ABSTRACT

Fluorinated polymers find tremendous research interest due to their several important properties like excellent water and oil repellency, resistance to acid, base, organic solvents, UV-light and flammability. Fluorinated polymers in the form of aqueous dispersion or emulsion can be used as specialty paints & coatings having excellent surface properties. In this context, this thesis describes the preparation of fluorinated homo and copolymers in emulsion via reversible addition-fragmentation chain transfer (RAFT) process. In this case, a number of fluorinated alkyl-acrylate monomers like 2,2,2-trifluoroethyl methacrylate (TFEMA), 2,2,3,3,3-pentafluoropropyl acrylate (PFPA), 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) were used. RAFT polymerization of HFBA was carried out in miniemulsion and the obtained PHFBA was used as macro-RAFT agent to polymerize butyl acrylate (BA) producing the fluorinated block copolymer, PHFBA-*b*-PBA. The block copolymer showed core-shell morphology and improved hydrophobicity compared to PHFBA. Fluoropolymer/Clay nanocomposite (FCN) based on PHFBA was prepared by RAFT miniemulsion polymerization using poly (ethylene glycol) methyl ether methacrylate (PEGMEMA) and 2-(acryloyloxy) ethyl trimethylammonium chloride (AETAC) as functional comonomers. In this case, nanoclay was armored in presence of AETAC, but it was encapsulated in presence of PEGMEMA. The FCN having armored morphology showed much higher water contact angle (WCA) than the same with encapsulated nanoclay. The FCNs based on PFPA and HFBA were prepared via RAFT mediated Pickering miniemulsion polymerization using nanoclay like Laponite and sodium montmorillonite (NaMMT) as emulsion stabilizer. Here, the polymer-clay interaction was achieved via electrostatic attraction. TEM and SEM analyses showed the formation of nanoclay-armored fluoropolymer particles. Polymerization-induced self-assembly (PISA) process was adopted to polymerize TFEMA in a surfactant-free emulsion. In this case, functional macro-RAFT agent based on 4-vinyl pyridine (4VP) was prepared and modified by quaternization to make it water-soluble. The successful synthesis and modification of the macro-RAFT agent was confirmed by ^{1}H NMR and GPC analyses. The water-soluble macro-RAFT agent took part in the PISA process in presence of TFEMA. Thus, a surfactant-free emulsion of PTFEMA was produced with very high yield. The particle size of PTFEMA latex was obtained by DLS, AFM and TEM analyses. PTFEMA-silica composite latex was prepared by grafting nanosilica onto the functionalized PTFEMA particles. The fluoropolymer film showed superhydrophobicity with WCA of 151.5°.

Keywords: RAFT polymerization, Fluorinated polymer, Emulsion polymerization, Core-shell morphology, Fluoropolymer/Clay nanocomposite, armored morphology, encapsulated morphology, nanosilica, Superhydrophobicity.