

Supporting Information

Simultaneously Tailoring Surface Energies and Thermal Stabilities of Cellulose Nanocrystals Using Ion Exchange: Effects on Polymer Composites Properties for Transportation, Infrastructure, and Renewable Energy Applications

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Derivation of Surface Energies

The Good-van Oss equation is given by equation S1, where N_A is Avogadro's constant, a is the cross sectional area of the probe molecule, γ_S^+ and γ_S^- are the electron acceptor and donor parameters of the surface and γ_L^+ and γ_L^- are the electron acceptor and donor parameters of the probe molecule. If monopolar probe molecules are used, γ_S^+ and γ_S^- can be calculated directly from only two probe molecules (one acid and one base). For this study, the ΔG values for dichloromethane and ethyl acetate, the γ_S^+ and γ_S^- values can be determined using equation S2. Because $\gamma_S^- = 0.0 \text{ mJ/m}^2$ for dichloromethane, equation S2 is reduced to equation S3. Upon rearranging, γ_S^- can be calculated using equation S4. Similarly, using the ethyl acetate ΔG value, equation S5 can be derived for the value of γ_S^+ . Equation S4 and S5 are combined to solve for the acid base component of the surface energy, using equation S6. Once the total surface energies are calculated, the work of adhesion (equation S7) and work of cohesion (equation S8) can be determined.

$$\Delta G = N_A * a * 2 * ((\gamma_L^+ * \gamma_S^-)^{1/2} + (\gamma_L^- * \gamma_S^+)^{1/2}) \quad (S1)$$

$$\Delta G_{DCM} = N_A * a_{DCM} * 2 * ((\gamma_{DCM}^+ * \gamma_S^-)^{1/2} + (\gamma_{DCM}^- * \gamma_S^+)^{1/2}) \quad (S2)$$

$$\Delta G_{DCM} = N_A * a_{DCM} * 2 * (\gamma_{DCM}^+ * \gamma_S^-)^{1/2} \quad (S3)$$

$$\gamma_S^- = (\Delta G_{DCM} / (N_A * a_{DCM} * 2))^2 * (1 / \gamma_{DCM}^+) \quad (S4)$$

$$\gamma_S^+ = (\Delta G_{EthAce} / (N_A * a_{EthAce} * 2))^2 * (1 / \gamma_{EthAce}^-) \quad (S5)$$

$$\gamma_S^{AB} = 2 * (\gamma_S^+ * \gamma_S^-)^{1/2} \quad (S6)$$

$$W_{AD} = 2 * (\gamma_{Sample1}^D * \gamma_{Sample2}^D)^{1/2} + 2 * (\gamma_{Sample1}^{AB} * \gamma_{Sample2}^{AB})^{1/2} \quad (S7)$$

$$W_{CO} = 2 \cdot (\gamma_{Sample1}^D \cdot \gamma_{Sample1}^D)^{1/2} + 2 \cdot (\gamma_{Sample1}^{AB} \cdot \gamma_{Sample1}^{AB})^{1/2} \quad (S8)$$

Molecular Dynamics Details

Molecular dynamics simulations were carried out using the NAMD molecular dynamics package[1] and a combination of the generalized CHARMM force field[2, 3] and the CHARMM force field for carbohydrates[4]. Parameters for polystyrene were readily available from the CHARMM generalized force field and parameters for CNCs were obtained from the CHARMM force field for carbohydrates. Parameters for the ionic surface modifications were initially determined from the cgenff program. However, upon discovering that a high penalty value was obtained for many of the partial charges, as well as the parameters, the force field toolkit (fftk)[5] protocol was used to determine appropriate parameter values and partial charges.

To build the simulation systems, unmodified CNCs were first generated using the cellulose-builder software[6] with the (110) surface exposed. Each cellulose chain consists of 10 repeat units and is periodic along the length of the chain (intrachain dimension of 103.8 Å). 14 cellulose chains are placed adjacent to one another to form a sheet/layer and periodic boundary conditions are also employed between chains (interchain dimension of 74.894 Å). Three of these so-called cellulose sheets are layered to form the final cellulose nanocrystal, with this dimension being chosen as the thickness is approximately equal to the cutoff distance for non-bonded interactions in simulation (12 Å). Once the unmodified CNC systems were created, the psfgen tool in VMD[7] was used to exchange 1 out of every 10 exposed hydroxyl groups with sulfate groups and place the appropriate cation in close proximity to this group. These modified CNCs were then equilibrated in vacuum for 2 nanoseconds to relax the structure and allow the ions to reach a minimum energy conformation on the CNC surface.

Polystyrene films were created by packing 60, 100-mer polystyrene chains in an appropriate volume having the same cross-sectional area as the periodic CNC (74.984 Å x 103.8 Å). Once the chains were

packed in this volume, the film was annealed in order to relax the chains and mitigate any potential edge effects by allowing the chains to migrate through periodic boundaries.

To generate CNC-polystyrene interfaces, the equilibrated polystyrene film and equilibrated CNC were merged into a single system file and moved such that the two surface were in close proximity. During simulation the bottom 15 Å of the PS film were fixed in order to hold the film in place. Upon running the simulation, the CNCs moved into close contact with the polymer film and formed a distinct interface. Similarly, for CNC-CNC simulations, the “bottom” CNC was fixed in place by constraining the backbone carbon atoms and the “top” CNC was allowed to move into equilibrium with the adjacent nanocrystal and form the CNC-CNC interface. These simulations were run for 5 nanoseconds to ensure that the interface formed completely and reached the minimum energy configuration. This was verified by plotting the interfacial energy as a function of simulation time and a determination that the energy had reached a plateau value.

References

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