

Understanding the Balance between Additives' Miscibility and Plasticisation Effect in Polymer Composites: A Computational Study

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Supporting Information

Model

In the coarse-grained (CG) model developed by Svaneborg et al.¹, atoms are lumped together into spherical beads, representing roughly a polymer monomer. The CG sites are described with the Weeks-Chandler-Andersen (WCA) pair potential:

$$U_{WCA}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \text{ for } r < 2^{1/6}\sigma \quad (S1)$$

where $\varepsilon = k_b T$ is the potential well depth and σ is the separation distance when the potential is zero. Bonded interactions between the beads are described through the sum of the WCA and the finitely extensible nonlinear elastic (FENE) potential:

$$U_{FENE}(r) = -\frac{kR^2}{2} \ln \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (S2)$$

where $R = 1.5\sigma$ is the maximum allowed distance between the bonded beads and $k = 30\varepsilon\sigma^{-2}$ is the constant force. The minimum of the sum of the two functions fixes the equilibrium bond length

equal to 0.965σ at a reduced temperature and density of $T^* = 1$ ($T^* = Tk_b \varepsilon^{-1}$) and $\rho_b = 0.85\sigma^{-3}$, respectively. An additional angle bending interaction is used to restrict chain conformations:

$$U_{bend}(\theta) = \kappa(1 - \cos\theta) \quad (S3)$$

where θ is the angle between subsequent bonds, κ is the stiffness parameter.

Simulation Details

The simulation box is an orthorhombic cell with a surface area of $17.15 \times 17.15 \text{ nm}^2$ in the xy the length, in the normal direction is ~ 2 times the dimension of the length in the x direction. The solid surface is located at the $z=0$ and it extends for 1.675 nm . Periodic boundary conditions are applied in all directions, confining the mixture of polymer and plasticisers (PLs) between two solid walls. Molecular overlaps of chain segments in the initial configurations are removed by energy minimisation in all the systems consisting of polymer, surface and flexible PLs. The final configuration of such systems is then used as starting configuration for the mixture containing rigid PLs where the bending potential is replaced with the harmonic potential as explained in the main text. In the production run the systems are simulated for up to $12 \mu\text{s}$, according to the system considered. To collect enough statistics, 2 different starting configurations have been employed: PLs randomly distributed in the polymer matrix and PLs adsorbed on the surface and PLs aggregated in clusters, if the surface is not present. In the simulations the number of particles, the volume and temperature are kept constant (NVT ensemble). The volume is selected to obtain the real density of each polymer in the bulk ($910, 969, 913 \text{ kg m}^{-3}$ for PI, PS and SBR, respectively). The systems evolve according to Langevin Dynamics. 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 $\Gamma = 0.5 m_b \tau^{-1}$.¹ Following the procedure of previous works^{2,3} the surface beads are frozen in all directions and pair interactions between surface beads are neglected. Simulations are performed using the software GROMACS 2016.⁴

We consider mixtures of polymer chains of PI comprised of 1-2-5-10-50-150 and 300 beads, polymer chains of 300 beads for PS and SBR and PLs (rigid or flexible) of different lengths (5, 7, 10 and 20) and concentration *phr* 5 in bulk. In addition, we simulate PI polymer chains comprised of 50 and 300 beads on planar surface with PLs.

Results

In Figure S1 we report the snapshots of 4 different systems. The systems R7 and R10 need more time to reach full adsorption. The aim of the figure is to show that in the case of rigid PL7, the PLs adsorb directly on the substrate, while rigid PL10 first form clusters and then adsorb.

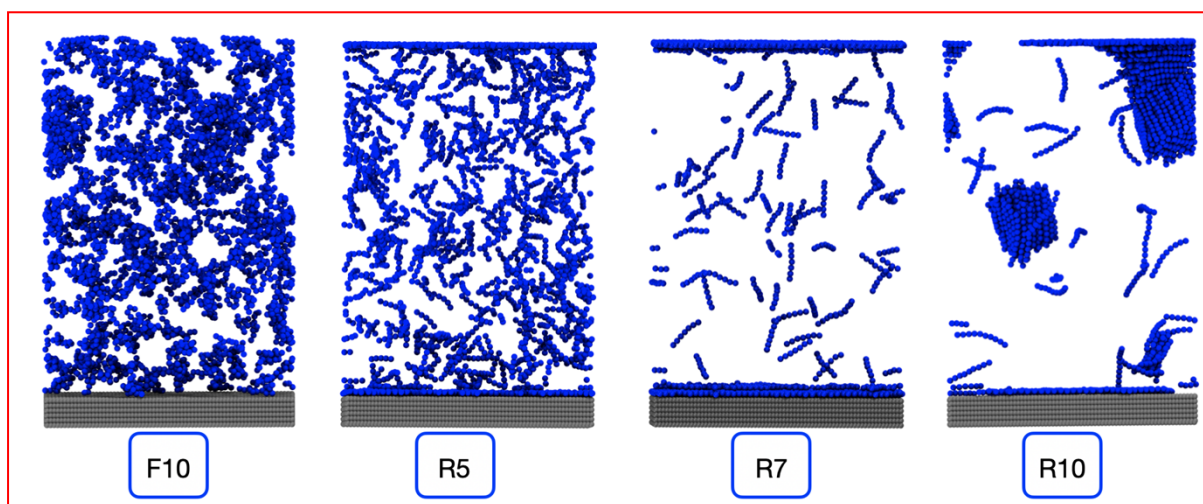


Figure S1 Configurations of the systems containing PI (not represented) and PLs (blue) ($p_{hr}=5$) at different PL conformations and lengths. In the bottom of the figure the letter refers to the flexibility of the PL molecules (F for flexible and R for rigid) and the number refers to the number of beads per PL.

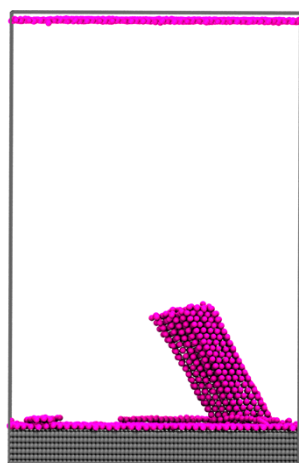


Figure S2 Configuration of the system containing PI (not represented) and PL20 (magenta) after pre-equilibration and 3.0 μ s of production run.

Table S1 Values of the end-to-end distance (R_{ee}) for different PLs immersed in PI300. The maximum value of the standard deviation of the R_{ee} is 0.06 nm.

System	PL Length (number of beads per PL)	R_{ee} Flexible PLs (nm)	R_{ee} Rigid PLs (nm)
PI300-PL	5	0.95	1.57
	7	1.21	2.37
	10	1.52	3.55
	20	2.28	7.49

A detailed description of the molecule arrangement inside the clusters is given by using the definition of orientational pair radial distribution function (Figure S3a):

$$g_{or}(r) = P_2(\cos\theta(r)) \quad (S4)$$

where P_2 refers to the second Legendre polynomial (*i.e.* $P_2(x) = \frac{1}{2}(3x^2 - 1)$) and $\cos\theta(r)$ is the angle between the directions of the rigid PLs as a function of the distance r between the central bead of the PLs as shown in Figure S3b.

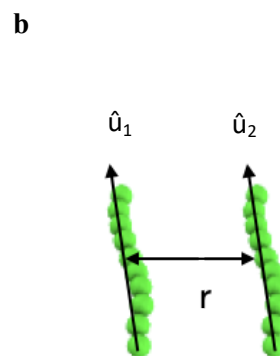
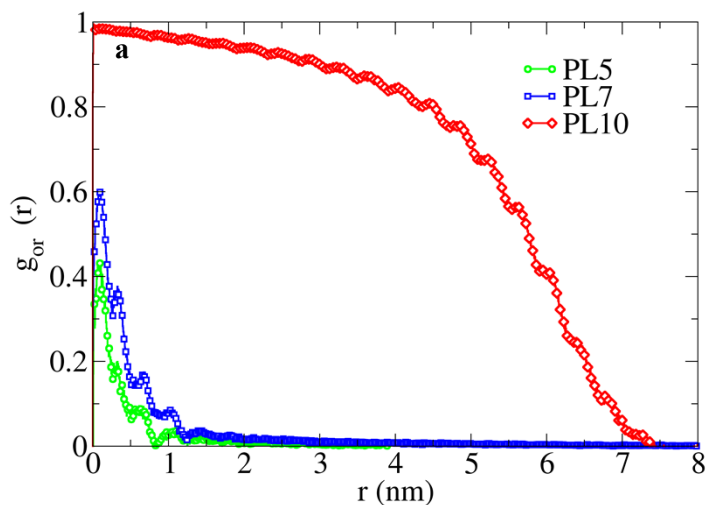


Figure S3 a) Plot of $g_{or}(r)$ in PI-bulk for different rigid PL lengths. In the legend the number refers to the number of beads per PL chain. **b)** Schematic definition of orientational pair radial distribution function $g_{or}(r)$.

In Figure S3b we show that by increasing the length of the rigid PLs, the probability of forming clusters in the bulk with vertically aligned PLs increases. In particular, when the PL length is 10, the value of $g_{or}(r)$ at short distance is approximately 1, hence the molecules are parallelly aligned. Such observations are confirmed using the definition of radial distribution function (RDF). In Figure S4a we notice that for PLs of length 5, the function reaches 1 at large distances, due to the random distribution of PLs in the bulk, while for PLs of length 10 (Figure S4b), the function reaches zero at large distances. It is interesting to notice that PLs in a cluster are tilted around the radial axis away from the centre of the cluster, as it is shown in Figure S5.

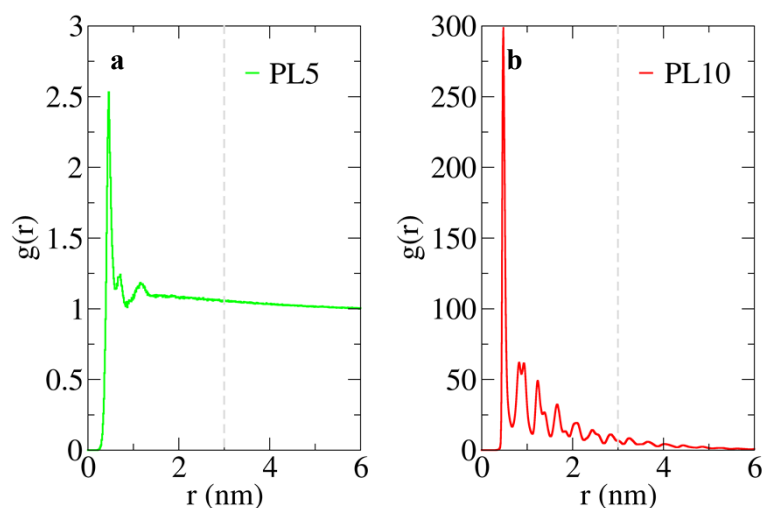


Figure S4 Radial distribution function $g(r)$ between the centre of mass of PLs in PI-bulk (300 beads per chain) **a)** PL5 and **b)** PL10. The grey dashed lines indicate the range over which the integral of the RDF is calculated.

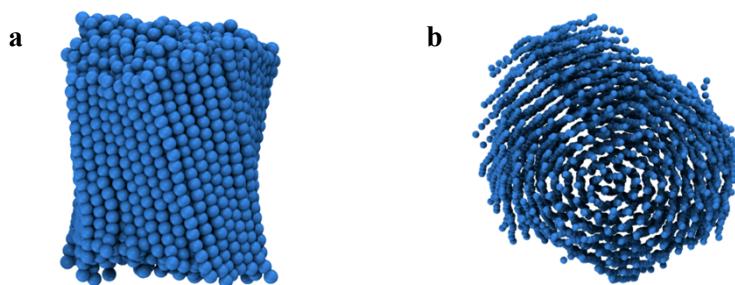


Figure S5 Snapshots of a cluster consisting of PL20 in PI300 where the rod-like chains are tilted around the radial axis away from the centre of the cluster: **a)** side view and **b)** top view.

Coarse-Grained Model of Banana-Shape PLs

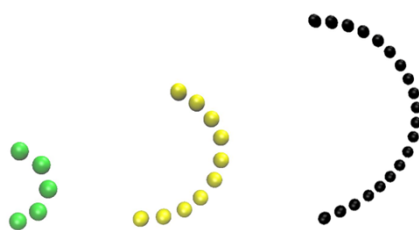
Examples of bent-core molecules that present banana shape are benzoates that contain five, six or seven benzene groups.⁵ To obtain such a shape we employ an additional proper dihedral potential (Equation S5) to restrain the angle between two planes (i,j,k and j,k,l) determined by four connected beads (i,j,k,l):

$$U_{dih}(\phi_{ijkl}) = k_{\phi}(1 + \cos(n\phi - \phi_s)) \quad (S5)$$

where ϕ is the angle between the two planes and k_{ϕ} is the force constant. In Table S2 we report the values of the bond and dihedral angles and the force constants for the banana-shape PLs analysed. In Figure S6 we show the configurations of systems composed of PI melt and banana-shape PLs of different length (5,10 and 20). As we have observed for rod-like PLs, PL5 are miscible in the polymer matrix, while PL10 and PL20 form clusters.

Table S2 Potential parameters of banana-shape PLs of different length, θ and ϕ denote the bond and dihedral angles, respectively; k_h and k_{ϕ} (in $\text{kJ mol}^{-1} \text{rad}^{-2}$) the force constant of the bond and dihedral potential, respectively.

PL Length	θ	ϕ	k_h	k_{ϕ}
5	140°	0°	3500	3100
10	160°	0°	3500	250
20	170°	0°	3500	40



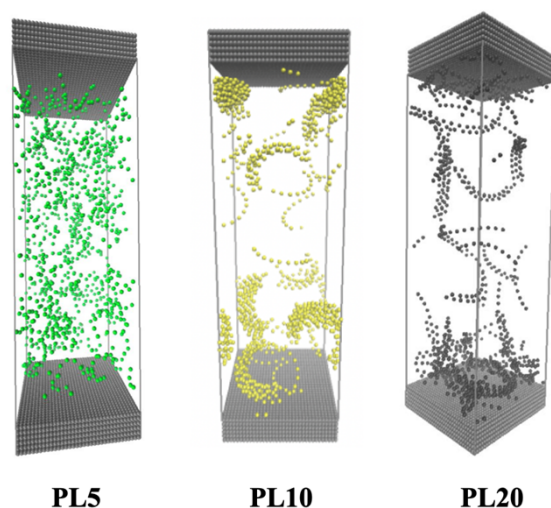


Figure S6 Configurations of the system with PI (not represented) and PL (green, yellow and black beads, representing PL5, PL10 and PL20, respectively) at $phr=5$. On the top panel the corresponding PL configurations are reported. The systems containing banana-shape PLs have been simulated for 400 ns.

References

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