

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The polyisoprene seed latexes were prepared by conventional emulsion polymerization to obtain different seed particles for kinetics studies of surface grafting reaction on these seeds by reaction calorimetric technique. The reactions were performed in the presence of sodium persulfate as an initiator, sodium dodecyl sulfate as a surfactant, sodium bicarbonate as a buffer and a small amount of n-dodecyl mercaptan as a chain transfer agent. The effects of the amount of monomer, surfactant concentration, initiator concentration, and reaction temperature on the latex size were investigated. The particle size decreases with increasing the surfactant and initiator concentration and reaction temperature whereas it increases with increasing the monomer concentration.

The graft copolymerization of DMAEMA onto a synthetic polyisoprene seed latex can be accomplished using the redox initiator system CHP/TEPA. The modified latexes displayed a dramatic increase in colloidal stability at low pH, which is attributed to the grafted hydrophilic polymer acting as an electrosteric stabilizer (i.e. a 'hairy layer'). The rate data are consistent with the grafting occurring as a rare event involving abstraction between a hydrophobic cumyloxyl radical and isoprene unit in

the interfacial phase to form a radical on the polyisoprene which can commence propagation with the water-soluble DMAEMA monomer: 'topology-controlled' polymerization. While this process produces the hairy layer grafted to the particles, most polymerization seems to lead to untethered poly(DMAEMA) in the water phase. There is evidence that the reaction between the pairs of the redox couple, TEPA and CHP, is relatively slow. Loss of radical activity after the redox feed is switched off is also slow, which is consistent with the slowness of redox reaction, and/or if one of the rate-determining step in termination includes transfer to a monomeric radical. Despite the simplification of the system achieved by working with synthetic polyisoprene rather than NRL, a consistent mechanistic picture to fully quantify the kinetic data obtained by calorimetry cannot be advanced until it is possible to quantify the aqueous-phase homopolymerization and redox initiation processes.

The graft copolymerization of hydrophilic vinyl monomers, DMAEA, DMAEMA, and HEMA onto the natural rubber latex were also carried out in the second-stage emulsion polymerization. The different redox initiator systems, CHP/TEPA, *t*-BHP/TEPA, and $K_2S_2O_8/K_2S_2O_5$ used to initiate the graft copolymerization, were investigated. The graft copolymer initiated with CHP/TEPA gave the highest percentage grafting efficiency. The more hydrophobic initiator, CHP, was observed to be more efficient than *t*-BHP and $K_2S_2O_8$, respectively, for grafting of the second monomer in the modified natural rubber.

The reaction parameters such as monomer and initiator concentrations and reaction temperature on the conversion, grafting performance and some properties

such as water absorption and contact angle of the grafted copolymers were investigated.

The grafting efficiency increases at the lower concentration range of monomers, reaches a maximum at 15 phr monomer concentration and decreases with further increase of the monomer concentration. The increase in the grafting efficiency might be due to the complexation of rubber with monomers. The decrease in grafting efficiency after 15 phr may be caused by the higher monomer concentration, the rates of the termination of macroradicals increase more quickly than the rate of grafting with rubber macroradicals. On the other hand, the rate of monomer diffusion is bound to be progressively affected in the polymer formed, which of course it grows most rapidly when high concentrations of monomer are used. The water absorption increases with increasing the monomer content and the contact angle of modified natural rubber films decreases correspondingly upon increasing the monomer content, implying that higher hydrophilicity was achieved with increasing monomers. The stability at the low pH increases when increasing the monomer content, which is grafted on the surface of the rubber particles due to the protonation of the amino groups increased.

The grafting efficiency increases with an increase in the degree of initiation because the radicals transfer to either rubber or monomer, producing macroradicals, which is enhanced by increasing the initiator concentrations, thus resulting in an increase in grafting. However, beyond the amount of 1.0 phr, the grafting efficiency decreases, which results from the increasing conversion of free homopolymer. On the

other hand, the probability for the rate of chain transfer for the free polymer radicals to the natural rubber backbone is less than the rate of termination of free polymer radicals, favoring the termination process of copolymers over the chain-transfer process. The water contact angle of the films decreased with increasing the initiator concentration. This can be attributed to the fact that the NR films with a more hydrophobic group were grafted by a more hydrophilic group in the second polymer. The water absorption of the modified NR film decreased initially and then subsequently increased with increasing the initiator concentration. The initial decrease was due to increase in the crosslink density of the rubber while the subsequent increase was due to increase in the hydrophilic content in the copolymer. The latex stability at low pH increases when the initiator content increases.

The higher reaction temperature usually produces the greater conversion because more radicals are generated to consume monomer molecules. With increasing in the reaction temperature, more alkyloxyl radicals are produced. The grafting efficiency increased as the polymerization temperature was increased up to 25°C and decreased with further increased in reaction temperature. The very rapid decomposition of the initiator yields an instantaneously high radical concentration and the radicals then might be acting as radical scavengers, which results in decreasing the radical flux after feed has stopped. Thus the result is a lower initiator efficiency which, however, fails to produce both the corresponding ungrafted homopolymer and graft copolymers. In addition, another possibility to lead the decreases in grafting efficiency decreases with increasing the reaction temperature could be caused by the nature of the grafting monomers. Because the polymers of DMAEA and DMAEMA

used have conformations which are temperature sensitive, which phase transition could occur when the reacting temperature reaches above the lower critical solution temperature, LCST. This reason supports the use of the redox initiator, which can initiate the polymerization at low temperatures. The water absorption and contact angle of the graft-modified NR films were not significantly different when the reaction temperature was increased.

For grafting of poly(HEMA) onto NR latex, the resulting latex coagulated during the polymerization even in the presence of SDS because this monomer can possibly reduce the extent of the hydration layer at the surface of NR particles and react with the indigenous stabilizer of the latex.

The functional groups in the grafted natural rubber were characterized by FT-IR spectroscopy. The appearance of new peaks in the FT-IR spectra of grafted natural rubber was at around 1160 cm^{-1} and 1730 cm^{-1} , due to the ether linkage and carbonyl group of poly(DMAEA) and poly(DMAEMA) grafted on natural rubber backbone. On staining with OsO_4 for the grafted rubber surface viewed by the TEM technique, the dark center particle is the natural rubber seed latex and the outer layer is a hairy layer of poly(DMAEMA) shell. Conversely, when the grafted rubber was stained by PTA, the darker areas are the surface of natural rubber particle and the lighter regions are the irregular outer layer of poly(DMAEMA) shell. Glass transition temperature of grafted natural rubber determined by DSC technique was at about -64°C .

5.2 Suggestions for Further Work

In the area of modification of natural rubber latex, further studies in the following aspects should be carried out.

- 1) More dilute NR latex (lower than 15%DRC) could be used to find out what differences from the simple polymerization behavior to the complex polymerization behavior in aqueous media could be observed. This may shine some light on polymerization mechanisms, especially if attempts were made to elucidate the polymerization mechanism for the monomers in aqueous media.
- 2) Stability of the modified natural rubber latexes in electrolytes or salts at constant and varied pH should be investigated.
- 3) Curing of the modified natural rubber latexes and properties of the cured films should be studied in order to compare with the uncured NR films.