

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

As the pristine clay aerogels were relatively fragile and difficult to handle without significantly damaging them, the addition of a polymeric component was prerequisite for attaining the appreciable reinforcement. Herein, the NR/clay aerogel composites were fabricated via the freeze-drying process, followed by the cross-linking reactions to bolster their mechanical strength while preserving the inherent properties of the individual components. Two cross-linking systems i.e. sulfur vulcanization (CV) and solution cross-linking with S_2Cl_2 were conducted to take the advantage of this. It was found that, through the sulfur-based cure system, the silicate layers had a tendency to adsorb part of the vulcanization ingredients (reactive species) onto the surface, causing a reduction in their cross-linking efficiency. Even though the great reinforcing effect was attained at 7 phr loading of Na^+ -MMT (with compressive modulus of 35 kPa), a longer cure time was necessitated for optimizing the materials structural integrity, when compared with the other aerogels reported up to date. This was due to the fact that the ice-templated material would possess an inferior thermal conductivity as compared to that of a dense polymer. For this reason, the solution cross-linking reactions were carried out using sulfur monochloride (S_2Cl_2) as a cross-linking agent. Depending on the experimental conditions, a series of cross-linked NR aerogels were produced, and it was seen that 1% (v/v) of S_2Cl_2 and reaction temperature of $-18^\circ C$ were the optimum condition for producing a very strong and tough rubber composites. The highest rigidity was attained for the 10 wt% NR aerogel with the compressive modulus and bulk density of 4500 kPa and 0.2 g/cm^3 , respectively. This demonstrated the much higher cross-linking efficiency of S_2Cl_2 against the isoprene units of rubber matrix, particularly at very low reaction temperature, as compared to that of the conventional sulfur-based cure system. Further, the swelling capacity and thermal motion of the rubber matrix were restricted on a basis of the formation of effective cross-links between different rubber chains. In brief, the combination of low density and appreciable mechanical and

thermal properties has encouraged the utilization of ice-templated materials for a wide variety of advanced applications e.g. thermal/acoustic insulation, low-pressure-drop catalysis, packaging and structural materials, high-volume absorption of liquids, controlled delivery, devices to chemical sensors, etc. where low density is of great importance.

As the neat rubber displayed the conductivity of 10^{-15} S/cm, being in the range of insulating materials, electrolytic admicellar polymerization was introduced for creating an ultrathin conductive polymer film on NR substrates. The results showed that the electrical conductivity was increased by more than eight orders of magnitude (from 10^{-15} to 10^{-6} Scm⁻¹) with the addition of conducting PPy. At the same time, the clay particles were introduced into the reaction mixture to determine whether the electrical, thermal, and mechanical behaviors could be simultaneously improved. It was seen that the mechanical integrity in terms of hardness, Young's modulus, and storage modulus at a given temperature was increased linearly with the amount of silicate layers, as expected for the typical composites. However, the electrical conductivity was strongly influenced by the mass fraction of silicate layer, its dispersion state, and the physical properties of the composites i.e. compactness and molecular orientation. For instance, as the clay particles were dispersed in the form of a highly exfoliated structure at lower PPy concentration and were essentially covered by a conductive adlayer, it would create more effective networks for electron conduction, leading to a much higher conductivity as compared to those of composites, comprising the intercalated structure with the conducting PPy being confined in the galleries of clay. Further, the addition of Na⁺-MMT imparted both the thermo-oxidative and thermo-shielding effects to the composites over the entire decomposition period. It is thus anticipated that the corresponding composites will be excellent candidates for applications ranging from anti-static devices to electromagnetic shielding, and tissue engineering.

9.2 Recommendations

Future work will be focused on the possibility for using the cross-linked NR aerogels as suitable sorbent materials in separation processes, where the separated

compounds or pollutants e.g. crude oil or petroleum products can be easily removed and recovered by compression the samples under piston. This is motivated by their unique features including interconnected pore structure, buoyancy, high rate of liquid uptake, hydrophobic nature of rubber matrix, durability in aqueous media (at least 3 days), and good retention over time. Besides, as these aerogel composites display the thermal insulation properties similar to those of polymer foam products e.g. Styrofoam or rigid polyurethane foams, which is about $0.03 \text{ W}\cdot\text{mK}^{-1}$, it is therefore very challenging to produce the more environmentally responsible foam-like materials, being a valid alternative to the conventional insulating foams. This is originally inspired by the increasing public preference for environmental protection, progressive dwindling of fossil resources, and limited landfill sites. Of particular interests are casein protein and poly[(*R*)-3-hydroxybutyrate]. The former is a naturally-occurring protein found in dairy products and is known to readily biodegrade when exposed to the environmental conditions (Gawryla, 2009a), while the latter is produced by a variety of bacteria from renewable resources like corn sugar and oil and biodegrade to carbon dioxide and water (Bordes *et al.*, 2009; Xie *et al.*, 2009). Therefore, utilization of these bio-based polymers would seem to be reasonable for replacing the currently widespread non-degradable petroleum-based polymeric foams in packaging or biomedical applications, where the environmentally friendliness is of importance. Further, if the electrical conductivity is of particular interest, the selection of carbon nanotubes (CNTs) as a second inorganic component might be an interesting task to make the composites conductive. This is because the CNTs are considered to be an ideal inclusion for the typical polymer composites due to their exceptional electrical, thermal and mechanical behaviors even at a very low nanotube loading (Gawryla *et al.*, 2009c; Liu *et al.*, 2009). However, it is important that the CNTs are homogeneously dispersed throughout the matrix without sacrificing their intrinsic aspect ratio or even disrupting the surface conjugated π network.

Future attempts may be made to find the optimum conditions for producing the flexible/stretchable smart materials with a better control of thickness, microstructure, and intrinsic properties so that they can be used as electrochemical or biosensors, mechanical actuators, or battery electrodes. The promising routes are (i) by replacing the rubber particles with more flexible and elastic substrates e.g.

textiles, fabrics, or other latex particles (ii) by properly selecting the reaction temperature, doping agents e.g. anionic or non-ionic surfactants, and doping level to improve the structural integrity, surface smoothness, and electrical conductivity of the resulting materials, (iii) by considering the CNTs as the alternate inorganic compartment instead of Na^+ -MMT clay so that the appreciable mechanical, thermal, and electrical behaviors can be realized. Further, as the copper electrode is inevitably corroded during the electro-polymerization, it is of fundamental importance to remove and/or separate the corresponding ions out of the reaction mixture to achieve the actual electrical and mechanical properties of the polymerized materials. Also, the time for refreshing the anode and cathode electrodes might be considered as another variable that influences the corrosion of electrode. Even though it was previously verified that no corrosion was detected at 2 hr period of time, we recommend that it should be reduced down to 1 hr instead to minimize the release of copper ions. As the pH of aqueous solutions must be kept constant i.e. less than 3.3, it is possible that some copper ions were evolved already under such acidic condition. However, their concentration is relatively low as compared to the others viz. rubber, pyrrole, and Na^+ -MMT, and thus the influence of copper ions on the materials electrical, mechanical, and thermal properties can be negligible.