Thermoresponsive coatings using green processing technologies: Application to bioseparation processes

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Stimuli-responsive materials represent a rapid variety of functional materials that are becoming increasingly important. In particular, temperature responsive membranes have received more and more interest from various scientific fields, because their permeation properties can be controlled or adjusted according to the external temperature environment [1,2]. Numerous applications to these membranes have been for drug delivery systems, biological and chemical separation, water treatment, chemical sensors and tissue engineering. Several design and production processes have been developed to prepare stimuli-responsive membranes and can be classified in two main categories: i) processing the stimuli-responsive materials to fabricate the membrane or ii) surface modification of previously prepared membranes by chemical or physical methods to incorporate the stimuli-responsive polymers.
Herein we report a PS/PAN blended membrane grafted with PDEAAm using a new green methodology by combining plasma surface activation and supercritical fluid technology.
Membranes with controlled morphology were previously prepared by supercritical carbon dioxide ($scCO_2$) induced phase inversion method. Activated membranes were coated via *in situ* polymerisation of poly(N-N'-diethylacrylamide) (PDEAAm) in supercritical carbon dioxide. XPS analysis confirmed the successful coating of the membrane surfaces with a PDEAAm layer. Coated and uncoated membranes were characterized by scanning electron microscopy, mercury porosimetry, dynamical mechanical analysis, swelling and contact angle measurements in order to study their morphology, hydrophilicity and viscoelastic properties. Contact angle measurements and phosphate buffer solution permeability were determined in order to characterize the structure hydrophobicity variations with temperature. The on-off mechanism was tested using a model protein (BSA) as a proof of concept for the ability to control pore apertures by temperature stimulus. In addition to temperature-dependent permeability of aqueous solutions, PDEAAm grafted chains also impart good antifouling properties to the PS/PAN blended membranes. By comparing the performance of analogous membranes prepared by conventional grafting polymerization technique with results obtained in this work, we demonstrate that much higher fluxes and extremely improved anti-fouling behavior can be achieved by plasma indeuced graft polymerization. The reported remarkable differences are due to the plasma surface activation that by preserving the morphological properties of the base membranes efficiently induced the active sites for PDEAAm grafting. The further polymerization in supercritical conditions allowed the formation of the homogeneous temperature responsive polymeric layer comparatively to the less controlled coating procedure using conventional solvents.

[1] T. Peng and Y. L. Cheng, J. Appl. Polym. Sci. 70 (1998) 2133.
[2] M. A. Cole, N. H. Voelcker, H. Thissen and H. J. Griesser, Biomaterials 30 (2009) 1827.

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