ZWITTERION-CONTAINING POLYMER ADDITIVES FOR FOULING RESISTANT ULTRAFILTRATION MEMBRANES: CHOOSING THE RIGHT CHEMISTRY AND ARCHITECTURE

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Fouling is likely the most significant obstacle to the wider use of membranes in many processes, especially when the feed contains large quantities of organic contaminants such as proteins, natural organic matter, and oil. Zwitterions, which have equal numbers of positively and negatively charged groups, are very hydrophilic and strongly resist fouling. Blending a zwitterion-containing polymer with a commodity polymer such as polyvinylidene fluoride (PVDF) during membrane manufacture by non-solvent induced phase inversion (NIPS) is a promising approach to making fouling resistant ultrafiltration (UF) membranes. It does not require any post-processing steps and can be plugged directly into existing membrane manufacturing facilities. A handful of studies demonstrate varying degrees of fouling resistance when zwitterion-containing amphiphilic copolymers are blended with PVDF to prepare membranes. However, we do not know how copolymer chemistry, architecture, and blending ratio with the base polymer affect final membrane properties. There are no guidelines on how to design and select a zwitterion-containing copolymer for optimal performance. In this study, we seek to identify the effect of several copolymer features on the performance of membranes prepared from its blends with PVDF: Zwitterion chemistry, hydrophobic monomer chemistry, copolymer composition (i.e. zwitterionic/hydrophobic monomer ratio), copolymer architecture, and blend composition. We synthesized several copolymers varying these parameters, and evaluated the morphology, permeance, selectivity and fouling resistance of resultant membranes. We have found design rules to direct the selection of best polymer structures and architectures for this use. First, we found that unlike past reports, a higher hydrophilic/zwitterionic monomer content in the copolymer does not necessarily lead to better performance. Copolymers with high zwitterion contents macrophase separate from PVDF during the NIPS process. The resultant membrane has poor performance. Second, we can identify the copolymer compositions where this problem will be avoided using thermal analysis of copolymer/PVDF blends. If the copolymer leads to a shift in the crystallization temperature of PVDF, this predicts good anchoring of the copolymer and improved fouling resistance. Third, even very small quantities of zwitterion-containing copolymers can lead to significant increases in permeance and exceptional fouling resistance. As little as 5 wt% zwitterionic copolymer can lead to 2x higher flux with little change in rejection, and show essentially complete resistance to irreversible fouling. Finally, this effect is more prominent with comb-shaped copolymers with the zwitterions are arranged as short side-chains attached to the hydrophobic backbone, in comparison with random copolymers of the same repeat units. This information is crucial for membrane companies considering such copolymer additives to improve the performance of PVDF membranes, enabling rational design of zwitterion-containing polymers for membrane applications. We are currently further exploring the responsive and self-cleaning properties of these membranes, and their performance in realistic applications such as wastewater treatment.