologies show rich microdomains of a single type of homopolymer chains separated by interphases. For the PS–PI system, when the volume fraction of a component increases (PS) relative to the other one (asymmetric copolymer), the interphase tends to become curve. This is because the chains of a component are more extended thus allowing the formation of a few planar interfaces. In this case, the conformational entropy loss of the majority component is too high. Therefore, to gain the conformational entropy, the chains of the majority component tend to expand along the direction parallel to interface. As a result, the polymer/polymer interface becomes convex towards the minority component. This interface curvature effect is more pronounced when the composition of the diblock copolymer is more asymmetric. The asymmetric copolymers display spherical morphology formed by body-centered-cubic (bcc) packing of the less dispersed component into the matrix of the majority component. When the volume fraction of the minority component continues to increase (relative chain length of the homopolymer) in the matrix of the majority component, hexagonal packed cylinder (Hex) morphology evolves. The bicontinuous cubic phase, sometimes called gyroid phase is generated from the hexagonal phase by interconnection of microdomains of the same component. Block symmetric copolymers (when volume fraction of both components are the same) exhibits a lamellar morphology consisting of alternating layers of different components. Upon increasing the PS fraction, the morphology appears in a reversed order

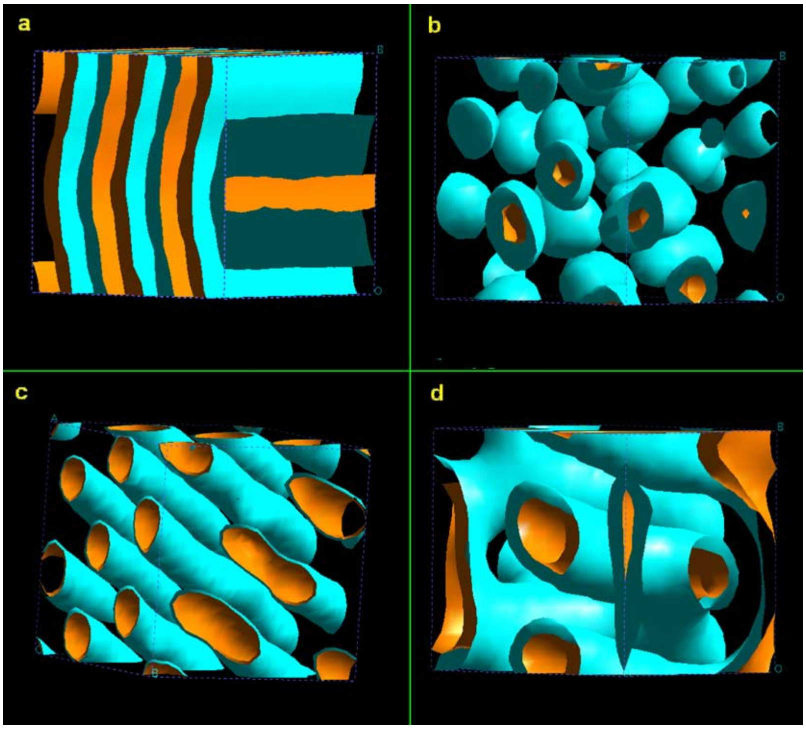

Fig. 3. Morphologies of the PS–PI diblock copolymer system obtained by simulation: (a) lamellar (Lam), (b) body-centered cubic (bcc), (c) hexagonal-packed cylinder (hex), (d) gyroids microstructure.

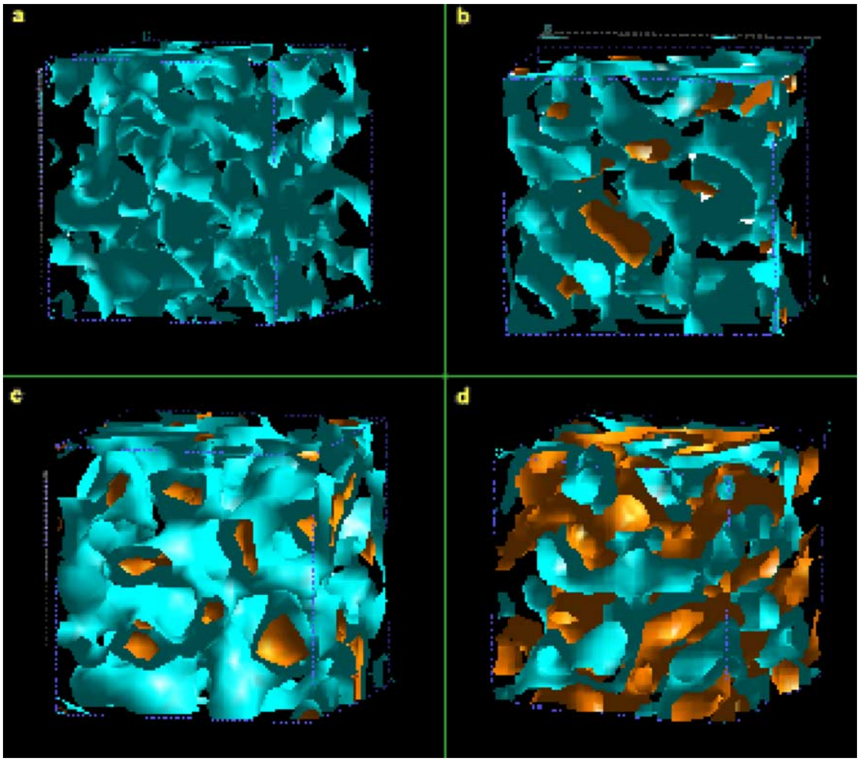

Fig. 4. Simulated morphologies of the PS–PMMA diblock copolymer system; (a) and (b) irregular microstructure, (c) Island type microstructure, (d) labyrinth microstructure.

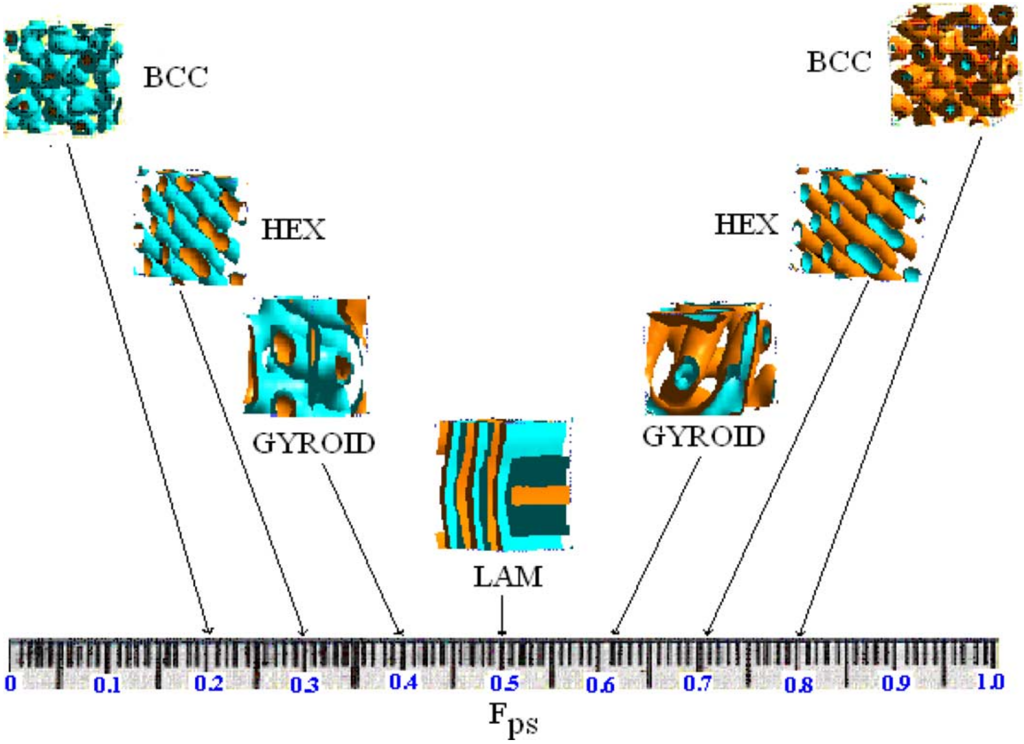

Fig. 5. Simulated morphologies of the PS–PI system and their composition domain.

and asymmetric systems evolve again; Fig. 5. These morphologies are similar with that published by Groot et al. [23], where they propose directly a model of beads, which is the base of the method used in the present work. Here, the model for the PS–PI system was obtained from the molecular structure of the copolymeric chain, where the bead–bead interaction parameter is acquired from the monomer–monomer interaction. Then, the use of a different monomer totally modifies the bead–bead interaction parameter and consequently the morphology, like is observed for PS–PMMA system.

Irregular morphologies of islands and labyrinth are characteristics for the PS–PMMA system, Fig. 4. The microphase separation as a function of the composition is partial because the minority component chains are mixed, in a certain degree, in the matrix of the majority component. This is attributed to the chemical nature of the components, see Fig. 6. The variety of self-assembled nanostructures of PS–PI and PS–PMMA diblock copolymer systems in bulk is very broad. The most important factor controlling the phase morphology is the composition. This is since the form of the polymer/polymer interphase changes with the relative chain length and because the segregation parameter (χN) is of fundamental importance for the formation and prediction of classic or partial microdomains.

The morphologies obtained by simulation for the diblock systems can be compared qualitatively with the morphologies reported by Khandpur et al. [31] and Weis et al. [32], see Fig. 7. This validates the diblock models, Gaussian chain parameters and interaction parameters used for each system. For the more complex block copolymer systems and other natural systems exhibiting the self-assembling phenomenon, the present representative factors of the molecular structure and segment–segment interactions, necessary for the simulation, can be extrapolated not only to the bulk but also to diluted solutions.

3.2. Mechanical properties: Shear, Young and Bulk modulus parameters

The mechanical properties are mainly due to the behavior exhibited by these polymeric materials under different testing modes of elastics properties; each one defining a characteristic modulus (Young (E), shear (G) and bulk (B)). In this work, the mechanical properties of the PS–PI and PS–PMMA diblock copolymers were obtained from the molecular structure models generating the representatives Gaussians models and specific morphologies. In order to estimate the mechanical properties we employed semiempirical and empirical relationships reported by Seitz et al. [26]. These relationships involve five fundamental molecular parameters. These are the molecular weight, van der Waals volume, the length and number of rotational bonds as well as the glass transition temperature (T_g) of the copolymer. These parameters have been determined by means of quantitative structure–properties relationships (QSPR) using connectivity index through interactive molecular modeling software available in the SYNTHIA package of Cerius2 software (from Accelrys Inc.). The use connectivity indices enable apply the Zeitz relationship to copolymers statistics systems [33]. The gradual increase in each modulus (E, G and B) as a function of the composition

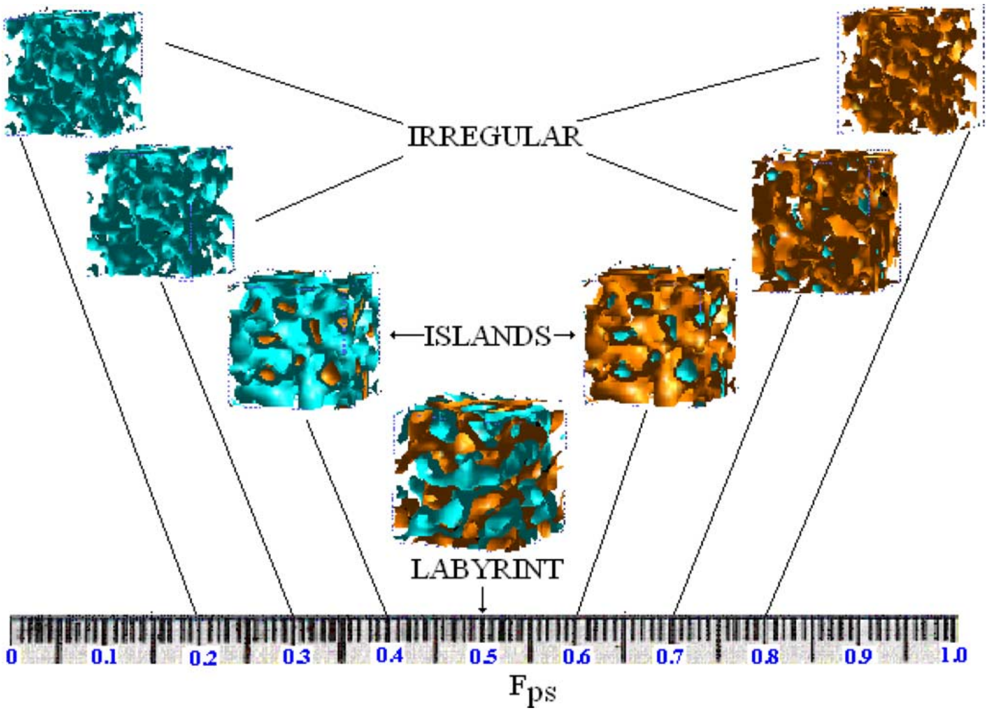

Fig. 6. Evolution of the morphology obtained from DPD simulation for the PS–PMMA diblock copolymer system and their composition domain.

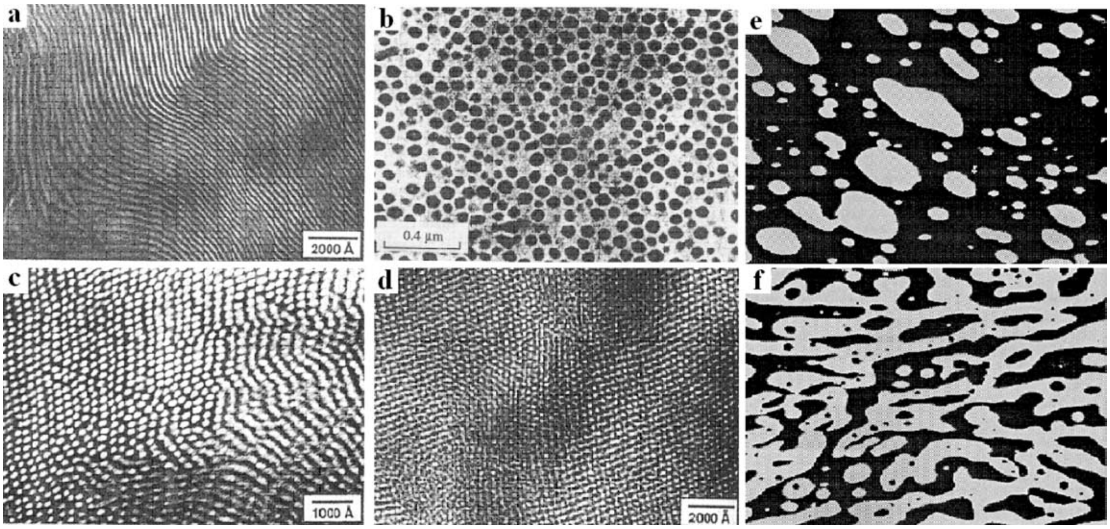

Fig. 7. TEM micrographs of the PS–PI and PS–PMMA systems taken from Refs. [31,32]; respectively: (a) lamellar (LAM) microstructure, (b) spherical (BCC) microstructure, (c) hexagonal-packed cylinder (EXH) microstructure, and (d) gyroids microstructure for the PS–PI system and; (e) island microstructure and (f) labyrinth microstructure for PS–PMMA.

is displayed in Figs. 8 and 9 for the PS–PI and PS–PMMA systems respectively; all modules were calculated at room temperature. The most important relation between the mechanical and morphology properties for diblock copolymer systems with linear architecture is the composition. This is directly expresses in the length of the homopolymer chain for each diblock system.

The mechanical properties exhibited by the block copolymers are affected by the morphology. In particular, the changes in the chain length (composition dependent) and segment–segment interactions strongly affect the final morphology. Those properties are generated in the interphase where different homopolymers chains coexist and where the individual properties are combined. When the interphase surfaces increase due to the morphology evolution of spherical to laminar and as a function of the composition, the material mechanical properties are maximized. This explains why the diblock copolymer systems properties are superior and more stable to the classical blends. The mechanical properties have been determined for the PS–PI and PS–PMMA diblock copolymer systems. The present procedure for predicting mechanical properties can be used to predict other important features of copolymer systems like thermophysical, transport and electrical properties which are of great importance in engineering applications. These additional properties can be evaluated under different predictive schemes that are also based on the quantitative properties structure relationships. The morphology and macroscopic properties of diblock copolymers predicted by numerical simulation can used to carefully tailor the chemical synthesis by controlling composition, molecular weight, and molecular architecture. The properties exhibited by these structured materials have not been widely studied and thus molecular modeling and

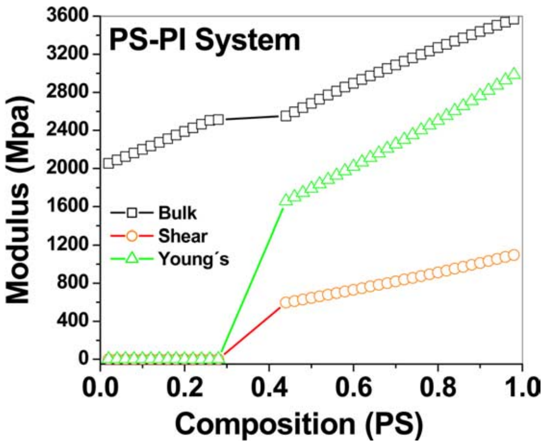

Fig. 8. Predicted behavior of composition dependence (PS block) of the mechanical properties (Young, bulk and shear modulus) for the PS–PI diblock copolymer.

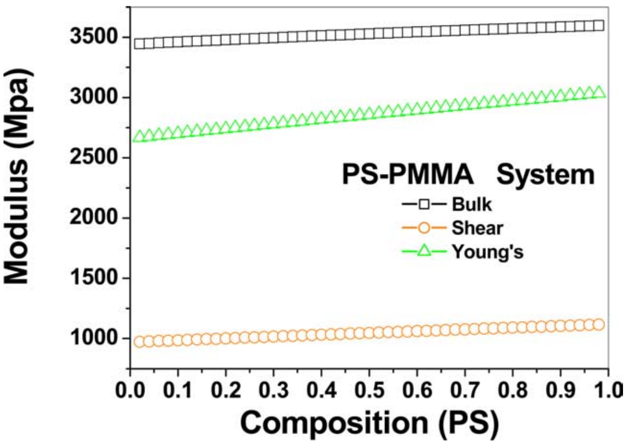

Fig. 9. Schematic representation of composition dependence (PS block) of the mechanical properties (Young, bulk and shear modulus) for the PS–PMMA diblock copolymer.

numerical simulations emerges as a new field able to provide important information to experimentalist. The simulated mechanical properties would have to be validated experimentally for the PS–PI and PS–PMMA diblock systems with linear architecture, however, up to our knowledge there are no experimental data reported for these copolymeric systems. Nevertheless, stress–strain curve, bulk and shear modules for homopolymers and copolymer blends that involve the monomers employed display a similar behavior [34–38].

4. Conclusion and outlook

Methods of molecular modeling and numerical simulation have been used to study the development and evolution of the structures with specific morphologies of the PS–PMMA and PS–PI diblock copolymer systems as well as their associated mechanical properties. The self-assembling phenomenon exhibited by these polymeric systems offers a wide variety of routes to structure materials into a mesoscopic scale. Starting from this assumption, the chains of the diblock systems were built considering the experimental parameters controlling the microphase separation. The validation of the representative models for each diblock system allowed one to predict mechanical properties by means of semi-empirical methods supported by structure–property relationships. The methodology employed in the present work can be extended to complex multi-block systems such as star, triblock, graft copolymer and random multiblock in bulk and solution. Those are more complex cases but have the common feature that the segment–segment interaction parameter controls the self-assembling process. Finally, note that the self-assembling phenomenon is not characteristic of synthetics polymers and it is also present in many natural systems and where the different main interactions are similar to those governing the self-assembling process of synthetic polymers. Therefore they can also lead to different structures at the mesoscopic scale. The present computational approach can also be used to study the morphology and mechanical properties of these natural systems.

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