Abstract

Fluoropolymers, since its serendipitous discovery in 1930 has attained enormous research and technological importance and important marketplace in the development of advanced materials having interesting structural and functional properties. Owing to the unique properties of fluoropolymers such as excellent water and oil resistance, chemical resistance and thermal stability they have been widely used in developing speciality coatings. This thesis reports on the preparation of well-defined functional fluoropolymers such as block and random copolymers based on fluoroacrylates and fluoromethacrylates along with different comonomers via reversible addition-fragmentation chain-transfer (RAFT) polymerization. The potential application of these fluoropolymers mainly as a coating material along with other different properties such as self-healing behaviour was studied. The functional copolymers bearing fluoroalkyl groups and other reactive groups were further modified by post polymerization modification using Diels-Alder chemistry to prepare polymers with self-healing property. The functional copolymers prepared were characterized using FT-IR, ^{1}H-NMR, GPC, TGA, DSC, SAXS, XPS and AFM analyses. The self-healing property was studied by scratch-and-heal analysis, which was monitored using optical microscopy (OM) and AFM analyses. At first, block copolymers comprising hybrid polyhedral oligomeric silsesquioxane (POSS) and 2,2,2-trifluoroethyl methacrylate (TFEMA) were prepared via RAFT polymerization. The morphological behaviour of the BCPs was studied in different solvents. The BCP thin films demonstrated core-shell type morphology when deposited from chloroform and lamellar type morphology when deposited from THF as the solvent. Further, the potential application of the BCPs as a hydrophobic coating material was studied by coating the BCPs over different substrates such as glass, cotton fabric and an aluminium metal plate via dip-coating. Interestingly, the BCPs showed hydrophobicity up to ~135° over cotton fabric. To develop a fluoropolymer with self-healing functionality along with the excellent hydrophobicity, random copolymer consisting of PTFEMA and poly(furfuryl methacrylate) (PFMA) was synthesized by RAFT polymerization. Further, the furfuryl moieties of this copolymer were modified via Diels-Alder (DA) reaction using varied content of POSS-maleimide (POSS-M). In addition, to increase in hydrophobicity the copolymers exhibited good self-healing efficiency (~78 %) due to dynamic DA covalent bonds between the reactive furan group in the copolymer and the maleimide group in POSS-M. Further, to prepare fluoropolymers with fast crosslinking efficiency BCPs comprising TFEMA and 2-hydroxyethyl methacrylate (HEMA) was prepared via RAFT polymerization. Then the hydroxyl groups of the BCP were modified with anthracenyl moiety and were crosslinked using 1,2,4-triazoline-3,5- dione (TAD) derivatives which led to faster dynamic conjugation with anthracenyl moiety. Interestingly, the hydrophobicity of the BCP was not changed even after incorporation of hydrophilic TAD moiety and the self-healing property was studied using AFM analysis. A multifunctional triblock copolymer (TBCP) comprising sodium 4-vinylbenzene sulfonate (SS), butyl acrylate (BA), and 2,2,2-trifluoroethyl acrylate (TFEA) was prepared via the polymerization induced self-assembly (PISA) process using RAFT polymerization. The TBCP film showed interesting mechanical properties with remarkable high elongation of 1500%. Moreover, the TBCP exhibits excellent hydrophobicity having a water contact angle (WCA) ~122°. The dielectric properties of the prepared copolymer were studied using AC-impedance analysis.

Keywords: *Fluoropolymers, RAFT, Diels-Alder Reaction, hydrophobicity, self-healing.*