

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The admicellar polymerization of polypyrrole on soft substrate which is, in this study, polymer particles from natural rubber latex was successfully prepared as evident by FTIR and optical microscope. However, admicellar polymerization has limit of low level of polymerization so that thin coating can be formed. The admicellar polymerization was carried out at several concentrations from 10 mmole/l (mM) to 70 mmole/l of pyrrole. This level of pyrrole accounts to approximately not more than 10 wt% PPy (mostly less than 1 wt%) in NR matrix.

To obtain processable and ductile PPy, attempts to increase PPy content in the admicellar system were brought about by using two methods of adding pyrrole. They are one-step and two-step mixing procedures; one-step means the scale-up of admicellar polymerization based on certain concentration of pyrrole (e.g. 20 mM) but with high initial weight of pyrrole adding just before polymerization. The two-step procedure includes first, preparation of admicellar polymerization to obtained PPy admicellar coated NR particles following the polymerization of pyrrole at the desired amount.

From the colloidal stability observation, admicellar and one-step polymerization showed good stability so that film formation could be made. The concentration limit for the stability was 60 mM for one-step polymerization. In contrast, two-step polymerization poorly exhibited colloidal stability even at low PPy content. Increasing pyrrole content led to phase separation with darkish hard solid of PPy and a big piece of NR so that homogeneous film formation was impossible. This was thought to cause by high initiator content at high pyrrole content (although the monomer:initiator ratio was kept constant at 3.4:1, lower than that (1:1) used in one-step polymerization) so that crosslinking in NR phase might be occurred slightly. However, the phase-separated samples could be shred and processed on two-roll mill and compression molding to get rather rough surface. The films were too brittle so rheological and tensile tests could not be applied.

Optical microscope reveals that PPy coating on NR particles (N2 at 5 mM) renders more homogeneous morphology (without dark domains) than the simple

mixing of PPy in NR (polymerization of pyrrole in NR latex without surfactant template). Increasing PPy concentration (from 10mM to 40 mM of N2) violated adsolubilization in the surfactant bilayers such that the dark domains of PPy were shown. Some inclusions of NR in the PPy domains were also found with increasing its numbers with more pyrrole concentration. This makes the admicellar samples become more heterogeneous. Adding salt (N3 samples) helps to gain more homogeneous morphology with the delay in dark PPy domains to form at relatively higher concentration suggesting that more PPy can be adsolubilized and admicellar polymerized on the NR particle surfaces. It is hard to say that the admicellar coating is uniform or not since the magnification is too low to zoom up the surface position.

SEM results for morphological study of two-step polymerization showed globular structure of PPy deposited and dispersed non-uniformly on PPy admicellar coated latex at low PPy content. As PPy content increased, PPy globules were seen clearly. In the presence of salt, the PPy globules became much smaller and were distributed more uniformly and densely. This suggests that the PPy admicellar coating with salt is more uniform (or covering more surface area) than that without salt. This should bring better properties, e.g. conductivity.

Processability of the PPy admicellar coated NR latex was characterized by dynamic rheological test using frequency sweep at 70 °C. Unfortunately, the samples of high PPy content were not able to prepare as homogeneous films. The admicellar products showed higher shear storage and loss moduli whereas their tan delta were slightly lower than pure NR and mixed PPy/NR (N1). Complex viscosities of these samples were higher than pure NR and mixed PPy/NR. This suggests that the admicellar products have better compatibility between two phases than the mixed PPy/NR and can be processed at moderate condition (using moderately higher shear force than NR). Moreover, results of N1 comparing to pure NR indicate that oxidation polymerization by ammonium persulfate has slight effect on NR crosslinking, probably due to low initiator content. However, the storage and loss moduli, $\tan \delta$, and complex viscosity of admicellar products without salt were not significantly different from those with salt. This is perhaps due to low PPy content. Surprisingly, N2 showed increase in these properties with PPy concentration while N3 did not and performed in the opposite way. This maybe

attributes to the breakage of brittle PPy globules under shear. This breakage can be occurred intensely in N3 because it contains more PPy globules.

The properties of the PPy admicellar coated NR latex, one-step and the two-step polymerization were characterized. The significant properties are thermal, electrical, and mechanical properties. NR showed one decomposition temperature while PPy showed two transitions. Thermal stability of N2 and N3 exhibited one decomposition temperature like NR but shifted to occur at higher temperature (clearly seen at high concentration of PPy for peak temperature) and were not much different with the trend that N3 exhibited slightly higher degradation temperature. One-step polymerization with 10 wt% PPy showed one transition like N2-N3 series with about same weight change. This could indicate better homogeneity by admicellar polymerization. Weight residue of N3 was greater than N2 indicating better adsolubilization of PPy. Interestingly, two-step polymerization of N2 for all compositions showed transition like the characteristic degradation of PPy but at lower temperature and higher wt% change except at high PPy content where degradation shift to high temperature and low wt% change. Contrarily, two-step polymerization of 10 wt% PPy from N3 showed one transition like that occurred in one-step polymerization but at relatively lower peak temperature (wider transition range) and weight change.

Since PPy is rigid and brittle material, its ductility should be improved by rubber toughening. Tensile testing provides information for strength and elongation that relates to toughness. Tensile modulus and 50% secant modulus of N2 and N3 were not much different, possibly due to small content of PPy; however they, especially N2-1 and N3-1, were relatively higher than pure NR, N1, Ctrl.1 and Ctrl.2 indicating better compatibility and insufficient effect of crosslinking in NR phase. Rigidity of these samples is clearly attributed to PPy. Importantly, N2 and N3 showed superior improvement in elongation that was greater than 1000% (compared to pure NR that is considered to be the best elastomer) indicating that PPy brittleness was diminished. The N2 and N3 products are superior in ductility or toughness. This was thought to be due to inclusion morphology like most rubber-toughen modifiers. The one-step polymerization at 10 wt% PPy from N2-2 showed inferior tensile strength, modulus but improved elongation.

As expected, surface resistivity of N3 samples were much higher than those of N2 samples. It is noted that N2 samples have higher conductivity with increasing PPy concentration.

The recommendation for the future work described below.

1. Initiator will be changed from $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to FeCl_3 and dopants will be added into the system while polymerization is carried out.
2. The admicelled latex sheet will be grinded into small pieces and extruded through extruder then compressed into a sheet so as to prepare the new composite.
3. Anionic surfactant (SDS) will be changed into nonionic surfactant.
4. Plastic emulsion will be used instead of NR latex particles.
5. Further test for piezoelectric property and ability to detect gas.