



CHAPTER II LITURATURE REVIEW

2.1 Syntheses of Fluorine Contained Polymer and Polymethyl Methacrylate Copolymer

In 1997, Park *et al.* successfully discovered a new method of synthesizing copolymer of poly(perfluoroalkylethyl methacrylate)(PFMA) with poly(methyl methacrylate). The polymer was prepared by using the macromonomer technique and emulsion polymerization method. PMMA macromonomers were prepared by the macromonomer technique via the radical oligomerization of methylmethacrylate with a chain transfer agent and then PMMA macromonomer was copolymerized with copolymers of perfluoroalkylethyl methacrylate and methyl methacrylate by the emulsion polymerization technique to finally obtain graft copolymer of PFMA-g-PMMA. This method can be used to obtain various compositions of PMMA and branch lengths. This technique is useful in the manufacture of surface modification agents.

In 1999, Haddleton *et al.* synthesized and characterized PFMA-r-PMMA by ATRP technique which gave a well defined copolymer and a predetermined molecular mass. By using a fluorinated initiator, they produced α -perfluoroalkyl functionalized PMMA chain which had a much lower water wettability at relative low %fluorine contained.

In 1999, Xia *et al.* found that ATRP of block copolymerization of FOMA-b-PMMA could be successfully carried out in $scCO_2$. Poly(FOMA) was prepared in $scCO_2$ as a macro-initiator. Dispersion polymerization of MMA in $scCO_2$ using ATRP was carried out in the presence of fluorinated polymeric surfactant. This system yielded stable PMMA latex particles with well controlled molecular weights and a narrow molecular distribution.

2.2 The Properties Studying of Fluorine Contained Polymer and Polymethyl Methacrylate Copolymer

In 1996, Sheiko *et al.* studied the self dewetting phenomena of perfluoroalkyl methacrylate films on glass. They found three states of dewetting behavior depending on film thickness: (i) at distances at least more than seven bilayers away from the flat substrate, the film melted according to the bulk isotropization temperature and demonstrated macroscopic dewetting of order sublayer. (ii) Sublayer was not stable above the isotropization transition, but collapsed in a peculiar stepwise manner. A bilayer started to dewet the next bilayer only after the top layer had collapsed into microscopic droplets. This repetitive process proceeded until (iii) a thin film with the thickness of only one and a half bilayers remained and covered the substrate. This layer was stable even when the temperature was raised 50°C above the isotropization temperature. Apparently, the geometric constraint by the “hard wall” and the interactions with the substrate caused this stabilization. The self-dewetting was discussed in terms of a progressive disordering of the side chains with increasing distance from the wall.

In 1998, Borruto *et al.* studied the effect of different materials on friction and wear behaviors with sliding friction of 100%. AISI 1050 and AISI 420 steels, pyrex glass, teflon(PTFE) and carbon fiber were chosen as the materials to be studied. All of them had the different surface wettability angles (θ). Testing was carried out on a pin-on-disc tribometer with homogeneous and heterogeneous couplings in dry conditions and with oil and water lubrication. The most important results achieved with the mechanical tests and the SEM examinations was that with couplings of a hydrophilic and hydrophobic material, water lubrication has a greatly positive effect, particularly with hydrophobic discs and hydrophilic pins the friction factor and the wear lower than those with oil lubrication.

In 1998, Park *et al.* investigated surface properties of PFMA-g-PMMA compare to of PFMA-r-PMMA and PFMA homopolymer. Surface energy of PFMA-g-PMMA was lower than the PFMA-r-PMMA but had a bit higher PFMA homopolymer. Annealing enhanced the graft copolymer's ability to lower surface free energy to the same level as that of the PFMA homopolymer. However,

annealing was less effective for the PFMA-r-PMMA copolymer. The reasons for the poorer surface modification activity of random copolymer were because of the less hydrophobicity of the random copolymer and the hindrance of perfluoroalkyl groups by methyl ester groups of MMA segments. The PMMA branches were also expected to increase blending miscibility to PMMA homomonomer.

In 2001, Brostow *et al.* studied the morphology, elastic, static and dynamic friction of polymer blends of a commercial epoxy resin and fluorinated poly(aryl ether ketone)(12F-PEK). The system was cured at 24 and 70 °C. The friction is 30% less than the value for the pure epoxy resin, at the 12F-PEK concentration of only 1% and after curing at 24°C. By contrast, after curing at 70°C, increases in both static and dynamic friction were observed. At 24 °C, the SEM analysis showed that a phase separation starts at 10%12F-PEK; completely phase-inverted morphology was found above 30% of fluoropolymer. The system cured at 70°C has more compact structure and the phase separation process was shifted towards higher fluoropolymer concentrations.

In 2002, Aoike *et al.* studied the tribological properties of series random copolymers. They chose to study a random copolymer because it has higher compositional homogeneity compared to block, graft copolymer and polymer blends. The materials used in this study were a series of random copolymer composed of methyl methacrylate (MMA) and n-butyl methacrylate. With the MMA fractions varied from 0-1. They found that tribological properties occurring when a stiff slider moved on a copolymer surface under both conventional macro- and nanotribological conditions can be controlled by the composition of random copolymer. Random copolymer surfaces may also be applicable to controlling surface dynamic behavior such as indentation and adhesion on macroscopic to nano scopic scale.