Supporting Information

Molecular dynamics simulations of copolymer compatibilizers for polylactide/poly(butylene succinate) blends

Orrasa Prasitnok and Khongvit Prasitnok*

Multidisciplinary Research Unit of Pure and Applied Chemistry, Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Mahasarakham University, Maha Sarakham, Thailand

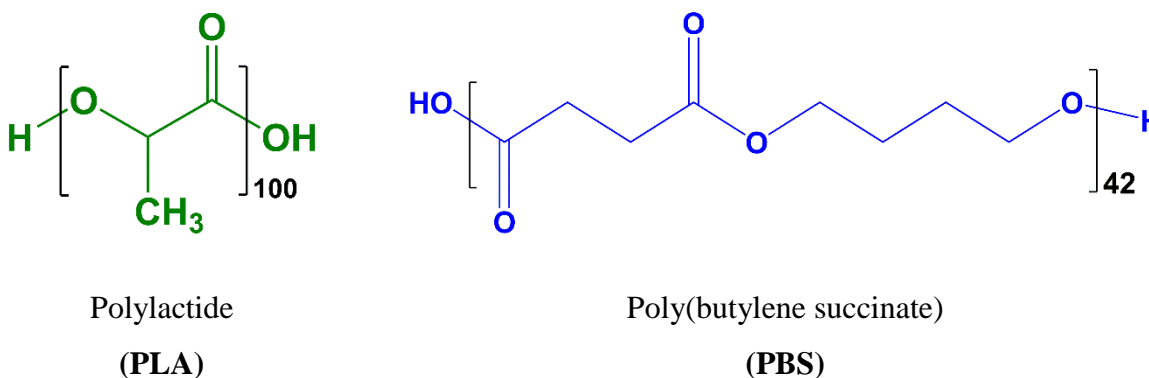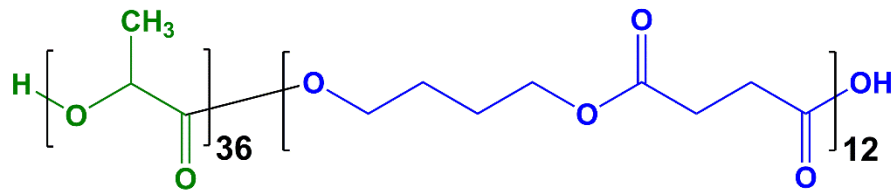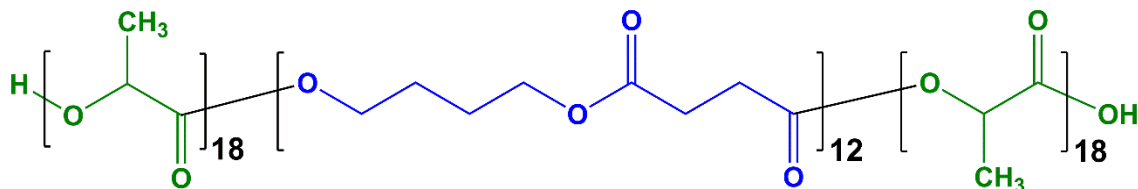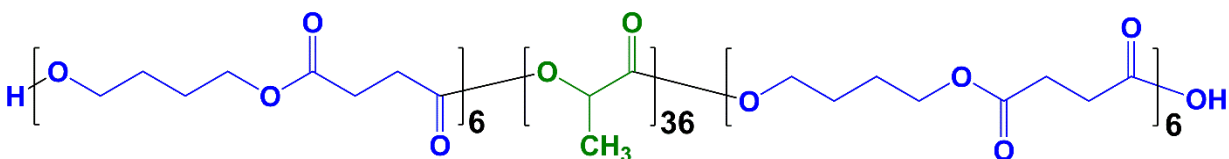*Corresponding Author. E-mail: khongvit.p@msu.ac.th

Polylactide

(PLA)

Poly(butylene succinate)

(PBS)

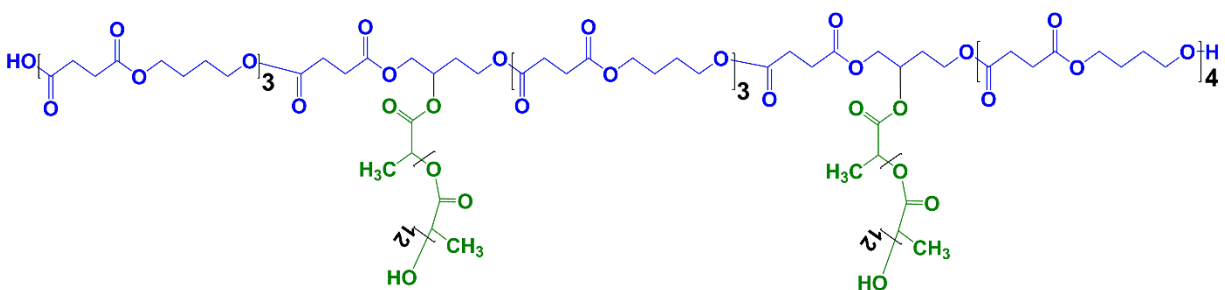**Fig. S1.** Chemical structures of PLA and PBS considered in this work.

(a) Poly(lactic acid)-*block*-poly(butylene succinate)
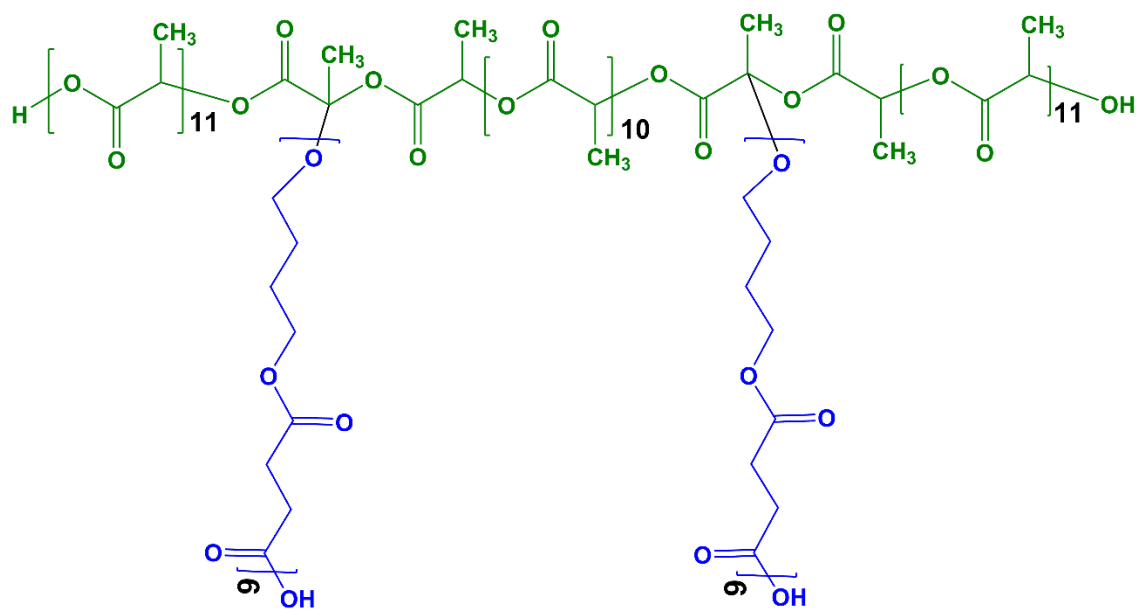
(L-*b*-B)

(b) Poly(lactic acid)-*block*-poly(butylene succinate)-*block*-poly(lactic acid)

(L-*b*-B-*b*-L)

(c) Poly(butylene succinate)-*block*- poly(lactic acid)-*block*- poly(butylene succinate)

(B-*b*-L-*b*-B)

(d) Poly(lactic acid)-*grafted*-poly(butylene succinate)

(L-*g*-B)

(e) Poly(butylene succinate)-*grafted*-poly(lactic acid)

(**B-*g*-L**)

Fig. S2. Chemical structures of the copolymer compatibilizers considered in this work.
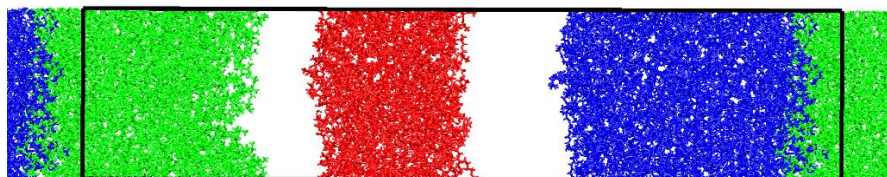

Fig. S3. An example of the initial structure of the blend simulated in this work (Blend/L-*b*-B-*b*-L system). The slab of copolymer compatibilizer (red) is located at the interface between the slabs of PLA (green) and PBS (blue) homopolymers.
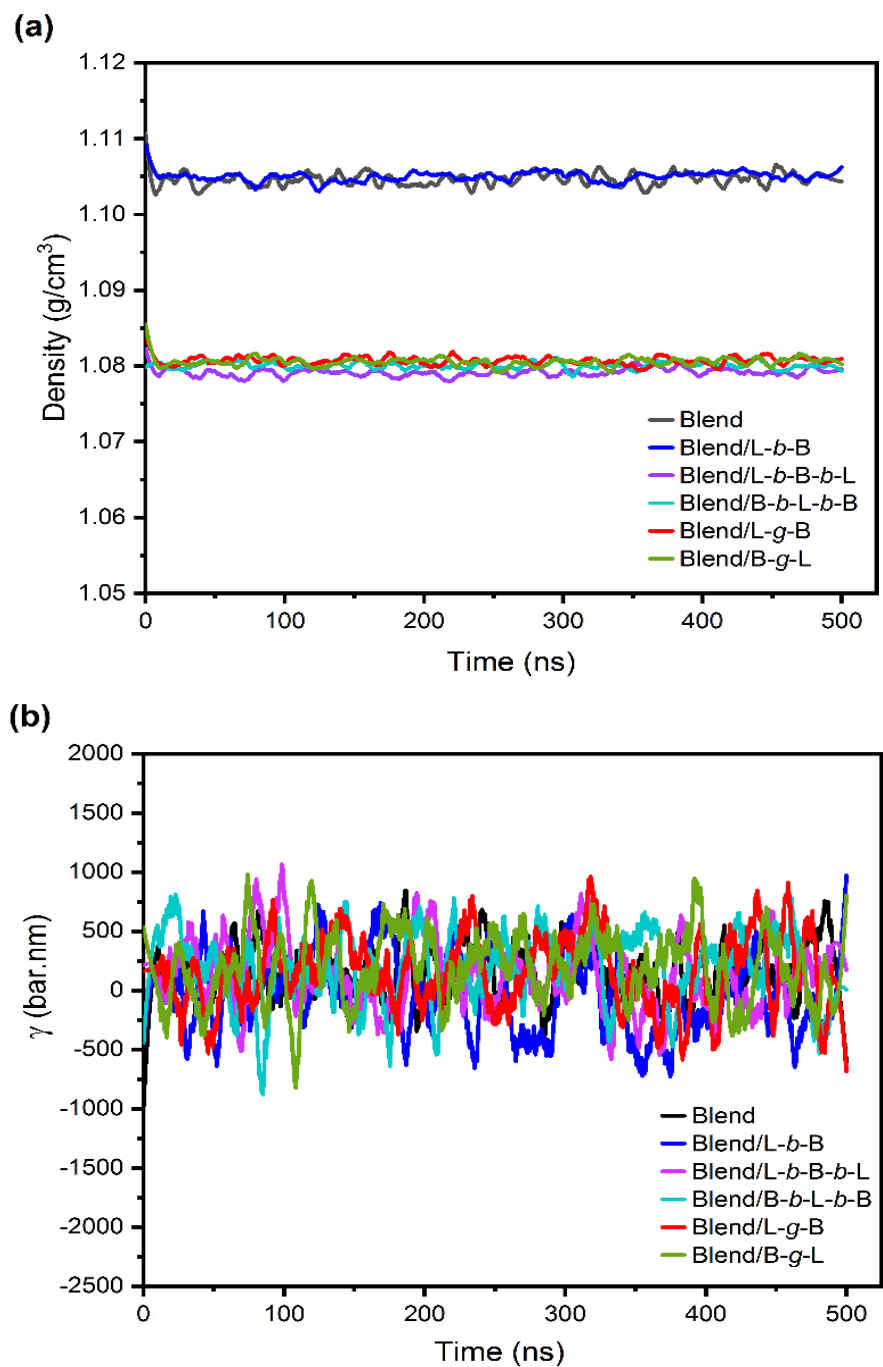
Fig. S4. Time evolution of density (a) and interfacial tension (b) from the 500 ns equilibration runs indicating sufficient equilibration for the simulated systems.
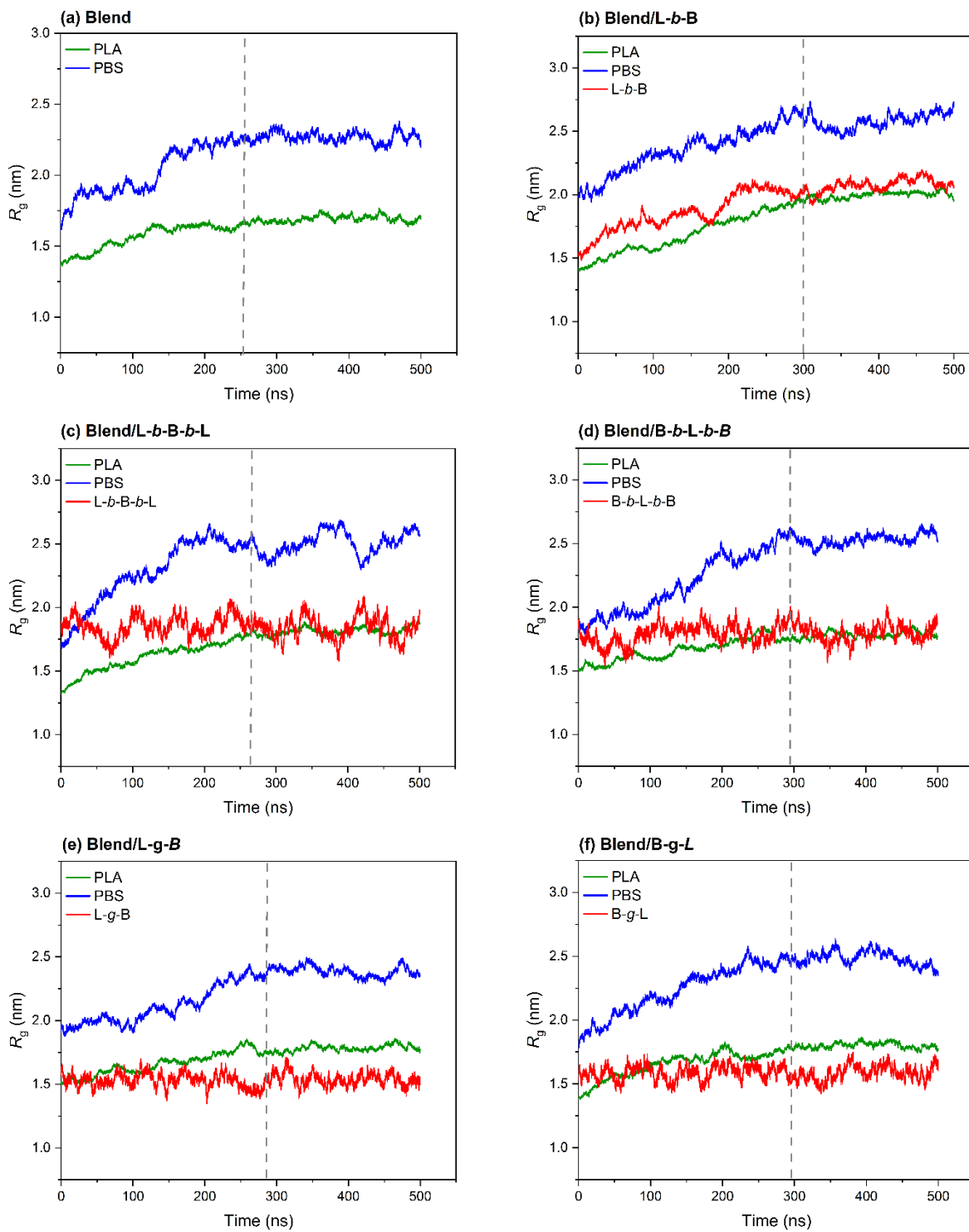
Fig. S5. Time evolution of the radius of gyration (R_g) for PLA, PBS, and compatibilizer chains from the 500 ns equilibration runs. The dashed lines indicate the equilibration time of the R_g.

Table S1 Comparisons of the average R_g of polymer chains and their corresponding box sizes for the simulated systems.

System	Box size $x \times y \times z$ (nm³)	Polymer	R_g (nm)
Blend	$6.0 \times 6.0 \times 12.1$	PLA	1.69 ± 0.02
		PBS	2.27 ± 0.04
Blend/L-*b*-B	$6.0 \times 6.0 \times 15.9$	PLA	2.00 ± 0.03
		PBS	2.58 ± 0.06
		L-*b*-B	2.08 ± 0.05
Blend/L-*b*-B-*b*-L	$6.0 \times 6.0 \times 16.4$	PLA	1.80 ± 0.03
		PBS	2.51 ± 0.09
		L-*b*-B-*b*-L	1.84 ± 0.09
Blend/B-*b*-L-*b*-B	$6.0 \times 6.0 \times 16.3$	PLA	1.81 ± 0.03
		PBS	2.53 ± 0.04
		B-*b*-L-*b*-B	1.80 ± 0.07
Blend/L-*g*-B	$6.0 \times 6.0 \times 16.4$	PLA	1.77 ± 0.03
		PBS	2.38 ± 0.04
		L-*g*-B	1.54 ± 0.05
Blend/B-*g*-L	$6.0 \times 6.0 \times 16.4$	PLA	1.78 ± 0.02
		PBS	2.48 ± 0.06
		B-*g*-L	1.59 ± 0.06

Orientational autocorrelation function

Equilibration of the systems has also been attested through the orientational autocorrelation function[1, 2] (the first Legendre polynomial) of a vector connecting two next-nearest atoms in the backbone of the polymer chains (1-3 vector). The autocorrelation function is calculated through

$$P_1(t) = \left\langle \frac{\mathbf{v}(t+t_0) \cdot \mathbf{v}(t_0)}{|\mathbf{v}(t+t_0)\|\mathbf{v}(t_0)|} \right\rangle$$

where $\mathbf{v}$ is the 1−3 vector and the bracket $\langle ... \rangle$ denotes an average over different time origins t_0 as well as for the 1−3 vectors belonging to the same chain. This function measures the decorrelation of the vector at time $(t + t_0)$ with reference to its position at time t_0.

$P_1(t)$ for PLA, PBS, and compatibilizer chains of each system are depicted in Fig. S6. It can be seen that $P_1(t)$ functions of polymer chains in all blends decorrelate (reach to the value of 0) within the 500 ns of the equilibration run. This indicates relaxation of polymer chains and confirm that the blends are in equilibrium.
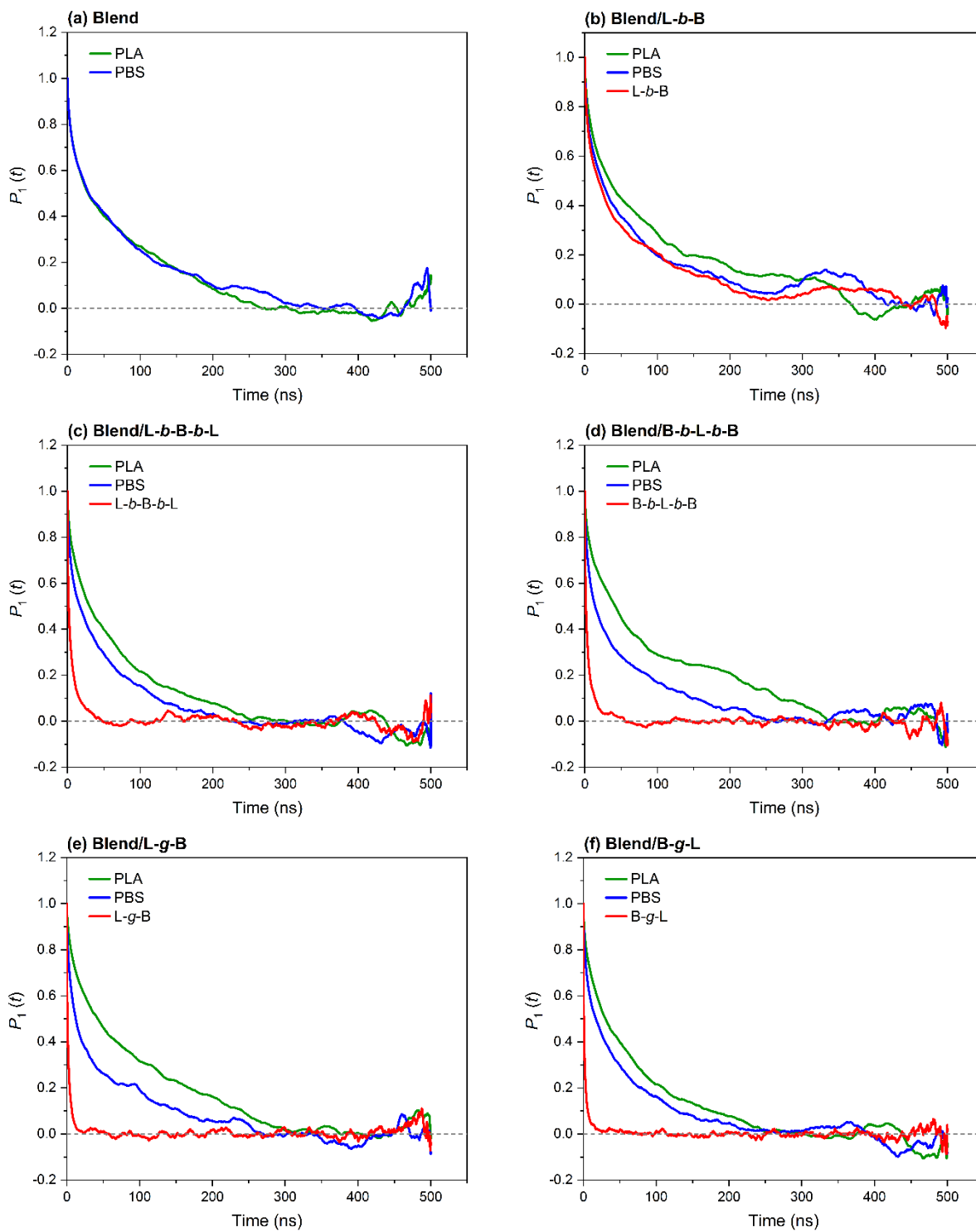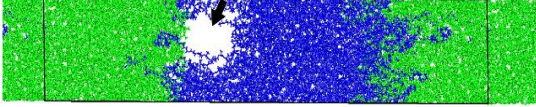
Fig. S6. Orientational autocorrelation functions for PLA, PBS, and compatibilizer chains from the 500 ns equilibration runs.
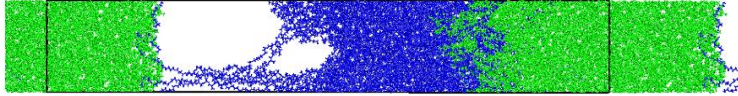
(a) Blend

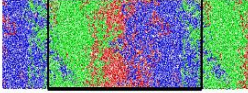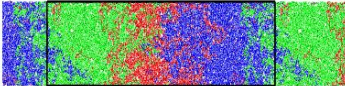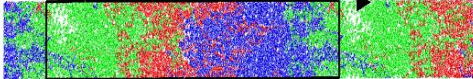Strain = 0
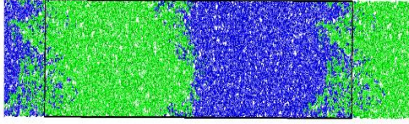
Strain = 0.5

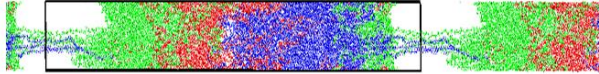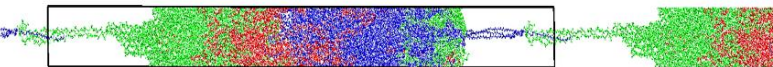Strain = 1.0

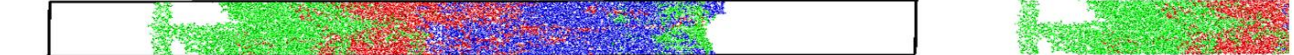Strain = 2.0

(b) Blend/L-*b*-B

Strain = 0
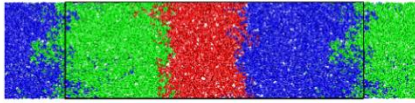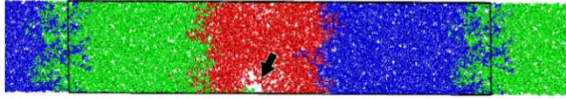
Strain = 0.5

Strain = 1.0

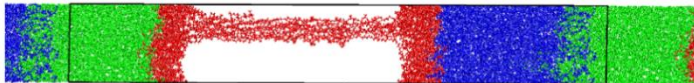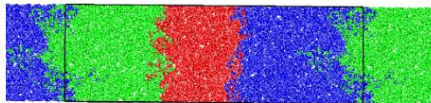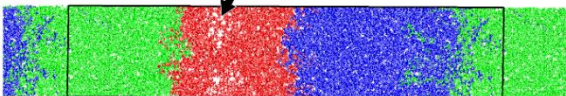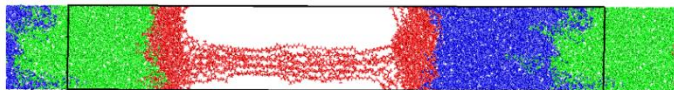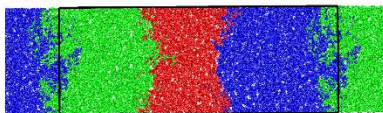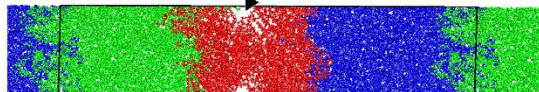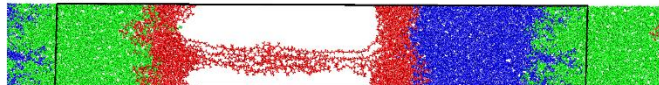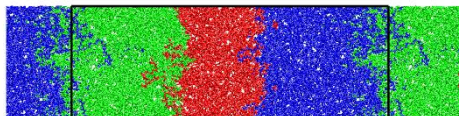Strain = 1.5

Strain = 2.0

Strain = 3.0

(c) Blend/L-*b*-B-*b*-L

Strain = 0

Strain = 0.5

Strain = 1.0

Strain = 2.0

(d) Blend/B-*b*-L-*b*-B

Strain = 0

Strain = 0.5

Strain = 1.0

Strain = 2.0

(e) Blend/L-*g*-B

Strain = 0

Strain = 0.5

Strain = 1.0

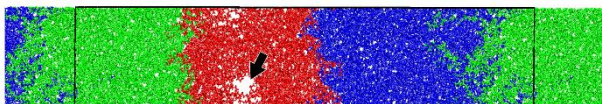**Strain = 2.0**

(f) Blend/B-*g*-L
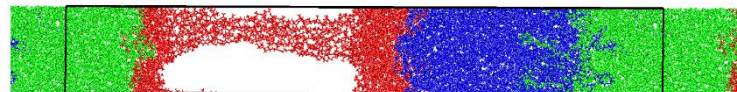
Strain = 0

Strain = 0.5

Strain = 1.0

Strain = 2.0

Fig. S7. Evolution of the systems during uniaxial deformation along the direction normal to the PLA/PBS interface (green, red, and blue colors are PLA, compatibilizer, and PBS chains, respectively). The black arrow indicates the region where the fracture initiates.

Reference

1.   B. Hess, C. Kutzner, D. van der Spoel and E. Lindahl, *Journal of Chemical Theory and Computation*, 2008, **4**, 435-447.
2.   R. Boyd and G. Smith, *Polymer dynamics and relaxation*, Cambridge University Press2007.