Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Optical properties of heterogeneous thin film structure composed of three optically transparent components with corresponding volume fractions f_a, f_b and f_c can be characterized within the Bruggeman effective media approximation (EMA) being of the form:

$$0 = f_a A + f_b B + f_c C \tag{1a}$$

where $A = \frac{n_a^2 - n_1^2}{n_a^2 + 2n_1^2}$, $B = \frac{n_b^2 - n_1^2}{n_b^2 + 2n_1^2}$, $C = \frac{n_c^2 - n_1^2}{n_c^2 + 2n_1^2}$, n_a, n_b and n_c are the bulk refractive indices of the three components correspondingly; n_1 is the refractive index of the heterogeneous three-component substance. The volume fractions of these components are mutually dependent and are related through a by the trivial relation

$$\sum_{i=1}^{n} f_i = f_a + f_b + f_c = 1 \ . \tag{2a}$$

The system of equations (1a) (2a) can be used to solve the inverse problem of the determination of the volume fractions for separate components. Obviously, the unique solution of this problem exists only for a two-component structure:

$$f_a = \frac{B}{B - A} \text{ and } f_b = 1 - f_a \tag{3a}$$

However, unknown volume fractions of two components of a multicomponent system can also be defined, if the values of the volume fractions of all the rest components are known. In particular, solution of this problem for a three-component structure is of the form:

$$f_a = \frac{B(f_c - 1) - f_c C}{(A - B)}; \qquad f_b = 1 - f_a - f_c. \tag{4a}$$

where, f_c is the known value of the volume fraction for a separate component (void, air or solvent) obtained by an independent method.

The Bruggeman EMA-formalism can be useful also to study the conformational changes (swelling or collapse) of the grafted copolymer coating due to the wetting. The course of such processes is strongly determined by the initial structure of the grafted layer, since the only parameter that remains constant during the conformational changes of wet coating is the composition ratio:

$$R = \frac{f_a}{f_b} \tag{5a}$$

Changeable parameters are not only the volume fraction of a solvent f_c' that substituting air in the voids of the layer but also the volume fractions of monomers f_a' and f_b' that compose the complex copolymer structure. It should be noticed that, the ratio of these fractions $f_a'/f_b' = R$ remains unchanged for any conformational changes.

Equations (1a), (2a), (5a) allow one to find a unique solution for the three unknown values f_a', f_b' and f_c', if the composition ratio R as well as the bulk refractive indices of both copolymers n_a and n_b, refractive indices of immersion media n_c and the grafted coating n_1 are known:

$$f_c' = \frac{M}{M-C}; \qquad f_a' = \frac{B(1-f_c')R}{R+1}; \qquad f_b' = \frac{f_a'}{R} \tag{6a}$$

where $M = \dfrac{RA+B}{R+1}$.

In other words, this system of equations provides a functional link between the refractive index n_1 of the grafting coating and its structural changes due to wetting.

Obviously, any structural (conformational) change of the grafted surface layer is unambiguously related to a change in its thickness.

The heterogeneous structure of the grafted coating can be divided virtually into three homogeneous layers of corresponding thickness d_a, d_b and d_c. The change in the coating volume is completely determined by its thickness, since the surface area of the coating is constant. Therefore, the volume fraction of any component can simply be expressed through the relation of virtual layer thickness to the total thickness of the heterogeneous coating:

$$f_a' = \frac{d_a}{d}, \qquad f_b' = \frac{d_b}{d}, \qquad f_c' = \frac{d_c}{d} \tag{7a}$$

Therefore the procedure for establishing of the functional link between the values of possible change of the volume composition of the coating $f_a' / f_b' / f_c'$ in the immersion media on one hand and corresponding changes of its thickness d and refractive index n_1 on the other hand should be as follows:

- first, one has to determine the refractive index of wet coating n_1^w at the condition of full filling of the voids by immersion liquid at the constant thickness (conformation) for a sample with established thickness $d^w = d^d$, porosity $f_c' = f_c$ and composition ratio $R = f_a / f_b = f_a' / f_b'$ in its dry state;
- then, one has to calculate new values f_c', f_a' and f_b' using (6a) for the fixed *R*-ratio and arbitrary n_1^w-value from the selected range.
- the thickness of wet coating after conformational change can be calculated in this case using one of three relationships:

$$d^w = \frac{d_a}{f_a'} = \frac{d_b}{f_b'} = \frac{d_c}{f_c'}, \qquad (8a)$$

where $d_a = d^d f_a$, $d_b = d^d f_b$, $d_c = d^d f_c$.