Sulfonated polyethersulfone (SPES) was used as an additive to prepare hydrophilic poly(ethersulfone) (PES) hollow fiber membranes via non-solvent assisted reverse thermally induced phase separation (RTIPS) process. The PES/SPES/N,N-dimethylacetamide (DMAc)/polyethylene glycol 200 (PEG200) casting solutions are lower critical solution temperature (LCST) membrane forming systems. The LCST and phase separation rate increased with the increase of SPES concentrations, while the casting solutions showed shear thinning. When the membrane forming temperature was higher than the LCST, membrane formation mechanism was controlled by non-solvent assisted RTIPS process and the also membranes presented a more porous structure on the surface and a bi-continuous structure on the cross section. The membranes prepared by applying SPES present higher pure water flux than that of the pure PES membrane. The advantages of the SPES additive are reflected by the relatively high flux, good hydrophilicity and excellent mechanical properties at 0.5 wt.% SPES content.