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Giuliana Giunta, Carsten Svaneborg, Hossein Ali Karimi-Varzaneh, Pietro Carbone

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Published in: ACS Applied Polymer Materials

DOI: 10.1021/acsapm.9b00815

Publication date: 2020

Document version: Accepted manuscript

Citation for pulished version (APA): Giunta, G., Svaneborg, C., Ali Karimi-Varzaneh, H., & Carbone, P. (2020). Effects of Graphite and Plasticizers on the Structure of Highly Entangled Polyisoprene Melts. ACS Applied Polymer Materials, 2(2), 317-325. https://doi.org/10.1021/acsapm.9b00815

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ACS Appl. Polym. Mater., Just Accepted Manuscript • DOI: 10.1021/acsapm.9b00815 • Publication Date (Web): 23 Dec 2019 Downloaded from pubs.acs.org on January 6, 2020

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is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Effects of Graphite and Plasticizers on the Structure of Highly Entangled Polyisoprene Melts

G. Giunta^{a*}, C. Svaneborg^b, HA. Karimi-Varzaneh^c, P. Carbone^{a*}

^a School of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, M13 9PL, Manchester, United Kingdom

^b Department of Physics, Chemistry and Pharmacy, University of Southern Denmark (SDU), Campusvej 55, Odense M 5230, Denmark

^c Continental Reifen Deutschland GmbH, Jädekamp 30, D-30419 Hannover, Germany

KEYWORDS Polyisoprene, graphite, plasticizers, coarse-grained, entanglements, loops, trains, tails

Abstract

Using a simple and efficient way to optimise a chemically-specific bead-and-spring model for polymer/surface systems, we analyse the structural properties of high molecular weight polyisoprene (PI) in contact with graphite. We find that, in the vicinity of the graphite, the adsorbed PI chains assume a *pancake structure*, are highly packed and highly entangled. The addition of plasticizers even with moderate surface affinity guarantees an almost complete surface coverage and forces the polymer chains to detach from the surface and to become less entangled. The softening effect of the plasticizers is observed also in bulk when they are added to the system but are not adsorbed on the surface. Finally, we show that the definition of the thickness of the interface is not unambiguous but depends on the observable used to characterized the melt: it is function of the polymer molecular weight if defined looking at the chain conformation but it becomes independent on the polymer chain length if defined looking at the entanglement density.

*giuliana.giunta@manchester.ac.uk

*paola.carbone@manchester.ac.uk

Introduction

In order to improve mechanical and rheological properties of polymeric materials, inorganic particles with linear dimension up to 1µm can be mixed in the polymeric matrix^{1,2}. The addition of these fillers enhances the mechanical response of the compound by improving for example hardness and tear resistance but may be also used to modify other properties such thermal, electrical conductivity and optical properties^{1,3}. The polymer/filler interfacial area and the chemical nature of the particles-polymer matrix interactions⁴ are the two parameters directly responsible for the modification of the properties. However due to the complexity of the experimental characterization and of the material itself, which often contains polymer chains with large distribution of molecular weights, particles of different sizes and geometry and different type of additives, it is currently difficult to identify design rules for such materials¹ and thus their development is still very much empirical⁵.

To cut short the laboratory testing experimental time, there is therefore an increasing need of predicting computational tools able to provide reliable models linking filler geometrical and chemical characteristics with composite properties. Computer modelling has been widely applied to achieve a rapid and accurate prediction of the properties of the nano-composites before their preparation, processing and characterization^{4,5}. Nevertheless, molecular simulations of many body systems using chemically detailed all-atom models are still limited to polymers with low molecular weight due to the prohibitively long relaxation times associated to the macromolecules⁶. The use of efficient coarse-grained (CG) models, where atomic details are lost by grouping atoms into single interaction sites (beads, superatoms), is therefore invaluable in order to overcome the spatiotemporal limitations of large systems whose behaviour is in the mesoscale⁷⁻⁹. Several examples of systematic CG models are already in the literature. Bisphenol-A-polycarbonate on nickel¹⁰ and PI on graphite¹¹ are examples of CG models of specific polymer-surface systems derived by means of the Iterative Boltzmann Inversion (IBI) technique¹². Although these CG models accurately reproduced the structural properties of atomistic simulations, the IBI technique is generally a high time consuming CG method as it is based on a bottom-up approach that requires reference atomistic simulations to be performed^{7,13,14}. On the other hand, top-down CG methods such as the SAFT- γ^{15} and MARTINI¹⁶ in principle, do not require atomistic trajectories as a reference to develop the CG intermolecular potential derivation. These approaches are instead based on the reproduction of macroscopic thermodynamic properties of small molecules that can be considered as building blocks to construct bigger molecular systems. In both cases, the intramolecular potentials usually require a structure-based parameterisation⁶. These models are used when maintaining some chemical details of the system is essential to investigate the properties of interest¹⁴. For example in the MARTINI model developed by Gobbo et al.¹⁷ the authors describe the adsorption of organic molecules on graphite. In this model the interaction parameters are obtained by fitting the adsorption enthalpies from the gas phase and the wetting enthalpies of the pure compounds.

For the specific case of CG of polymer melts, one of the most used CG model is the bead and spring (or Kremer-Grest, KG) model¹⁸ where bonded interactions are described by the finite-extensible non-linear elastic (FENE) potential and the non-bonded beads interact through the

Weeks-Chandler-Andersen (WCA) potential¹⁹. This model not only reduces the number of degrees of freedom, but it is also computationally advantageous since does not include the calculations of the expensive long-range interactions between polymer beads and the square root operations involved in the harmonic potential⁶. In the majority of cases, this simple CG model is used to study generic (i.e. non-chemically specific) polymeric and polymer/surface systems^{20–23}. The lack of chemical details in the model is not a problem when looking for scaling laws or universal behaviour and the KG model has helped to clarify many aspects of the structure and dynamics of polymer chains in the immediate vicinity of surfaces ^{11,20–22,24,25}. Svaneborg and co-authors^{26,27} have recently showed that is it possible, by tuning the chain stiffness (i.e. the Kuhn length), to adapt a generic bead-and-spring polymer model to simulate melts of chemically-specific (at and above the Kuhn length) polymers. The authors developed a set of KG model parameters for several commodity polymers and showed that following their parameterization procedure it is possible to use the KG model to reproduce entanglement moduli comparable with the experimental data.

Here we are interested in investigating the structural features of a typical elastomeric composite comprised of (*cis*-)polyisoprene and graphite. This composite material is widely used in the automotive industry, as the incorporation of carbon black (nano) fillers in natural rubber enhances the mechanical properties of tyres (rolling and wear resistance, wet grip, etc.)²⁸. The graphite is in this instance, considered as a model for the surface of carbon black fillers¹¹.

The aim of this work is double folds: on one side we propose a new coarse-graining procedure for polymer/surface systems that allows the inclusion of chemical specificity into the mesoscopic description of the KG model; we then use the model to investigate the structural properties of highly entangled PI chains in contact with an homogeneous graphitic surface paying particular attention to the effect that low molecular weight diluents (plasticizers) have on the conformation and entanglement density of the adsorbed polymer chains²⁹.

Models and Methodology

PI (100% *cis-1,4*) is represented using a KG bead-and-spring model adapted to match the universal properties of a wide range of specific polymers species developed by Svaneborg et all²⁶. The PI KG model is parameterized to match the conformation properties of cis-PI at and above the Kuhn scale. In particular the entanglement density will emerge naturally since the simulation model reproduce the correct Kuhn length and the correct density of Kuhn segments of cis-PI. The details of the model can be found in reference 26 and a summary of the model strategy is reported in the Supporting Information. Here we just summarize the parameters relevant for the current work.

In the PI KG model, atoms are lumped together into spherical beads in such a way that a CG bead contains 67% of the mass of polymer repeating unit (i.e. the mass of the bead is m_b =45.62 g mol⁻¹). The choice of the bead mass, along with other parameters of the force field is the result of the coarse-graining scheme that allows the reproduction of the Kuhn length and the Kuhn segment density of the real polymer²⁶.

The CG sites interact through the WCA pair potential:

$$U_{WCA}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] for \ r < 2^{1/6}\sigma$$

$$\tag{1}$$

where $\varepsilon = k_B T$ (k_B is the Boltzmann constant) is the potential well depth and σ is the separation distance when the potential is zero. The topology of the chain is maintained by introducing bonded interactions described trough the FENE potential:

$$U_{\text{FENE}}(r) = -\frac{kR^2}{2} \ln \left[1 - \left(\frac{r}{R}\right)^2 \right]$$
(2)

where $R=1.5\sigma$ is the maximum permitted distance between two bonded beads and $k=30\varepsilon\sigma^{-2}$ is the constant force of such potential²⁶.

The sum of the WCA and FENE potentials results in an anharmonic potential, where the minimum of the sum of the two functions set the equilibrium bond length equal to 0.965σ at a reduced temperature of $T^* = 1$ ($T^* = Tk_B \varepsilon^{-1}$) and bead density of $\rho_B = 0.85\sigma^{-3}$.

In order to restrict chain conformations, an additional angle bending interaction is used. The potential for such bonded degree of freedom is given by:

$$U_{\text{bend}}(\theta) = -\kappa (1 - \cos\theta) \tag{3}$$

where θ denotes the angle between subsequent bonds, the stiffness parameter is $\kappa = 0.206\varepsilon$. The bending stiffness is chosen such that the model matches the number of Kuhn segments per Kuhn volume of cis-PI²⁶. This leads to bead containing 67% of the mass of polymer repeating unit (i.e. the mass of the bead is m_b =45.62 g mol⁻¹).

The polymer/graphite interactions are described via the standard Lennard-Jones (LJ) (12-6) potential:

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{for } r < r_{cutoff}$$

$$\tag{4}$$

where $r_{\text{cutoff}} = 2.4\sigma$, the parameters ε , σ and r_{cutoff} are derived from atomistic simulations of a binary system of benzene and isoprene as detailed below.

To develop the polymer/surface intermolecular potential, a procedure akin to that used to derive the inter-bead force field parameters in Dissipative Particle Dynamics $(DPD)^{30}$ and more recently in the MARTINI force field¹⁶ is followed. Initially an atomistic model of the binary mixture of benzene (representing a surface unit) and isoprene (representing the monomer of the polymer) is set up. Atomistic simulations are then carried out in *NPT* (*P*=1 bar and *T*=300 K) and the system is allowed to equilibrate. The degree of benzene/isoprene mixing is then quantified by calculating the mixing ratio, *x*, using the equation below:

$$x = \frac{n_I}{n_I + n_B} \tag{5}$$

where n_I and n_B refer to the number density of the components isoprene, *I*, and benzene, *B*.

This binary mixture is then coarse-grained as LJ fluids, where both the benzene and isoprene molecules are mapped as one CG bead with a constant σ value of 0.47 nm. The ε values describing the benzene/benzene and isoprene/isoprene interactions are 3.7 and 2.9 kJmol⁻¹, respectively. These values guaranteed that the density of each liquid corresponds to the experimental ones of 876 kg m⁻³ and 681 kg m⁻³, respectively. The parameter for modelling the cross interactions, ε_{B-I} , is selected in order to replicate the mixing ratio, *x*, obtained from the atomistic simulations. A final value of $\varepsilon_{B-I} = 3.5$ kJ mol⁻¹ allows for the reproduction of the atomistic results, reported in Figure S1 in the supporting information.

Once the polymer/polymer and polymer/surface interactions are defined, we proceed in modeling the full system. In our CG simulations, the graphite surface is initially modeled as six hexagonal layers of graphene with a lattice constant D=0.245 nm set in order to keep constant the ratio between the carbon atom (bead) size σ_C (σ_B) and the bond distance (lattice constant) d (D) as it is shown in the equation below:

$$\frac{\sigma_{\rm C}}{\rm d} = \frac{\sigma_{\rm B}}{\rm D} \tag{6}$$

where σ_c is the carbon atom diameter (0.28 nm), d is the carbon-carbon bond distance (0.142 nm), σ_B is the bead size (0.47nm) and *D* is the lattice constant (0.245 nm). The mapping of the graphite surface is reported in Figure 1.



Figure 1 Mapping of the solid substrate: *D* is the distance between connected beads, σ_C is the carbon atom size d is the bond distance and σ_B is the bead size.

To model the PI-Graphite (PI-G) interactions, the initial value of $\varepsilon_{B-1} = 3.5$ kJ/mol obtained from the liquid mixture simulations is then rescaled based on two considerations: (*i*) as in the PI KG model used here a single PI bead represents 67% of the real monomer mass, a multiplying correction term of 0.67 is introduced to account for the difference between the mass of a PI bead and that of the isoprene bead used in the liquid binary LJ simulations, (*ii*) the benzene ring forming part the graphene hexagonal lattice shares its atoms with 3 neighbouring rings. Thus when a benzene bead is used to form a CG surface with the same hexagonal symmetry, the energy parameter of the bead is scaled by factor of 1/3. The resulting epsilon parameter is given by $\varepsilon_{PI-GH} = 0.67 \times \varepsilon_{B-I}/3$.

To test this approach we simulate two different CG surface configurations: one hexagonal lattice (H) (described above in Figure 1) and a square lattices (S) with a different number density of beads. The scaling factors used to rescale the original ε_{B-1} parameter for the different configurations are selected to maintain constant the surface energy density, i.e.

$$\varepsilon_{PI-G_H} \times \eta_H = \varepsilon_{PI-G_S} \times \eta_S \tag{7}$$

here ε_{PI-G_H} and ε_{PI-G_S} are the values of the PI-graphite LJ potential for the hexagonal (H) and square (S) lattice respectively, and η_H and η_S correspond to the number of beads in each graphene layer.

In Table 1 the values of the final set of parameters are reported.

Interactions	σ (nm)	ε (kJ·mol ⁻¹)
PI-PI	0.4136	2.477
PI-G _H	0.47	0.78
PI-G _S	0.47	0.63

Table 1 Potential parameters.

Simulation Details and Entanglement Analysis

Atomistic Simulation of Polymer/Surface Systems

To model the PI-graphite systems we employ the united atom force field developed by Hager et al.¹, the details of the force field can be found in reference¹. The production runs are performed in the *NVT* ensemble at 300 K with the Berendsen thermostat for up to 200 ns. The generation of the initial configuration and subsequent equilibration follow the procedure reported by Meyer et al.³¹ which consists of generating the chains with a "polymerization" algorithm and a series of annealing simulations from 600 K. The simulation box is an orthorhombic cell with a surface area of $5.71 \times 5.71 \text{ nm}^2$ in *xy*. Periodic boundary conditions are applied in all three directions. The graphite slab, located at *z*=0 consists of six graphene layers and extends for 1.675 nm along *z* direction. The length in the normal direction is 35.33 nm so the polymer melt is in contact with the surface on one side and to a vacuum to the other²⁵. Following the procedure reported by Harmandaris et al.²⁵ the film is built sufficiently thick to contain a region far from the interfaces whose structural and thermodynamic properties are identical to that of bulk polymer and to ensure that the influence of the two interfaces is isolated.

The list of the atomistic systems simulated in the present work is reported in Table S1 in the Supporting Information.

Atomistic Simulation of the Isoprene/Benzene mixture

The OPLS-AA force field is used to model both benzene and isoprene molecules under *NPT* conditions using the Berendsen thermostat and barostat³² to maintain a constant temperature of 300 K and a pressure of 1 bar, respectively. The OPLS-AA force field accurately reproduces the experimental density of the pure isoprene and benzene fluids.

Coarse-Grained Simulation of the Polymer/Surface Systems

The simulation box is an orthorhombic cell with a surface area of $20.67\sigma \times 20.77\sigma$ for the hexagonal lattice and $20.72\sigma \times 20.72\sigma$ for the square lattice in the xy plane, the length in the normal direction, z, is 3 times the dimension of the length in the $x^{11,20}$. In order to avoid effects due to the box size, the biggest systems are simulated in a bigger surface area of $41\sigma \times 41\sigma$ for the square lattice. The graphite slab, located at z=0 is 1.675 nm thick along z direction with an interlayer spacing of $\Delta z=0.335$ nm^{33,34} in order to be larger than the value of r_{cutoff} . Periodic boundary conditions are applied in all directions, therefore the polymer resulted confined between two solid walls. Molecular overlaps of chain segments in the initial configurations are removed by energy minimization. During the equilibration period (of duration of $3 \times 10^{4}\tau$) the polymer/surface interactions are temporarily switched off to allow a quick equilibration of the polymer melt. In the production runs the systems are simulated for up to $14.6 \times 10^5 \tau$ depending upon the system size. In the simulations the number of particles, the volume and temperature are kept constant (NVT ensemble) and the volume is selected to obtain the real density of the polymer (910 kgm⁻³)²⁶. The system evolved according to Langevin Dynamics³⁵. The equations of motion are integrated with a time step of 0.01τ , where $\tau = \sigma (m_b \varepsilon^{-1})^{0.5}$ and a friction coefficient $\Gamma = 0.5 m_b \tau^{-1}$. In our approach, pair interactions between surface beads are neglected and the surface beads are frozen in all directions.

Table S2 in the Supporting Information summarized the systems simulated. All the simulations are carried out using the software GROMACS 5.0.4³⁶.

Coarse-Grained Simulation of the Polymer/Surface Systems with Plasticizers

Plasticizers (PL) are small organic molecules added to the polymer composites and used to lower the polymer glass transition temperature and increase dispersion of the filler particles in the polymer matrix. Since common plasticizers used in elastomer compounds include a variety of short hydrocarbons with various degree of affinity to the filler's surface, we represent the plasticizer molecules as short PI chains with increasing affinity to the graphitic surface. We simulate three different plasticizers length (5, 10 and 20 beads per chain) with a concentration typically found in the industrial samples of 5*phr* (plasticizers per hundred rubber): assuming that M_p is the total mass of the polymer, the mass of plasticizers for a 5*phr* concentration is $\frac{M_p}{100}$ × 5. The plasticizers/graphite affinity is varied by modifying their LJ epsilon value (ε_{PL-G}). In Table S3 of the Supporting Information, the number of plasticizers in the system for different lengths is reported.

Equilibration of the PI Melt

Long chain polymers require both thermodynamic and configurational equilibration. One way to check whether the configurational equilibration is achieved is to analyse the mean square internal distances along the chains³⁷. The simulations with the sole PI bulk and those with the surface have been run until both equilibrations are achieved. Figure S2 in the supporting information shows the plot of the mean square internal distances (MSID) of different chain lengths as a function of the number of bonds along the chain. The value of MSID increases monotonically with the number of bonds along the chain towards a plateau value, hence the simulations have been run sufficiently long that the chains are equilibrated at each length scale.

Primitive Path Analysis

To topologically characterise the melts and the interface, we perform the Primitive Path analysis³⁸ (PPA). We apply a variation of the original PPA method³⁸ which we briefly outline here. More details about the original procedure can be found in Ref. ³⁸.

The beads at the end of each polymer chain as well as in the vicinity of the surface are initially constrained in their positions. A set of energy minimizations are then carried out initially switching off all pair interactions between nearest beads along the chain, subsequently we remove next-nearest pair interactions, and finally pair interactions within a chemical distance less than ten beads are removed. The advantage of this process compared to the original formulation of the procedure is that it gently converges to the PPA mesh of the melt by gradually reducing the excess length of the chains due to thermal fluctuations. Secondly, this PPA method preserves distant entanglements along the PPA, e.g. self-entanglements that are caused by the periodic boundary conditions. The results are averaged over 40 independent conformations. A detailed explanation of the theory can be found in the supporting information in the section "Entanglement Analysis".

Results and Discussions

Validation of the Coarse-Grained Model

We first study the structural features of the melt in order to validate the KG model²⁶. Figure 2 shows the mean squared radius of gyration (R_g) (Equation 8) calculated for the different polymer molecular weights.

$$\langle R_g \rangle^2 = \frac{b^2 N}{6} \tag{8}$$

where *b* is the value of the Kuhn length and *N* is the number of beads.





Figure 2. Variation of the radius of gyration, R_g , calculated in the bulk as a function of molecular weight, M_w . The values are fitted using Flory's law (dashed lines).

It can be seen that as the length of the PI chains is increased the R_g increases and the trend follows the power law predicted by the Flory theory³⁹ $R_g = aN^{\nu}$, where ν is the Flory exponent, N is the polymer chain length and a is a fitting parameter. In our CG simulations, the estimated exponent for chains in the bulk is ν =0.52, which agrees with the Flory exponent value of 1/2, characterizing the size of polymers in ideal solvents. Furthermore, the KG model is able to reproduce the radius of gyration (R_g) obtained from the atomistic simulations (3.64 ± 0.07 nm against a value of 3.07 ± 0.03 nm for the KG model, both for a chain containing 200 beads). The small discrepancy between the atomistic and CG R_g values arises from the difference in the mapping schemes as it is explained in section 2, i.e. in the KG model, one bead contains 67% of the mass of one monomer (about 4 carbon atoms), whereas in the mapping applied in our atomistic simulations, the double bond of two successive carbon atoms of the same monomer is used as the CG interaction site (5 carbon atoms per bead). Finally, the bulk value of the end–to-end distance per chain molecular weight, $\langle R_{ee}^2 \rangle / M_w$, is equal to 0.00653 mol nm²g⁻¹ (where $R_{ee} = 7.72 \pm 0.16$ nm for a chain consisting of 200 beads) which is also in good agreement with experimental value of 0.00679 mol nm²g⁻¹ ²⁶.

We then validate the polymer/surface CG model. This can be done comparing the atomistic and CG polymer density profile calculated across the simulation box in the direction perpendicular to the graphitic surface (Figure 3). Both models predict, as expected, that moving away from the surface the density asymptotically reaches the uniform local mass density corresponding to that of the polymer melt (910 kg m⁻³), in agreement with previous studies^{11,20,25}.



Figure 3 Local mass density distribution of PI on graphite for atomistic (dashed line) and CG systems (hexagonal lattice H (green line) and the square lattice S (red line)).

In the vicinity of the graphite surface the density profile exhibits an oscillatory behaviour with three evident peaks and a fourth peak with a considerably smaller height. This spatial arrangement of particles indicates the formation of quasi-discrete layers adjacent to the surface, whose influence extends up to about 5 times the bead diameter σ as predicted by generic CG models of adsorbed polymers²⁰. Within the first layer, atomistic and CG models predict the position of the first peak at the same distance from the surface and, although the CG peak appears to be narrower, its integration yields to equal mass of adsorbed polymer in the atomistic $(4.08 \times 10^{-7} \text{ kgm}^{-2})$ and CG models $(4.05 \times 10^{-7} \text{ in the hexagonal lattice and <math>3.96 \times 10^{-7} \text{ kg m}^{-2}$ in the square lattice). The second and third peaks lay at a slightly shorter distance from the surface in the CG model compared to the atomistic one due to better packing of the bead-and-spring chain, but bulk density is reached at almost the same distance. Finally, we noticed that increasing the polymer molecular weight, the positions of local maxima in the density profile does not change. Similar results have been observed in previous simulations of polyethylene on graphite²⁵.

Interfacial Structural Properties of Entangled Polyisoprene Chains

Due to the presence of the attractive surface, the polymer chains present shape anisotropy and adopt different conformations in relation to the polymers in the bulk phase.



Figure 4 Profile of the components of the R_g in the perpendicular (z) $(R_{g,\perp})$ (top figure) and in the parallel $(R_{g,\parallel})$ (bottom figure) directions to the surface as a function of the distance from the surface for different polymer lengths: 50 (green triangles), 100 (red squares) and 300 (purple diamonds). The values of R_g are scaled by the corresponding components in the bulk.

Figure 4 shows that the adsorbed chains assume a *pancake structure*⁴⁰ flat in the direction parallel to the surface (*xy*). The value of the *xy*-component of the radius of gyration is higher at the interface than in bulk and quickly decreases approaching the bulk value, conversely the *z*-component increases in the proximity of the surface to reach the average value approaching the bulk. It can be noticed that the effect of the surface on the conformation of the chains vanishes at distances $z > R_g$ (indicated by the dashed black line in Figure 4).

A more detailed description of the adsorbed PI melt on graphite is obtained by analysing the statistics of conformations of adsorbed chains in the interfacial layer. Following previous studies²⁵ we define the length of the "adsorbed region" as the location of the first minimum in the density profile, corresponding in our case to a distance of 0.625 nm from the surface. In terms of polymer chain conformations, three polymer conformations are possible: *trains, loops and tails*. A train of length *s* is defined as the s+1 successive beads with the middle point of their bonds lying within the adsorbed region. A loop of length *s* is a sequence of s+1 interconnected beads between two trains having their *s* bonds outside the adsorbed region. Finally, tails of size *s* are sequences of s+1 segments outside the adsorbed region and terminated at one side by a bead connected to a train. A schematic representation of the definitions given above is shown in Figure S3 in the supporting information.



Figure 5 Average length of trains, loops and tails as a function of PI molecular weight (N).

Our results (Figure 5 and Figure S4 in the supporting information) follow the prediction of Scheutjens and Fleer⁴¹ and indicates that the average length of loops slightly increases with the polymer molecular weight, the tails present a strictly linear dependence on the chain length with a slope of 0.32 (against 0.34 predicted by Scheutjens and Fleer), while the length of the trains reaches a plateau for chains longer than 200 beads. Since it has been shown that the average length of trains and loops depends on the strength of the polymer-surface interaction²⁰, it is also important to notice that the average length of trains predicted by our model (5.4 and 5.7 segments for squared and hexagonal surface lattice respectively, see Figure S5 in the supporting information) is in good agreement with the atomistic data of Pandey et al (6 ca.).¹¹

Effects of the Plasticizers

Plasticisers with variable affinity to the surface are added to the system consisting of 300 beads per chain. We defined ε_p as the ratio between the values of the Plasticizer-Graphite interaction parameter (ε_{PL-G}) and that of the PI-Graphite (ε_{PI-G}). The value ε_p is varied from 1 (plasticizer and polymer beads have the same affinity to the surface) to 2.5 (plasticizer beads are 2.5 times more attracted to the surface than the polymer ones). Plasticizers of different lengths are simulated (see Table S3 and Figure S6 in the supporting information).

We calculate the amount of adsorbed plasticizers by using the definition of surface coverage γ .

$$\gamma = \frac{N_{pl}\sigma_{pl\,\pi}^2}{4L_x L_y} \tag{9}$$

where N_{pl} is the number of plasticizer beads in the adsorbed region, σ_{pl} is the size of the plasticizer bead, L_x and L_y are the lengths of the box in x and y directions, respectively.





Figure 6 Surface coverage, γ , as a function of ε_p for the three different plasticizers lengths (see Table S3). The dashed line is a guide line.

As expected, upon strengthening the interactions between plasticizers and graphite, the amount of surface coverage increases (Figure 6). Interestingly increasing the graphite/plasticizers affinity by more than 50% does not seem to increase the value of γ which remains around 0.8 even when the affinity for the surface is significantly high. Our simulation results therefore indicate that plasticizers with a filler affinity between 30-50% more than that of the polymer, may ensure already good filler surface coverage. This result is likely to be specific for the PI/graphite composites where the attraction between the polymer and the filler is fairly weak and due to dispersion interactions only, and we expect that different results might be obtained with different surfaces such as silica.

The effect that the adsorption of plasticizers has on the polymer structure is quantified calculating the chain *loops trains* and *tails* (Figure 7).





Figure 7 Variation of the average length of PI *trains* (a) *loops* (b) and *tails* (c) as a function of the percentage of the surface coverage (γ).

As the percentage of plasticizers adsorbed on the surface increases, the average length of *trains* decreases, indicating that the polymer chains desorb from the surface forming either longer *loops* and *tails*. For γ larger than 0.7 the polymer chains almost detach from the surface and form *trains* of just 1 or 2 bonds, *tails* of increasing lengths while the number of *loops* decreases to zero. The length of the plasticizers seems to have only a minor effect.

Entanglements Analysis

The primitive path analysis allows to quantify the number of entanglements in a polymer melts calculating the Primitive Path mesh size, ξ_{pp} , which is a value directly related to the inverse of the entanglements density⁴². In the PPA analysis we remove all plasticizers and only study entanglements between polymer chains. This is due to the fact that short chains only contribute to transient topological constraints analogously to the concept of dynamic dilution known from branched polymers^{43,44}.

Figure 8a reports the value of the ξ_{pp} , as a function of the polymer molecular weight and surface distance. Far away from the surface the value of ξ_{pp} obtained from the simulations is in good agreement with the one expected for *cis*-PI, $\xi_{pp-bulk}=1.11$ nm²⁷. This result strengthens the argument for the melt equilibrium, since matching the right entanglement density is a tough criterion which is sensitive to both the local and global chain structure, as it has been shown by Hoy and Robbins⁴⁵. The value of ξ_{pp} drops close to the surface indicating that the adsorbed chains are more strongly entangled here than in the bulk⁴⁶. The presence of strongly entangled chains influences the behaviour of the polymer which results stiffer in the vicinity of the surface^{47,48}. Figure 8a highlights also another important feature of the thickness of the interfacial layer. Figure 4 indicates that this thickness depends on the polymer M_w and specifically scales as the polymer R_g ; however, Figure 8a seems to indicate that the interface thickness is independent on the polymer M_{w} . This result reveals that the definition of interfacial layer is not unambiguously defined but depends upon the observable with which we characterize the melt. The radius of gyration is sensitive to the large scale conformational statistics of the whole chain, whereas the ξ_{pp} mesh size is sensitive to the mesoscopic conformational statistics on the entanglement scale. Figure 8a shows that the ξ_{pp} decays to the bulk mesh size value on the length scale of the bulk mesh size, $\xi_{pp-bulk}$, itself (~1.2nm). If we for instance had analysed the nematic order parameter of bonds as function of the distance from the surface, we could have obtained an even more microscopic definition of "interfacial width" ²⁰. Finally, we notice that at high molecular weight (above 200 beads per chain) the curves collapse on a master curve, as in the case of the probability distribution of loops (Figure S4b). This is also in agreement with what we observe in Figure 5 and Figure S4a (inset) where the average length of trains reaches a plateau for polymer longer than 200.

By analysing the entanglements for the systems containing the plasticizers we can see a different behaviour (Figure 8b).



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Figure 8. (a) Primitive Path mesh size (ξ_{pp}) as a function of the surface distance (z) calculated for pure melt. The maximum standard deviation for ξ_{pp} calculated in the bulk is 0.3 nm, while in the interfacial layer, up to 1.2 nm ca. from the interface, is negligible. In the inset the surface distance values are scaled by the R_g of the different polymers. (b) Primitive Path mesh size (ξ_{pp}) as a function of the surface distance (z) calculated for melt containing plasticizers (PL) with different surface affinity (ε_P) . Error bars indicate the standard deviation

Despite the high standard deviation in the values of the entanglements close to the surface, we notice a clear trend on the behaviour of the polymer entanglements when plasticizers are added in the system. When the interactions plasticizers/graphite are strong enough that the plasticizers are adsorbed on the surface ($\mathcal{E}_{P} \ge 1.25$), the number of polymer entanglements in the proximity of the surface decreases dramatically (Figure 8b). This is due to the fact that the adsorbed plasticizers create a layer of non-adsorbing molecules on the graphitic surface that prevent the adsorption of the PI directly on the surface. As a consequence, the plasticizers effectively locally dilute the PI chains, hence increasing the distance between entanglements, making the polymer chains less entangled and hence "softer" compare to the system without plasticizers. On the contrary, when the plasticizer molecules do not adsorb on the surface but are dispersed in the polymer bulk in high concentration, the number of bulk entanglements decreases (ξ_{pp} is higher) indicating that the whole melt becomes softer (effect that is experimentally expected when plasticizers are added to a polymer melt). More information is included in the supporting information in the section titled "Entanglements Analysis". Finally, by performing the PPA analysis on the systems with different length of plasticizers we notice that again the length of the plasticizers seems not to have any noticeable effect.

Conclusions

In this work we present a simple and efficient way to optimise a chemically-specific CG model for polymer/surface systems. The procedure builds upon that proposed by Svenborg at el. ²⁶ which, by matching the Kuhn lengths of a bead-and-spring model to the experimental values,

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 creates a simple KG models able to reproduce the mechanical response of a set of commodity polymers. We expand the procedure to polymer/surface system and use a thermodynamic (or bottom-down) approach to develop the polymer/surface interaction parameters. Following this approach we develop a model that represents a melt of poly-isoprene in contact with graphite. Due to the simplicity of the model, simulations of highly entangled polymer melts in contact with graphite are possible.

Using this model, we show that the width of the interfacial polymer layering depends on the polymer molecular weight and it is roughly the size of the chain radius of gyration. Within this interfacial volume the polymers melt forms loops, trains and tails and it is characterized by a higher number of entanglements.

Adding plasticizers with high surface affinity leads to their adsorption onto the graphitic surface and the subsequently detachment of the polymer chains. We however show that the percentage of adsorbed plasticizers never exceed 80% even if the affinity with the surface is significantly high. Interestingly just a fairly moderate surface affinity leads to an almost full coverage of the surface. The polymer detachment monitored analysing the length of loops, trains and tails, monotonically increases as the surface converge increases until the surface coverage reaches 80% at which point the polymer chains almost completely detach. The presence of the plasticizers affects also the entanglement density both in the bulk and at the interface. The adsorption of the plasticizers onto the surface dramatically decreases the polymer entanglement at the surface by a factor of 5 for surface coverage equal 80%. When the surface coverage is instead around 10%, the interfacial properties are barely affected but the presence of a large number of plasticizers in the bulk affects the entanglement network reducing its density. These results are system specific as the model correctly reproduces the adsorption behaviour of the atomistic models and have important consequences on the ability of different plasticizers to modify the glass transition temperature and rheological properties of the composites. Finally, we show that the definition of the thickness of the interface is not unambiguous but depends on the length scale of the observable used to characterized the melt: it is function of the polymer molecular weight if defined looking at the chain conformation but it becomes independent on the polymer chain length if defined looking at the entanglement density.

Supporting Information

Additional information on simulations performed; results of mean squared internal distance, distributions of loops, trains and tails; details of entanglement analysis.

Acknowledgments

Computational facilities for this work are provided by the Computational Shared Facility (CSF) of the University of Manchester. The authors thank the EPSRC funded Centre for Doctoral Training "Materials for Demanding Environments" EP/L01680X/1 and Continental Tyre Division for the financial support.

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