Density Functional Theory Study of Catechol Polymer Adhesion onto γ-Alumina (110) Surfaces

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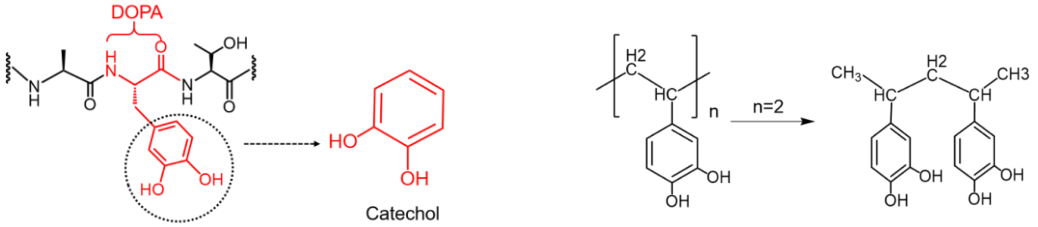
Understanding the adhesion mussel's adhesion mechanism is vital for developing advanced moisture-resistant bioadhesives. Mussels adhere strongly to various surfaces in aqueous environments due to adhesive proteins like mfp-3 and mfp-5, enriched with catecholic amino acid 3,4-dihydroxy-L-phenylalanine (DOPA).[1] The catechol group in DOPA, with two benzene rings and ortho hydroxy groups, enhances adhesion to both hydrophobic and hydrophilic surfaces. Hence, the adhesion mechanism of catechol dimer to dehydroxylated and hydroxylated γ-alumina (110) surfaces was investigated using periodic density functional theory calculations. Catechol dimer is modeled after the experimentally synthesized poly(vinyl catechol), as shown in Figure, which mimics the catechol side of DOPA[2].

The results showed stronger adhesive force on dehydroxylated γ-alumina (110) surface than on hydroxylated surface. Crystal Hamilton orbital population (COHP) analysis confirmed robust hydrogen bonding, with integrated COHP (IpCOHP) values of 1.58 eV for dehydroxylated and 1.92 eV for hydroxylated surfaces. The energy of optimized adhesion interfaces was calculated by removing hydrogen atoms from the catechol dimer's hydroxy groups and observing chemisorption on γ-alumina (110) surfaces. The energy profile showed that the structure retaining hydroxy groups and maintain the hydrogen bonds are more stable than those with hydrogen removal, resulting to the formation of water, surface hydroxo ligand, molecular hydrogen, and coordination chemisorption.



1) J. Yu, *Nat. Chem. Biol.* **2011**, *7*, 588. 2) H. Takeshima, *Macromol.* **2017**, *50*, 4206.