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# Cracking polymer coatings of paper-like surfaces: Control via block co-polymer structure and system composition



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#### ABSTRACT

Dissipative particle dynamics simulations are employed to examine the self-assembly of a three-component polymeric coating on a hydrophilic surface. The examined suspension is composed of an amphiphilic di-block co-polymer, a hydrophobic polymer, and a hydrophilic stabilizer in water. For technological relevance, the basis hydrophobic and hydrophilic polymer contents correspond to poly(styrene-co-n-butyl acrylate) and to starch, respectively, while the hydrophilic surface resembles unmodified cellulose. We show that the amphiphilic di-block co-polymer is key in controlling the assembling coating structure: symmetric co-polymers form wellordered lamellar coatings, while asymmetric ones lead to advanced patterning in the film. This response persists over a broad composition range of additional hydrophobic material. We also map the sensitivity of the results to polymer chemistry by variation of the interaction parameters. Finally, we show that the presence of excess free stabilizer in the coating solution can disrupt the homogeneity of the film, potentially deteriorating coating quality in practical applications. The findings stress the importance of block compositions and component concentrations as fundamental means to tune surface coating films and their internal structure.

#### 1. Introduction

Block co-polymers, composed of distinct polymer segments, are commonly used for producing functional and protective coatings [1-4]. Acting as surface modifications and barrier films, these coatings often form lamellar layers via self-assembly [5-7]. Such coatings are paramount in preventing oil and moisture penetration, in self-cleaning and antifreeze surfaces, in controlling the fouling of surfaces, but also in many bio-interfaces applications. One interesting surface material, for which barrier coatings are especially crucial because of its porous and hydrophilic nature, is paper. Cellulose-based paper offers a biobased, environmentally friendly, and inexpensive materials solution for, e.g., packaging materials, reasons for which we focus here on its barrier coatings.

Recently, computer simulations have become a powerful in silico laboratory for mapping the dependencies and assembly guidelines of polymer materials, including barrier coatings. For a recent review, see Ref. [8]. A particularly handy computational approach for examining barrier coatings of paper is dissipative particle dynamics (DPD) simulations, which allows the study of polymer systems at length and time scales capturing properties at materials level [9,10]. Compared to field-theory approaches, such as self-consistent field theory [11-16] and classical density functional theory approaches (most recently, e.g., Refs. [17-20]) that also capture relatively extended scales in structure and dynamics of polymer assemblies, DPD retains the particle-like character of the polymers, thus yielding advanced structural details. Indeed, DPD has been widely used to study microphase separations and self-assembly of block co-polymers (recent works include, e.g. Refs. [21-31]).

Block co-polymers are common in paper coating processes that target protecting paper and cardboard substrates against water, oil, and gases, such as oxygen or carbon dioxide [32-35]. In relation to block co-polymer based surface films and barrier coatings, DPD simulations have been used to study the behaviour of co-polymers grafted to a substrate in the presence of a selective solvent, revealing, e.g., the determining effects of attractive and repulsive interactions between the components on the conformational behaviour of the copolymers [36,37]. Block co-polymers adsorbing on a substrate can also form films with various internal morphologies. For example, Huang

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Full length article

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et al. [23] obtained, by alternating the stacking of two different diblock co-polymer chains, multilayered nanostructures. Additionally, by changing the repulsive forces, corresponding to chemical specificity in this framework, they revealed that the obtained morphologies are directly affected by the chemical incompatibilities between the building blocks. Wang et al. [26] mapped the influence of co-polymers surface affinity and concentrations on adsorption and ordering of selfassembled films. Furthermore, Yu et al. [38] demonstrated the critical effect of block length ratios on self-assembly and morphologies of block co-polymer membranes as another tuning factor, consistent with later findings of Scacchi et al. [39]. The importance of the effect of the constructing blocks lengths on the adsorbing behaviour of block copolymers is also shown in Ref. [40]. Block co-polymer self-assembly in a selective solvent can also be regulated by introducing a non-adsorbing polymer species into the system [41]. DPD simulations allow also charting the effect of substrate hydrophilicity and adsorbate concentration on the adsorbing surface films [42].

Block co-polymer coatings can be applied on paper-like surfaces by, e.g., polymer latex film formation, a process in which self-assembled polymer particles adsorb and spread on a surface [43-46]. We examine here the polymer system composition dependencies of self-assembling block co-polymer barrier coatings by DPD simulations, targeting producing a hydrophobic barrier on hydrophilic surfaces. The study system is composed of starch, a natural bio-based polymer with high affinity towards paper [47-49], poly(styrene-co-n-butyl acrylate), known to provide good barrier properties [50-52], a linear di-block co-polymer, namely starch-block-poly(styrene-co-n-butyl acrylate) [49,53-55], water as the solvent, and a cellulose-like flat substrate modelling paper surfaces. The work takes a practical block co-polymer barrier formation system on a technologically relevant surface (paper) and maps the system composition dependencies of the barrier coating structure, providing direct design guidelines for self-assembling coatings. This computational approach can be readily extended to also other polymer systems.

#### 2. Methods

#### Dissipative particle dynamics simulations

DPD is a mesoscale coarse-grained molecular simulations method first proposed by Hoogerbrugge and Koelman [56]. This methodology provides an efficient framework for addressing a variety of phenomena involving, e.g., phase separation, self-assembly, and transport in polymeric, surfactant, nanoparticle, and biomolecular systems [57], as well as applications associated with microchannel flow, electrospinning, free-radical polymerization, polymer electrolyte fuel cells, and biomedical materials [10]. In DPD, a group of atoms, a solvent region, or a selection of polymer monomers, are coarse-grained into beads. To achieve time and length scales comparable to those in experiments, the non-bonded interactions between beads are modelled via soft repulsive potentials [56,58]. The total force exerted on bead i is

$$\mathbf{F}_{i} = \sum_{i \neq j} \left[ \mathbf{F}_{ij}^{\mathrm{C}} + \mathbf{F}_{ij}^{\mathrm{D}} + \mathbf{F}_{ij}^{\mathrm{R}} \right], \quad i, j = 1, \dots, N,$$
(1)

where  $\mathbf{F}^{C}$  describes conservative interactions,  $\mathbf{F}^{D}$  dissipative contributions,  $\mathbf{F}^{R}$  random noise, and *N* is the total number of beads in the system. The model assumes pairwise interactions, which are truncated at a cutoff distance  $r_{C}$ .  $\mathbf{F}^{C}$  acts on the centre of the beads and has the form

$$\mathbf{F}_{ij}^{\mathrm{C}} = a_{ij}(1 - r_{ij})\hat{\mathbf{r}}_{ij},\tag{2}$$

where  $a_{ij}$  correspond to the maximum repulsion between beads *i* and *j*,  $r_{ij} = ||\mathbf{r}_i - \mathbf{r}_j||$  their distance, measured in units of  $r_{\rm C}$ , and  $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$  the directional unit vector. The coefficients  $a_{ij}$  are connected to the Flory–Huggins mixing parameter  $\chi_{ij}$  via

$$\chi_{ii} \approx (a_{ii} - a_{ii})/3.27,$$
 (3)

Table 1

The repulsive interaction parameters  $a_{ij}$  employed here. Beads A and B are hydrophilic and hydrophobic, respectively. Bead C model the hydrophilic substrate and bead D the solvent (water).

Bead	А	В	С	D
А	25	56.15	25	35
В		25	56.15	107
С			25	35
D				25

for a fixed total number density  $\rho r_{\rm C}^3 = 3$  (used here). We set  $a_{ii} = 25$  based on the compressibility of water [59]. Values of  $a_{ij}$  exceeding the self-repulsion in magnitude correspond to higher immiscibility between different bead types.

The dissipative force is given by

$$\mathbf{F}_{ij}^{\mathrm{D}} = -\Gamma \omega^{\mathrm{D}}(\mathbf{r}_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij},\tag{4}$$

where  $\Gamma$  is a viscosity related parameter (here  $\Gamma = 4.5$  [59]),  $\omega^{\rm D}$  is a weight function taking a value of zero at  $r = r_{\rm C}$ , and the relative velocity between beads  $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ .

The random force is described by

$$\mathbf{F}_{ij}^{\mathrm{R}} = \sigma \omega^{\mathrm{R}}(r_{ij})\xi_{ij}\hat{\mathbf{r}}_{ij},\tag{5}$$

where  $\xi_{ij}$  is a zero-mean Gaussian random variable with unit variance,  $\sigma^2 = 2\Gamma k_{\rm B}T$ ,  $k_{\rm B}$  is the Boltzmann constant, and *T* the temperature. The weight functions follow the relation  $\omega^{\rm D}(r_{ij}) = \omega^{\rm R}(r_{ij})^2 = (1 - r_{ij})^2$  for  $r_{ij} < r_{\rm C}$ . The combination of  $\mathbf{F}^{\rm D}$  and  $\mathbf{F}^{\rm R}$  provides a thermostat. In the case of polymers, two consecutive beads in the same chain perceive an additional spring force  $\mathbf{F}_i^{\rm S}$  of the form

$$\mathbf{F}_{i}^{\mathrm{S}} = -\kappa \sum_{j^{*}} (r_{ij} - r_{0}) \hat{\mathbf{r}}_{ij},\tag{6}$$

where  $\kappa$  is the spring constant,  $r_0$  the equilibrium distance, and  $j^*$  refers to the nearest neighbours in the chain. Here we set  $\kappa = 80$  [17] and  $r_0 = r_{\rm C}$ . For simplicity, the cutoff radius  $r_{\rm C}$ , the bead mass *m*, and the thermal energy  $k_{\rm B}T$  are set as 1, leading to a time unit  $\tau = (mr_{\rm C}^2/k_{\rm B}T)^{1/2} = 1$ .

#### Interaction parameters and simulations details

The DPD beads and the polymer constructs examined here are summarized in Fig. 1. Four chemically different beads were defined. The hydrophilic A and hydrophobic B beads model starch and a random co-polymer composed of styrene (42 wt%) and n-butyl acrylate (58 wt%), respectively. The substrate beads C and the solvent beads D were parametrized on unmodified cellulose and water, respectively.

The interaction parameters between beads are based on all-atom molecular dynamics simulations. The parametrization protocol is provided in Ref. [39]. Each polymer bead corresponds to 5 atomistic detail monomers in length, whereas each D bead represents 33 water molecules. The repulsive interaction parameters  $a_{ij}$  between all beads are summarized in Table 1. Moreover, the repulsive parameters were varied following the film stability analysis of Ref. [39], to map the stability of our findings and address the film formation response to the chemical characteristics of the components. The examined range was selected considering a sensible miscibility range and covering reasonable values for the hydrophilicity and hydrophobicity of the compounds. It should be mentioned that this range is not comprehensive.

Different amphiphilic di-block co-polymer chains  $A_iB_j$ , where *i* and *j* define the number of A and B beads, respectively, were examined under the length constraint i + j = 7, as shown in Fig. 1. The hydrophobic and hydrophilic polymers were fixed in length, namely  $B_{19}$  and  $A_4$ , respectively. The solutions were prepared separately by placing the polymeric content and water (random initial configuration)

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**Fig. 1.** Chemical composition of the DPD beads and the bead representations of the system components in the simulations. Bead A models starch, bead B poly(styrene-*co*-n-butyl acrylate), bead C cellulose, and bead D water. The amphiphilic di-block co-polymer  $A_iB_j$ , where *i* and *j* are the number of hydrophilic and hydrophobic beads, has a length i + j = 7 beads, but the ratio *i* : *j* may vary. The hydrophobic polymer chain  $B_{19}$  is 19 beads long. Beads C and D are used to model surface and solvent, respectively, whereas  $A_4$  represents free starch chains.



**Fig. 2.** A time series of simulations snapshots visualizing the self-assembly of the film on a hydrophilic substrate. The first snapshot shows an example configuration resulting from the polymer solution first let self-assemble to polymeric micelles at time when the hydrophilic substrate is introduced. The snapshot time sequence demonstrates the subsequent film formation via self-assembly taking place on the hydrophilic substrate. The system concentrations are 11.25% of  $A_3B_4$  and 10% of  $B_{19}$ . The colour scheme follows Fig. 1. Water beads are not shown for clarity.

in a simulation box of  $40 \times 40 \times 35 r_{\rm C}^3$ , equilibrated for  $10^6$  time steps. During this time, micelles with a hydrophobic core and hydrophilic corona form and equilibrate in their structure. Separately, the substrate was constructed using 24,000 C beads (random placement into a large simulation volume of  $(100 r_{\rm C})^3$  deformed to  $40 \times 40 \times 5 r_{\rm C}^3$ , preserving the total number density). The complete simulation box was constructed by combining the substrate slab and the solution box containing the micellar structure to a  $40 \times 40 \times 40 r_{\rm C}^3$  system. The positions of the substrate beads were fixed, and the simulations ran for  $1.5 \times 10^6$  time steps. A time series of snapshots illustrates the simulated film formation process in Fig. 2.

For integration, the velocity-Verlet scheme with an integration time step  $dt = 0.05\tau$  was used. Periodic boundary conditions were used along all axes. Moltemplate [60] was used to construct the models, LAMMPS [61] to run the simulations, and VMD [62] for visualization. System equilibration was checked by visual analysis of the evolution of the assembly structures during the simulation.

Analyses were performed by time-averaging over the last  $5 \times 10^5$  time steps of the simulations. Average probability distributions  $\mathcal{P}(z)$  of the beads along the *z*-axis (perpendicular to the surface), were defined via

$$\int_0^{L_z} \mathcal{P}(z) dz = 1. \tag{7}$$

Similarly, the two-dimensional average probability distributions  $\mathcal{P}(x, y)$  were defined via

$$\int_{0}^{L_{x}} \int_{0}^{L_{y}} \mathcal{P}(x, y) dx dy = 1.$$
 (8)

The average coating thickness  $\langle h \rangle$  over time was assessed by averaging over n = 50 frames, while its fluctuation, which is an indicator of stability, via

$$\Delta h = \frac{1}{n} \sqrt{\sum_{t=1}^{n} \Delta h_t^2},\tag{9}$$

where  $\Delta h_t$  is the standard deviation of the height of the film in frame *t*. Since all polymers were assembled into the film for the entirety of the sampling period, the totality of the solid content was considered.

Water penetration was calculated by monitoring water beads within a  $2r_{\rm C}$  slab in the *xy*-plane centred at the *z*-axial centre of the film formed on the surface. Finally, we obtain the effective tension between film and water via

$$\gamma = \frac{1}{2} \int_{z_1}^{z_2} \left( P_{\perp} - P_{\parallel} \right) dz, \tag{10}$$

where  $P_{\perp} = p_{zz}$  correspond to the perpendicular stress and  $P_{\parallel} = \frac{1}{2} (p_{xx} + p_{yy})$  to the tangential stress [59]. The values of  $z_1$  and  $z_2$  are



**Fig. 3.** Polymer coatings self-assembling on the substrate at co-polymer  $A_iB_j$  concentration 11.25% and hydrophobic  $B_{19}$  polymer concentration 10% for different di-block co-polymer block length ratios *i* : *j*. The DPD bead colour scheme follows Fig. 1, with substrate beads in grey, hydrophilic and hydrophobic beads of the amphiphilic co-polymer in blue and red respectively, and hydrophobic polymer beads in yellow. Water beads are not shown for clarity.

chosen far from the film-water interface (where the pressure difference is zero).

#### 3. Results

#### Effects of di-block co-polymers block length ratio

First, we focus on the coating spreading and coating structure dependency on system composition. We choose  $B_{19}$  at 10% and  $A_i B_i$ at 11.25% concentration, and vary the block length ratio of the amphiphilic co-polymer. The  $A_i B_j$  concentration of 11.25% is sufficient for achieving a full substrate coverage by a lamellar film for A<sub>4</sub>B<sub>3</sub> copolymer structure in the absence of the B<sub>19</sub> polymer [39]. Assembly and coating spreading differences rising from the co-polymer block length ratio *i* : *j* variation are presented in Fig. 3. The data shows that the block length ratio of the di-block co-polymers is key to the polymer coating spreading on the substrate. Namely, the asymmetric A<sub>6</sub>B<sub>1</sub> and A<sub>1</sub>B<sub>6</sub> di-block co-polymers lead to droplets on the surface (Fig. 3(a) and (d)). On the other hand, more symmetric structures  $(A_5B_2)$ and  $A_2B_5$ ) promote the spreading of  $B_{19}$  chains over the hydrophilic substrate, panels (b) and (e). Notably, while A2B5 leads to incomplete coverage, A<sub>5</sub>B<sub>2</sub> forms a complete film. This is due to the higher fraction of hydrophilic beads in their structure, providing a stronger affinity towards the hydrophilic surface. Finally, the most symmetric structures,  $A_4B_3$  and  $A_3B_4$ , both lead to  $B_{19}$  spreading efficiently into a welldefined lamellar coating on the substrate, panels (c) and (f). This is in line with previous findings [39]. The determining effect of block length ratios on the morphology of the assemblies was also addressed by Pearson et al. [63], who studied film-forming latex particles.

The results suggest that the di-block co-polymers act as surface modifiers, bridging the hydrophobic content with the incompatible surface. The right balance between the hydrophilic and hydrophobic block lengths of the amphiphilic co-polymers is crucial. From simple geometrical consideration, one can expect that the optimal block length ratio for coating a flat surface is  $\approx 50\% - 50\%$ , assuming similar volumes for both blocks. This ratio will change for different geometries, such as curved surfaces as demonstrated by, e.g., PEGylated lipid packings on surfaces and assembly structural changes [64,65].

#### Effects of polymer component concentration variation

As the  $A_3B_4$  co-polymer structure leads to the best spreading of the hydrophobic coating material, for the rest of the work we focus on the latter setup. Fig. 4 presents an assembly phase diagram of  $A_3B_4$  and  $B_{19}$  concentration dependency, while Table 2 reports the corresponding film thicknesses and water beads penetration into the coating film. Concentration of  $A_3B_4$  was varied between 9 and 15% and that of  $B_{19}$  between 7 and 15%. The assembly phase diagram reveals three assembly regions in the examined concentration ranges. The first region, named *Incomplete*, corresponds to incomplete, discontinuous coatings where the polymer material forms droplet-like assemblies. The second, named *Complete*, corresponds to formation of complete lamellar coatings with a uniform hydrophobic layer between two di-block copolymer layers. The third, named *Cracked*, contains the concentration range in which the hydrophobic layer assembles as nonuniform and cracked.

The region *Incomplete* corresponds to low di-block co-polymer concentration (9%). Here, the co-polymer content in the solution is insufficient for forming a complete film on the substrate. The lack of amphiphilic co-polymers drives the coating to discontinuous patchy coverage. For the entire variation range of the B<sub>19</sub> concentration (7– 15%), coverage remains discontinuous. Notably, due to the periodicity of the simulation box, the patches emerge as infinite hemicylinders spanning the simulation box along the surface plane. It is worth mentioning that for a system which is not subject to periodic boundary conditions, the shape of these patches is determined by the molecular curvature of the amphiphile molecules. The effects of molecular curvature on assembly on surfaces are discussed, e.g., in Ref. [66].

Increasing the concentration of  $A_3B_4$  to the range 10–11.25% results in the formation of films that cover the entire substrate. Except for



Fig. 4. Assembly phase diagram for surface coatings resulting from varying  $A_3B_4$  and  $B_{19}$  concentrations. Simulated data points are presented by squares and representative snapshots of the corresponding films formed on the surface. The assembly response in the examined concentrations range can be classified into phase diagram regions where the polymer solution self-assembles to an *Incomplete* region with discontinuous coating by droplets, a *Complete* region with lamellar coatings, and a *Cracked* region with broken lamellar coatings.

**Table 2** Average thickness and average number of water beads in the centermost  $2r_{\rm C}$  slab of the formed films for the polymer systems showing complete surface coatings.

A3B4 [%]	B <sub>19</sub> [%]	Thickness $[r_C]$	Water [beads]	Region
11.25	7	$5.8 \pm 0.7$	$9.0 \pm 13.4$	Cracked
11.25	10	$6.7 \pm 0.6$	0.0	Complete
11.25	15	$8.3 \pm 0.6$	0.0	Complete
15	7	$7.1 \pm 0.7$	$23.5 \pm 6.5$	Cracked
15	10	$8.1 \pm 0.6$	$25.6 \pm 6.9$	Cracked
15	15	$9.7 \pm 0.7$	$17.8 \pm 5.2$	Cracked

the lowest studied  $B_{19}$  concentration (7%), the formed films contain uniform and continuous layers of hydrophobic polymer  $B_{19}$ , which are sandwiched between the di-block co-polymer leaflets at all examined  $B_{19}$  concentrations (8–15%). These cases all correspond to the *Complete* region. Moreover, the thickness and water penetration data presented in Table 2 demonstrates that the observed self-assembly response is very stable against changes in polymer system composition. For example, increasing the concentration of the  $B_{19}$  results in an increased thickness of the films, i.e. the excess material packs sandwiched between the amphiphile co-polymer layers. Furthermore, no water beads can be found inside the coatings in the *Complete* region. This is consistent with Bakker et al. [52], reporting good water-blocking characteristics of paper barrier coatings produced with poly(styrene-*co*-n-butyl acrylate) as the hydrophobic component.

Increasing the amphiphilic di-block co-polymer concentration to the range 12.5–15% results in a disrupted  $B_{19}$  layer. Marked as *Cracked* in Fig. 4, this region shows that having an excess amount of  $A_3B_4$  di-block co-polymer promotes the formation of cracks into the hydrophobic layer and makes the  $B_{19}$  layer non-uniform. This is reflected also in the water penetration data reported in Table 2.

#### Internal structure of the films

Analysis of the internal structure of the self-assembled films provides a better understanding of the coatings. Fig. 5 shows the averaged

one-dimensional probability distribution  $\mathcal{P}(z)$ , perpendicular to the substrate, of A and B beads, and the corresponding two-dimensional  $\mathcal{P}(x, y)$ calculated for B19. The systems corresponding to Complete coverage, Fig. 5(a) and (b) exhibit sharp peaks of  $\mathcal{P}(z)$ , indicating the formation of a well-ordered lamellar assembly and strong separation of the polymer components into layers. The hydrophilic segment of the amphiphilic co-polymers A3 packs next to the relatively hydrophilic substrate, as indicated by the peak slightly beyond  $z = 5r_{\rm C}$  in  $\mathcal{P}(z)$ . At  $z \approx 6.5r_{\rm C}$ , the second peak corresponds to the hydrophobic blocks B<sub>4</sub>. The distribution indicates that A3B4 self-assembles at the substrate into a brush-like conformation. Similar clear layering peaks form at the other side of the film, in the opposite order with the hydrophilic component facing the aqueous solution phase. The hydrophobic coating material spreads between the two amphiphilic co-polymer leaflets with the increase in the concentration of  $B_{19}$  from 10 to 15%, essentially changing the layer thickness, see also data in Table 2.

Fig. 5(c) presents the corresponding data for a system in which the hydrophobic slab is disrupted due to excess co-polymer content (here 15% of  $A_3B_4$ ). The disturbance of the hydrophobic layer in comparison to panels (a) and (b) is evident, showing the presence of disordered patches of  $A_3B_4$  throughout the coating film. Uniformity of the resulting  $B_{19}$  layers was examined also by addressing the 2D probability distribution  $\mathcal{P}(x, y)$ , Fig. 5 right column, for complete and cracked systems. Consistent with the one-dimensional data, uniform and complete layers form for the panels (a) and (b), whereas the strongly nonuniform hydrophobic layer formation is evident in  $\mathcal{P}(x, y)$ , corresponding to panel (c).

#### Effect of miscibility changes between segments

The mixing compatibility between the polymer components is known to affect both the self-assembly structures and the quality of the films [67]. DPD simulations allow modelling the effect of miscibility readily via varying the repulsive parameter  $a_{ij}$  in Eq. (3). The sensitivity of the results to changes in polymer component miscibility



Fig. 5. Left, P(z) of the solid content. Right, P(x, y) calculated for B<sub>19</sub> layer within the film. First row correspond to A<sub>3</sub>B<sub>4</sub> and B<sub>19</sub> at concentrations 11.25% and 10%, second row at 11.25% and 15%, and third row at 15% and 10%, respectively. The insets show cross-sections of each film.

was examined for the setup corresponding to concentrations of 11.25%  $A_3B_4$  and 10%  $B_{19}$ . This system is such that  $B_{19}$  readily spread to form a uniform hydrophobic layer using the benchmark parameter values (system ii of Fig. 6).

Fig. 6(a) summarizes the findings of varying  $a_{ij}$  over a total of 27 different combinations. The data shows that complete and uniform coverage takes place over a broad range of interaction parameters. The good response is promoted by the incompatibility of the hydrophilic and hydrophobic components. In the examined system, this also coincides with a larger immiscibility of the substrate and the hydrophobic B beads. The findings indicate that a sufficient incompatibility between the hydrophilic and hydrophobic polymer components is needed for the formation of uniform well-defined lamellar films, quite expected for segregation of polymer species.

Further analysis focuses on three systems marked as i, ii, and iii in panel (a). System i corresponds to the smallest  $a_{ij}$  values, indicating the smallest immiscibility. System ii is the previously characterized and benchmark system, while iii corresponds to the largest values of  $a_{ij}$ , or greatest incompatibility. Fig. 6(b) shows the corresponding pressure component differences for systems i, ii, and iii, and the corresponding values of  $\gamma$  are reported in Table 3. Increasing immiscibility increases the effective tension monotonically. This is, unsurprisingly, directly related to the mixing characteristics of the components. The measure correlates with hydrophobic coating design: e.g., Rodrigues et al. [53] have reported that increasing the hydrophobicity of the coatings increases the tension between the film and water, simultaneously decreasing water absorption.

Fig. 6(c) shows the comparison of the distribution of components  $A_3$ ,  $B_4$ , and  $B_{19}$  for these systems. As expected, increased incompatibility of the components leads systematically to sharper and narrower density peaks, enhancing the segregation within the different layers.

#### Table 3

Average thickness, mean number of water beads in the centermost  $2r_{\rm C}$  slab of the coating film, and effective tension between the coating film and water,  $\gamma$ , calculated for the systems i, ii and iii. Immiscibility increases from i to iii.

Model name	$A_3B_4$ [%]	B <sub>19</sub> [%]	Thickness $[r_C]$	Water [beads]	$\gamma ~[k_{\rm B}Tr_{\rm C}^{-2}]$
i	11.25	10	$6.9 \pm 0.9$	$7.5 \pm 5.8$	0.3
ii	11.25	10	$6.7 \pm 0.6$	0.0	0.6
iii	11.25	10	$6.6 \pm 0.5$	0.0	1.3

Table 3 collects the corresponding thickness and water penetration data for the systems, data indicating that the average thickness of the film and its fluctuation both decrease as the chemical incompatibility increases. Panel (d) presents a comparison of  $\mathcal{P}(x, y)$  to characterize the uniformity of the hydrophobic layer formed by B<sub>19</sub>. The latter property increases as the immiscibility increases ( $i \rightarrow ii \rightarrow iii$ ). These differences in uniformity reflect directly in the amount of water within the film, see Table 3. The effective tension between the film and water ( $\gamma$ ) calculated via Eq. (10), provides yet another measure for assessing the effects of miscibility.

#### Effect of free stabilizer

In industrial coating processes, starch is commonly used as stabilizer material, and is present in the solution [68]. Also, in the latex preparation process, some starch chains can remain free [54]. Consequently, the coating solutions often contain extra free starch, possibly affecting the assembly response [53]. We next examine the effect of excess free starch on film formation. The examined systems contain  $A_4$  polymers in concentrations between 3% and 10% in a fixed composition of 10%  $A_3B_4$  and either 10% or 15% of  $B_{19}$ . These concentrations all



**Fig. 6.** Dependency of the hydrophobic coating on DPD interaction parameter  $a_{ij}$  between the different beads. The examined solution contains 11.25%  $A_3B_4$  and 10%  $B_{19}$ . The bead nomenclature A, B, C, and D refers to Fig. 1. In (a), the blue dots mark the formation of a continuous hydrophobic layer, while the green dots a nonuniform or cracked hydrophobic coating. Three example systems i, ii, and iii are identified, ii being the previously characterized benchmark system. Panel (b) summarizes pressure differences that allow calculating the effective tension for systems i, ii, and iii. Here  $P_{\perp}$  and  $P_{\parallel}$  are the normal and tangential pressure components, respectively. Panel (c) shows  $\mathcal{P}(z)$  of the solid content, namely  $A_3$ ,  $B_4$ , and  $B_{19}$  for systems i, ii, and iii. Panel (d) shows  $\mathcal{P}(x, y)$  corresponding to  $B_{19}$ , measuring the degree of uniformity of the hydrophobic layer.

correspond, in the absence of the added free starch, to the *Complete* region of Fig. 4 (uniform hydrophobic layer).

Fig. 7 shows that small amount (3 and 5%) of free  $A_4$  does not affect the structure of the films or the hydrophobic layer. However, at 10%  $A_4$ , the excess hydrophilic fragments are responsible for breaking the film. The excess hydrophilic content acts as a bridge between the solvent and the hydrophilic substrate, penetrating into the  $B_{19}$  layer and readily allowing water to penetrate the film. Essentially, the excess hydrophilic chains puncture the coating. This suggests that the amount of free hydrophilic stabilizers, such as starch, should be kept at low concentrations to avoid film rupture. Indeed, Cheng et al. [54] have shown that reducing the amount of free starch by starch degradation improves the coating quality.

#### 4. Conclusions

In this work we examined, by DPD simulations, the composition dependencies in the self-assembly structure of block co-polymer based barrier films, using a paper surface coating system composed of linear amphiphilic di-block co-polymers, hydrophobic polymers, and extra hydrophilic stabilizer fragments in water as the focus case. Namely, the benchmark system parametrization modelled di-block co-polymers corresponding to starch-*block*-poly(styrene-*co*-n-butyl acrylate), hydrophobic polymer to poly(styrene-*co*-n-butyl acrylate) and extra hydrophilic fragments to starch.

The most important findings of the work are the key role of even block length ratio in the amphiphilic di-block co-polymer in ensuring spreading of the coating film on the substrate, and the assembly ranges that indicate a broad optimal range for uniform film formation in terms of composition. Consistent with the presented findings, assembly morphologies dependencies on the block lengths have been demonstrated in numerous experimental studies, see e.g. Refs. [69-75]. These demonstrate that the assembly structure and phase separation [69-71], but also microscopic properties, such as the microporous character [72,73] and pore organization in porous films [75], bear block length dependency. Besides assembly structure, also polymer materials properties, such as glass transition temperature, depend on block length ratio, see e.g. Ref. [76]. Here we mapped surface coatings assembly response at microscale, showing analogous microstructure dependency, but also the component wise contributions of the polymer system to the assembly response. It is worth pointing out that the organization dependencies of the block length ratio extend to also other interfaces, such as airwater interface, see e.g. Ref. [74], and surface morphology of solid state assemblies, see e.g. Ref. [77]. Additionally, architectures more complex than linear, such as comb-like [78] and brush assemblies [79-81], have similar assembly dependencies.

For applications of the polymer films, the findings on the disrupting effects rising from the lack of amphiphilic co-polymer or hydrophobic mass in the system, and the equally damaging effects of excess amphiphile or hydrophilic stabilizer, are noteworthy. These effects rise



**Fig. 7.** Effect of excess free hydrophilic polymer  $A_4$  in the solution on the formation of the coating. Two-dimensional probability maps  $\mathcal{P}(x, y)$  of the formed  $B_{19}$  hydrophobic layer and a snapshot of the corresponding simulation system are presented.  $A_3B_4$  concentration is 10% and  $B_{19}$  concentrations 10 and 15%.  $A_4$  concentrations vary, from top to bottom, between 3, 5 and 10%.

from molecular packing, in practise curvature effects. Priorly, e.g. solvent and presence of ions has been demonstrated to tune assembly shape [82], but analogously, vesicle-to-bicelle transitions dependent on polymer packing are well known, see e.g. Ref. [65]. The findings generalize to assembly changes on curved surfaces, see e.g. Ref. [83].

Since the DPD approach and parametrization are by construction very general and at the mesoscale level, the results generalize to large variety of polymer systems, as demonstrated by the performed parameter sensitivity examination. Altogether, the findings present a mapping to design barrier coatings on hydrophilic surfaces, and guidelines for optimizing characteristics such as spreading and cracking.

#### CRediT authorship contribution statement

Kourosh Hasheminejad: Investigation, Software, Methodology, Formal analysis, Data curation, Visualization, Writing – original draft. Alberto Scacchi: Conceptualization, Software, Methodology, Writing – review & editing, Supervision. Sousa Javan Nikkhah: Conceptualization, Methodology, Writing – review & editing. Maria Sammalkorpi: Conceptualization, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Maria Sammalkorpi reports financial support was provided by Business Finland, Finland. Maria Sammalkorpi reports financial support was provided by Academy of Finland, Finland.

#### Data availability

Data related to the manuscript plots and the input script file for the DPD simulations are provided at fairdata.fi (https://doi.org/10.23729/63ca8eab-1ab9-4197-acea-f5c811954ce4). If using the inputs or the open data, we request acknowledging the authors by a citation to the original source (this paper).

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