

CHAPTER I

INTRODUCTION

Elastomer is a term used to describe the vulcanized polymeric materials that have the following characteristics: elasticity, flexibility, and toughness. Each elastomer displays its own unique elastic properties and often requires a large number of additives to again the appropriate performances for the different practical applications. Rubber compounding is considered as one of the most important topics since the early days of the rubber industry. Its ingredient can be categorized as cross-linking agents, processing aids, fillers, antioxidants, plasticizers, and other specialty additives (Mai and Yu, 2006). Fillers in the form of particulates have been widely introduced in rubber compounding not only to reduce the cost but also to improve the rubber processing, to enhance the mechanical properties, to change the electrical conductivity, and to increase the barrier properties. Those behaviors are strongly dependent on the volume fraction, particle shape and size, structure of particle aggregates, surface activity, and extent of interactions with the rubber matrix, which play a key role in determining the overall reinforcement (Valentín *et al.*, 2010).

Carbon black is the most extensively used reinforcing filler in rubber technology because of the fractal nature of carbon black aggregates (in the range of 100 nm to micron scale) and high surface area with a number of functional groups (Mai and Yu, 2006; Valentín *et al.*, 2010). As the carbon black is derived from the petroleum resource, it has been replaced by cheaper and more environmental friendly inorganic fillers such as synthetic silicon dioxide, so-called 'silica'. However, their uses as reinforcing filler instead of carbon black are limited by a tendency to form large agglomerates with a much reduced surface affinity towards the rubber components and to cause the adsorption of the polar materials such as the curatives on the surface, which leads to a reduction in the cross-link density and delays the scorch time of the rubber compounds. For these reasons, the use of bi-functional organic molecules for surface modifying the inorganic fillers is crucial in order to improve their dispersion state and the surface affinity towards the rubber matrices through the formation of covalent linkages. It is well understood that a minimum of 20 wt% of the fillers is usually required to attain the significant properties enhancement (Mai and

Yu, 2006); however, this high loading level may lead to the following drawbacks: an increase in melt viscosity, a more difficult for rubber compounds to be processed, and cause more weight to the end products. Accordingly, elastomer nanocomposites based on layered silicates are well-reviewed class of materials of great interest, as they offer the possibility for achieving the properties that cannot be realized with their micro-composite counterparts. By using a very low concentration of clay particles (≤ 5 wt%), this allows us to achieve the exceptional improvements in terms of mechanical strength, thermal stability, gas barrier properties, and flammability resistance as compared to the neat or conventional composites, which in turn display the similar behavior only at much higher volume fraction. The above qualitative differences are explained by the nano-scope dimensions and high aspect ratio (length to width ratio) of the clay layers. Thus, the nanocomposites stand out as good candidates for a variety of applications such as the packaging materials, antistatic surface coatings, corrosion protections, electrochemical capacitors, and so on (Teh *et al.*, 2004; Garai *et al.*, 2006; Sun *et al.*, 2008; Soundararajah *et al.*, 2009).

In this regard, clay and clay minerals such as montmorillonite, hectorite, saponite, etc., have been widely used for the preparation of elastomer nanocomposites by means of their ability to undergo the ion exchange reactions with organic or inorganic cations to render them more organophilic and to separate them into individual layers with very high aspect ratio. An intercalated structure is formed upon the insertion of the polymer chains into the silicate galleries, while an exfoliated structure is achieved when the clay layers are dispersed individually throughout the matrix. It is the latter that is often cited as the desired goal for the clay-containing composites. Interestingly, clay can be converted into an aerogel structure in one step with water through a freeze-drying process. This leads to a structural change from the granular appearance of clay particle to a lamellar structure of clay aerogel, being a replica of the ice crystal morphology. Since the clay aerogel is relatively fragile, it has to be calcined or reinforced with the polymeric components in order to produce resilient and perfect foam-like materials (Gawryla, 2009a). The combination of low density and appreciable mechanical and thermal properties signifies that these ice-templated materials are promising for a wide variety of advanced applications ranging from thermal/acoustic insulation to packaging and structural materials. In the present

study, natural rubber (NR) was selected as a source of reinforcement for the neat clay aerogel, and two vulcanization techniques; that is, conventional vulcanization (CV) system and solution cross-linking process, were then applied to increase the structural integrity of the foam-like materials. This is originally inspired by the possibility for generating the highly stiff/tough NR based foam-like materials without significantly harming their microstructure and bulk density. Depending on the experimental conditions, a series of cross-linked NR/clay aerogel composites were fabricated and then interpreted in terms of the swelling capacities, mechanical behaviors, microstructure, and thermal properties, taking the rubber and composites behaviors as references.

It was well demonstrated that NR is an electrical insulating material with the electrical conductivity of $\sim 10^{-15} \text{ Scm}^{-1}$. At the same time, electrically conducting polymers (CPs) have attracted a considerable attention in both academia and industry because of their conjugated electronic structure and unique electrical properties. However, the pristine CPs possesses some drawbacks that further limit its potential applications; for instance, the typical polypyrrole (PPy) has poor processability, and is brittle, insoluble, and infusible. It is therefore very challenging to use the moldable NR latex as a substrate for accommodating the conducting PPy film through admicellar polymerization in order to overcome the poor processability of PPy and, at the same time, to efficiently improve the electrical conductivity of NR substrates. Besides, previous studies have shown that the incorporation of clay particles, being an insulating substrate, offers the potential for creating a high degree of polymer ordering through the constrained environment (2-dimensional clay galleries) and thus facilitating the electron hopping along the main chains (Jia *et al.*, 2002; Boukerma *et al.*, 2006; Mravčáková *et al.*, 2006). To take the advantage of this, the present work aims to systematically investigate the influence of weight fractions of PPy and clay on the morphology and microstructure formation, electrical conductivity, and thermal and mechanical behaviors of the elastomer nanocomposites, synthesized through an electrolytic admicellar polymerization.