

1. Introduction

1.1. Composites

A composite material is defined as a macroscopic combination of two or more distinct materials having a recognizable interface between them. However, because composites are commonly used for their structural properties, the definition can be restricted to include only those materials that contain reinforcement, such as fibers or particles, supported by a binder or matrix material.

Rubber compounding is essentially the science of selecting and combining ingredients to produce a useful polymer according to its end use. In today's complex world of rubber goods formulation, fillers have achieved enormous importance as a compounding ingredient. Fillers are, in general, solid substances that are embedded in polymers to improve performance or reduce costs. It can be distinguished between non-reinforcing (extender) fillers, which are mainly used to reduce costs and reinforcing fillers that improve or generate new properties in the composites. Crucial parameters in determining the effect of fillers on the properties of composites are the filler size, shape, aspect ratio and the filler-matrix interactions [1].

Generally, powder minerals are used as non-reinforcing fillers such as china clay, calcium carbonate (whiting), barites (barium sulphate), mica and titanium dioxide (TiO₂).

Reinforcement is especially important for the application of elastomeric materials because the mechanical strength of unfilled elastomers is generally poor. Generally the inclusion of reinforcing fillers into polymers leads to an increase in modulus, improvement in abrasion, tear, cutting resistance and hardness. Isometric fillers like carbon black and high structure silica are commonly used for reinforcement of elastomers. Fibers have been used as fillers and are found to improve the properties of the composites in one dimension.

Thus, rubber composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase. In order to provide reinforcement, there generally must be substantial volume fraction (~10% or more) of the reinforcing agent. In composites, the combining of two or more existing materials is done mainly by physical means. A true composite might be considered to have a matrix

surrounding the reinforcing material in which two phases act together to produce characteristics not attainable by either constituent acting alone.

Almost all high-strength or high-stiffness materials fail because of the propagation of flaws. A fiber of such a material is inherently stronger than the bulk form because the size of the flaw is limited by the small diameter of the fiber. In addition, if equal volumes of fibrous and bulk material are compared, it is found that even if a flaw does produce failure in a fiber, it will not propagate to fail the entire assemblage of fibers as would happen in the bulk material. Furthermore, preferred orientation may be used to increase the lengthwise modulus, and perhaps strength, well above isotropic values.

Since this material is also lightweight, there is a tremendous potential advantage in strength/weight and/or stiffness/weight ratios over conventional materials. The desirable fiber properties can be translated into practical application when the fibers are embedded in a matrix that binds them together, transfers load to and between the fibers and protects them from environments and handling.

High-performance rigid composites made from glass, graphite, Kevlar[®], boron, or silicone carbide fibers in polymeric matrices have been studied extensively because of their application in aerospace and space vehicle technology [2-4]. The reinforcement of rubbers using particulate fillers such as carbon black or precipitated silica has also been studied at length [5, 6]. However, studies on composites based on fiber and rubber matrices need to be strengthened. The fiber-reinforced rubber composites are characterized by the extremely low stiffness of the rubber matrix compared to that of the reinforcing cords. Both continuous and discontinuous fibers are used to reinforce the rubber matrix; the most significant example for the former is the use of fiber-reinforced rubber in pneumatic tires. The discontinuous fiber-reinforced rubber composites are usually referred as short fiber–rubber composites.

1.1.1. Types of conventional reinforcing fillers for polymers

There are several ways to classify the various types of filler particle, such as based on their origin (natural or synthetic), chemical composition (organic or inorganic), size (micrometers or nanometers) or based on the shape (spherical, platelet or fiber) or aspect ratio. The aspect ratio is the ratio between the longest and

the shortest dimension of the particle, and is an important factor for the composite properties. According to aspect ratio, fillers can be classified as:

1.1.2. Low aspect ratio fillers (aspect ratio ~1)

Particulate fillers are mainly in this group, e.g., carbon black, silica, ground calcium carbonate, precipitated calcium carbonate, traditional clay fillers (mostly limited to kaolinite, which is used after a calcinations process in between 500-1000 °C that changes the crystal structure of the clay or makes it amorphous) [7, 8].

1.1.3. High aspect ratio fillers (aspect ratio ≥ 100) or fibrous fillers

Fibers such as nylon, polyester, glass fibers, carbon fibers, aramid etc. are used in large amount as fillers. Because of the high aspect ratio and high modulus, they can provide a large increase in modulus and strength, without affecting the toughness too much. Carbon fiber has a much higher modulus than glass fiber while having a much lower density. It is therefore an excellent reinforcement for reaching very high modulus at lower weight. But the higher price of carbon fiber and aramid somewhat limits the use [9]. When the function of the filler is taken into account, it becomes clear that there is a difference between particles with low aspect ratios (approximately spherical particles) and particles with high aspect ratios (platelets and fibers). Low aspect ratio fillers are not very effective in increasing the modulus of a compound, so they are often cheap fillers used in large quantities, while large aspect ratio fillers are effective in smaller quantities and can provide large increases in the modulus at higher filler loadings. *Nylon and polyester fibers are the most abundantly used organic fibers in tire industries. In this thesis, we are focusing on these two fibers.*

1.1.4. Platelet shaped fillers

Talc is a common platelet shaped filler. Talc seems to be a very soft material because it consists of layers that can be very easily cleaved. However, the magnesium-silicate structure within the layers is very strong and stiff. The milling process used for talc results in decreasing the size of the particles but also in delamination into moderately high aspect ratio platelets. The aspect ratio combined with the high modulus in the platelet direction is the reason that talc can give a significant increase in modulus to the compound, combined with a reduction in shrinkage.

Mica has a similar very stiff platelet-shaped structure as talc, and therefore it is also used to increase the modulus or reduce the shrinkage of the compound. Mica can be coated with organo-silane to obtain a better adhesion between particle and polymer. The aspect ratio and therefore the efficiency of reinforcement, depends on the milling process and the compounding step [7, 8].

1.2. Nanocomposites

Nanotechnology is recognized as one of the most promising arena of 21st century. Polymer nanocomposites are a relatively new type of composite material, of which the possibilities are numerous but not yet fully explored.

The term nanocomposite is in the broadest sense referring to every type of material with fillers in the nanometer range at least in one dimension [10]. More specifically, polymer nanocomposites are polymers that are reinforced with highly anisotropic rigid inorganic particles, which have at least one dimension in the nanometer range. The dimensionality of a nanocomposite is one of the most basic classifications that can be assigned to it. A nanoparticle-reinforced system serves as an example of a zero-dimensional nanocomposite. Nanofibers or nanowhiskers in a matrix constitute a one-dimensional nanocomposite, while an interpenetrating network is an example of a three-dimensional nanocomposite. Finally, the two-dimensional case is indicated as being based on individual layers of nanoscopic thickness embedded in a matrix. It is this case on which we will focus, as this is the most basic description of a polymer / fibrous nanoclay nanocomposite.

1.2.1. Nanocomposites compared to conventional filled polymers

Nanocomposites can show excellent properties at very low filler loadings (<10 wt%). Nanofillers are necessarily nanoscopic and have a high specific surface area. The specific surface area gives the reason why the nature of reinforcement is different in nanocomposites. In typical micro- and macro-composites, the properties are dictated by the bulk properties of both the matrix and the filler. This relationship between the properties of the composite and the properties of the filler is what leads to the stiffening and lower elongation. In the case of nanocomposites, the properties of the material are instead tied to the interface. Terms like “bound polymer”, “bound rubber”, and “interphase” have been used to describe the polymer at or near the interface, but the basic idea is a simple one. Interfacial structure is known to be

different from bulk structure, and in polymers filled with fillers with extremely high specific surface areas (that is, hundreds of meters squared per gram), most of the polymer present is near an interface, even with only a small weight fraction of filler. If the interaction at the interface is a strong one, or if the structure of the interfacial polymer is very different from the bulk, one can expect to see markedly different properties in the material as a whole. These changes have a fundamentally different origin than those found in micro- and macro-composites, where the volume of the interphase is only a small fraction of the overall volume of the material, and therefore nanocomposites are often referred to be “different” from other conventional composites.

The main difference between conventional clay fillers for polymers is the particle size and the aspect ratio of the fillers. In the case of conventional fillers, the dispersed particles are relatively large aggregates of primary particles. Although these aggregates can be cleaved into smaller particles, there is a limit to this break-up by mechanical methods. The mechanical break-up also limits the aspect ratio of the sheets of conventional clay fillers, since the particles do not only cleave between the layers, but also break up in the long direction. But the primary particles of layered silicates such as mica and many types of nanoclays such as smectite clays are crystalline layers of approximately one nanometer thickness. The characteristic property of layered silicate nanocomposites is the fact that these 1 nm thin silicate sheets (the primary particles) are individually dispersed in the polymer matrix [11]. To achieve this fine dispersion, mechanical forces alone are not enough; there should be a thermodynamic driving force as well to separate the layers into the primary silicate sheets [12].

1.2.2. Nanofillers

The fillers used in polymer nanocomposites are usually inorganic fillers, although carbon nanotubes and carbon nanofibers (extensively used in rubbers) are also there. Nanofillers can have different shapes:

1. **Spherical** (nanosilica, polyhedral oligomeric silsesquioxanes, POSS)
2. **Rod / fiber** (synthetic whiskers, carbon nanotubes, boehmite, sepiolite, attapulgite)

3. **Sheet / platelet** (layered silicates such as smectite group clays, synthetic mica etc.).

In this thesis, attention has been paid to fibrous nanofiller, 'attapulgite'.

1.2.3. Attapulgite (AT)

Attapulgite belongs to the family of fibrous hydrous magnesium silicates, palygorskite. It is an inorganic fibrous material. The structure of attapulgite was first proposed by Bradley early in 1940 [13]. The chemical structure of attapulgite is shown in Figure 1.1. Its theoretical half-unit cell formula is $Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ and is a natural fibrous silicate material. The smallest structural unit of attapulgite is fibrillar single crystal with a length of 500-2000 nm and 10-25 nm in diameter. It is containing ribbons of a 2:1 phyllosilicate structure different from other layered silicates such as montmorillonite. Each ribbon is connected to the next by the inversion of SiO_4 tetrahedra along a set of Si-O-Si bonds and extends parallel to the X-axis to form rectangular channels. Unlike the layer-layer interaction existing in layered silicates, the interaction between AT single crystal is extremely small due to a similar line-line contact, which could result in a weak interaction and facilitate the separation of AT micro-agglomerates into single crystals upon large shear, physical and chemical modification. In addition, it has a large surface area and strong absorptive capacity that is greater than any other natural mineral [13, 14].

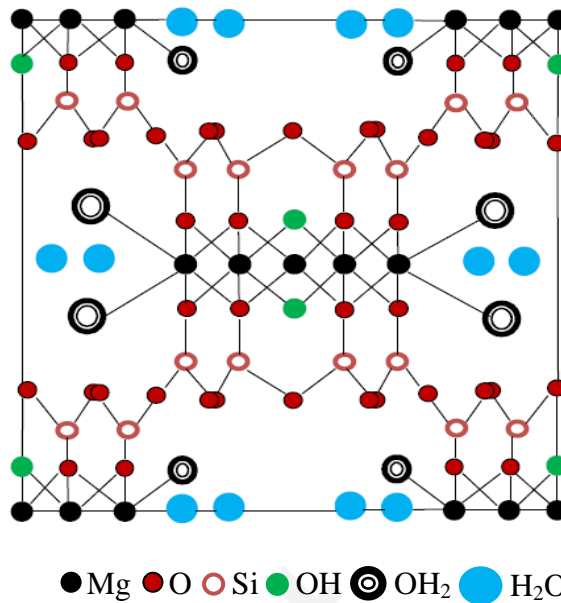


Figure 1.1. Chemical structure of attapulgite

1.3. Hybrid composites

Hybrid composites are those composites which have a combination of two or more reinforcing fillers.

The most common hybrid composites are carbon-aramid reinforced epoxy (which combines strength and impact resistance) and glass-carbon reinforced epoxy (which gives a strong material at a reasonable price). Hybrid composites are usually used when a combination of properties of different types of fillers to be achieved, or when longitudinal as well as lateral mechanical performances are required.

In this thesis, hybrid composites are developed with reference to tire applications in terms of better durability and rolling resistance.

1.4. Durability

Some of the factors involved in durability of a tire are ageing, temperature, fatigue etc. Fatigue and fracture of rubber composites can provide information for tire durability assessment in different ways. With some limitations due to the complexity and multiple factors involved with tire durability performances, the following investigations can often provide some insight: 1) fatigue properties of tire composites combined with tire finite element analysis for a tire life estimation, 2) fatigue of belt and ply composites to assess their relative performance, 3) to understand and establish the failure mechanisms of laboratory composites and to extend the same mechanism

to correlate with failure mechanisms in tires and 4) crack growth properties of rubber composites combined with detailed fracture mechanics analysis of the cord-rubber layers in tires.

1.5. Rolling resistance

Rolling resistance, sometimes called rolling friction or rolling drag, is the resistance that occurs when a round object such as a ball or tire rolls on a flat surface. It is caused mainly by the deformation of the object, the deformation of the surface, or both. Additional contributing factors include wheel radius, forward speed, surface adhesion, and relative micro-sliding between the surfaces of contact. It depends very much on the material of the wheel or tire and the sort of ground. In general, tire rolling resistance is responsible for 10% passenger car fuel consumption and 20% in case of fully loaded heavy trucks. A characteristic of a deformable hysteric material is that the energy of deformation is greater than the energy of recovery. The rubber compound in a tire exhibits hysteresis. As the tire rotates under the weight of the vehicle, it experiences repeated cycles of deformation and recovery, and it dissipates the hysteresis energy loss as heat. Hysteresis is the main cause of energy loss associated with rolling resistance and is attributed to the viscoelastic characteristics of the rubber. The force necessary to overcome hysteric losses in a rolling tire is known as rolling resistance. Rolling resistance directly affects the fuel economy of a vehicle. Scarcity of crude through out the world and increasing crude prices are a matter of concern for the customers as well as vehicle manufacturers. Again to make the matter worse, another important major issue is also connected to fuel consumption; i.e, environment protection. Fuel consumption is directly related to the green haouse gas emission that creates a threat to the enviornment. All these reasons demand for reduction in fuel onsumption and so reduction of rolling resistance of tires. Hence reduction of rolling resistance has become a key issue for OEMs(Original equiment Manufacturers as well as tire industries. Many legislations pertaining to rolling resistance are either implemnted or about to be implemented through out the world. This parameter became important to USA vehicle manufacturers with implementation of CAFE (Corporate average fuel economy) standards for new cars. From 2012 onwards all tires in Europe is going to have a labeling for rolling resistance. The aim of labelling is to directly grade tires in terms of rolling resistance and make the customer aware of the same. Rolling resistance is

usually expressed as a coefficient: resistance force per 1000 units of load. Rolling resistance is significantly influenced by inflation pressure. Tire rolling resistance can consume up to 20% of the energy required to drive at highway speeds.

Several factors affect the magnitude of rolling resistance a tire generates:

- **Material:** Different fillers and polymers are used in a tire and different compounds used have different hysteric characteristics. The replacement of some carbon black with the silica–silane system significantly reduces rolling resistance of a compound. So far silica-silane technology is the most important inventions concerned to material research for decreasing rolling loss due to a tire.
- **Wheel radius, forward speed, surface adhesion, and relative micro-sliding.** In fact rolling resistance increases drastically at higher speeds.
- **Design of a tire:** Rolling resistance in tires is related to the height of side walls and the contact area of the tire. Higher the height of the sidewall more will be the flexing and thus higher will be rolling resistance.
- **In tires, tread thickness has much to do with rolling resistance.** The weight of a tread is the maximum among all the rubber components in a tire. Thicker the tread, higher will be hysteresis and hence higher will be the rolling resistance of a tire.
- **Extent of inflation:** Lower pressure in tires results in more flexing of sidewalls and thus increases rolling resistance.
- **Heavy load:** Higher the load than the rated load, higher will be the deflection of the sidewall and more will be rolling resistance of a tire

In the last two decades there is a significant reduction in rolling resistance of tires. Besides implementation of low hysteretic compounds for rolling resistance reduction, it is also partly due to the substantial efforts made by tire researchers to understand the general principles governing the loss of energy in tires using new and modern tools like finite element analysis (FEA).

1.6. Literature search

1.6.1. Short fiber–rubber composites

Fibers find application essentially in all conventional rubber compounds. The functions of the rubber matrix are to support and protect the fibers, the principal load-carrying agent, and to provide a means of distributing the load among and transmitting it between the fibers without itself being fractured. The load transfer mechanism in short and long fibers is different. When a short fiber breaks, the load from one side of the broken fiber is first transferred to the matrix and subsequently to the other side of the broken fiber and to adjacent fibers. In short fiber–rubber composites, the shearing stress in the matrix contributes to load transfer. Typically, the matrix has a considerably lower density, stiffness (modulus), and strength than those of the reinforcing fiber material, but the combination of the two main constituents (matrix and fiber) produces high strength and stiffness, while still possessing a relatively low density. Different short-fiber composites are discussed below based on various rubber matrices.

In one of the first reports on fiber reinforcement of rubber, natural rubber (NR) was used by Collier [15] as the rubber matrix, which was reinforced using short cotton fibers. Some of the most commonly used rubber matrices for fiber reinforcement are NR, ethylene–propylene–diene monomer (EPDM) rubber, styrene–butadiene rubber (SBR), polychloroprene rubber (CR), and nitrile rubber (NBR) [16–19]. These rubbers were reinforced using short and long natural as well as synthetic fibers including jute, silk, cellulose, rayon, bamboo, sisal, glass fiber, carbon fiber, melamine, polyethylene terephthalate (PET) and nylon [20–32].

Rubber–rubber and rubber–plastics blends are also used as matrices for fiber reinforcement. Boustany and coworkers [33, 34] used NR–SBR blend as the matrix in the short fiber reinforcement using cellulose fiber. Ratnam et al. [35] prepared oil palm empty fruit bunch (OPEFB) fiber reinforced epoxidized NR (ENR)/ polyvinyl chloride (PVC) blend using electron beam irradiation. Arroyo and Bell [36] studied the effect of short aramid fibers on the mechanical behavior of isotactic polypropylene (PP) and EPDM rubber and their blends. Sreeja and Kutty [37] prepared NR—whole tire reclaim—short nylon fiber composites and studied the effect of urethane-based bonding agent on the cure characteristics and mechanical properties.

Sau et al. prepared conductive composites with NBR, EPDM and 50:50 NBR:EPDM blend and carbon fiber [38]. Physico mechanical and fracture properties of glass fiber reinforced nylon 6 and maleated EPDM blends were studied by Laura et al. [39, 40]. Short natural-fiber (cellulose) reinforced polyethylene and natural rubber composites were developed by Abdelmouleh et al. [41]. Chandran and Narayanankutty prepared an elastomeric conducting composite based on polyaniline coated nylon fiber and chloroprene rubber [42].

Some of the specialty elastomers which have been used as matrices for short fiber reinforcement are silicone rubber, fluoroelastomers, ethylene vinyl acetate (EVA) rubber, and polyurethane elastomer.

Zebarjad et al. [43] observed that the modification of PP with a combination of ethylene-propylene rubber and glass fiber could be used for improving the mechanical properties of the plastics. This is because, the reduction in the stiffness and strength due to the presence of rubber particles are compensated by the addition of short glass fibers.

Short fiber reinforcement of thermoplastic elastomers (TPEs) has recently opened up a new era in the field of polymer technology. Vajrasthira et al. [44] studied the fiber–matrix interactions in short aramid fiber reinforced thermoplastic polyurethane (TPU) composites. Campbell and Goettler [45] reported the reinforcement of TPE matrix by Santoweb fibers, whereas Akhtar et al. [46] reported the reinforcement of a TPE matrix by short silk fiber. The reinforcement of thermoplastic co-polyester and TPU by short aramid fiber was reported by Watson and Frances [47]. An elastomeric polyurethane- waste silk fiber composite was developed by Sahoo et al. [48]. Preparation and characterization of novel elastomeric polyurethane-carbon fiber composites are reported by Borda et al. [49].

Roy and coworkers [50-52] studied the rheological, hysteresis, mechanical, and dynamic mechanical behavior of short carbon fiber-filled styrene–isoprene–styrene (SIS) block copolymers and TPEs derived from NR and highdensity polyethylene (HDPE) blends.

Warrick et al. [53] reviewed the reinforcement of silicone elastomers with various types of discontinuous fibers, some of which were generated in situ by graft

polymerization. Polyester, cellulose, Kevlar[®] and carbon fibers were also used to reinforce silicone rubber [54, 55].

Tjong et al. [56] prepared and evaluated short glass fiber/ styrene–ethylene–butylene–styrene (SEBS)/PP hybrid composites. Rubber diaphragms, made up of fluorosilicone rubbers, can be reinforced using aramid fiber in order to impart better mechanical properties to the composite, though surface modification of the fiber is needed to improve the adhesion between fluorosilicone rubber and the fiber [57]. Bhattacharya et al. [58] studied the crack growth resistance of fluoroelastomer vulcanizates filled with Kevlar[®] fiber.

Malunka et al. [59] compounded ethylene–vinyl acetate (EVA) copolymer with short sisal fibers. Das et al. [60] prepared carbon fiber-filled conductive composites based on EVA and studied the electromagnetic interference shielding effectiveness of the composites.

Isham [61] and Leis [62] described how glass fiber reinforcement could broaden the performance spectrum in reaction–injection–molding (RIM) polyurethane rubbers as well as other elastomeric systems applied to automotive fascia. Marzocchi [63] developed glass fiber-reinforced polyurethane rubber. Short fiber reinforcement of polyurethane rubber was reported by Bledzki et al. [64] and Pan and Watt [65]. Suhara et al. [66] reported the thermal decomposition of polyurethane rubber reinforced with short polyester fiber.

Shonaike and Matsuo investigated the effects of fabrication conditions on mechanical properties of glass fiber reinforced thermoplastic elastomer composites [67]. Kutty and Nando studied the reinforcement of TPU using Kevlar[®] fibers [68]. López-Manchado and Arroyo [69, 70] prepared ternary composites based on isotactic PP-ethylene–octene copolymer TPE and poly(ethyleneterephthalate) (PET) textile fibers. The effect of matrix composition and fiber content on the final properties of the composite was investigated. They observed that PET fibers act as an effective reinforcing agent, giving rise to a sensible improvement in the tensile and flexural behavior, mainly in matrices with high copolymer percentages. They also observed that the analyzed mechanical properties depend more on the matrix composition than on the fiber percentage. Amornsakchai et al. [71] reinforced SEBS-TPE using aramid fiber. Increase in fiber loading caused a linear increase in the modulus of the

composites whereas the tensile strength was found to be decreasing with fiber loading. Hydrolyzing the fiber using NaOH and use of a compatibilizer, maleic anhydride-grafted SEBS (MA-g-SEBS) found improving the tensile strength of the composites. Thermoplastic elastomeric matrices like styrene-butadiene-styrene (SBS), SEBS, and Hytrel[®] were also reinforced using various short fibers including carbon, glass, and polyester [72-75].

In order to improve the flexibility of short glass fiber-reinforced epoxy composites, Kaynak et al. [76] modified the epoxy resin matrix with hydroxyl-terminated polybutadiene (HTPB) liquid rubber. A silane coupling agent was also used to improve the interfacial adhesion between glass fibers and epoxy matrix. However, Humpidge et al. [77] reported some unique processing problems for the resulting pasty mixtures when short textile fibers were incorporated in a liquid rubber medium.

Relation between work of fracture and fracture toughness of short-fiber reinforced polymers was theoretically studied by Lauke and Pompe [78]. Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites were investigated by Geethamma et al. [79]. Gusev and Rozman numerically studied the transverse elastic behavior of a unidirectional composite comprising non-overlapping silica fibers dispersed in a rubber matrix [80]. Effect of milling condition on mechanical and compression behavior of short-fiber reinforced rubber composites was studied by Moghe [81].

Fatigue of cord-rubber composites was investigated by Lee and coworkers [82, 83]. Hysteretic energy loss in cord/rubber composites under 2-D cyclic loading was studied by Gurvich et al. [84]. Mechanics of short-fiber reinforced composites was reviewed by Abrate [85].

Elastomer-based fibrous composites were characterized by a significantly nonlinear but usable deformation range under external loads using a micromechanical modeling approach to the entire stress-strain response of the composites based on knowledge of constituent fiber and matrix properties only [86]. Micromechanical behavior of short-fiber polymer composites was studied by Mehan and Schadler using Micro-Raman Spectroscopy [87].

1.6.2. Fibrous clay (Attapulgite)- nanocomposites

Though there are lot of literature based on layered-silicate nanocomposites [88-92], fibrillar nanoclay based rubber composites are less explored [93]. There are some reports of rubber–nanocomposites based on sepiolite. Reports on sepiolite composites based on PP [94], NR [95, 96], SBR [97], HNBR [98] epoxy [99] nylon-6 [100] are published. Very few literature is available for attapulgite based nanocomposites. AT has not received much attention as a filler in general purpose rubbers so far. Some studies have been reported in the field of thermoplastics and thermoset, which are discussed below.

Yang and Nelson successfully prepared polystyrene/attapulgite nanocomposites from micron size attapulgite clay [101]. Poly(acrylonitrile-co-methylacrylate)/AT nanocomposites have been prepared by mechanical blending by Yin et al [102]. The hydrogen bonding behavior between the copolymer and unmodified AT were investigated by Fourier Transform infra red spectroscopy. Synthesis of linear poly(ϵ -caprolactone)-attapulgite nanocomposites with well-defined structures was done by Chen et al. via a combination of controlled ring-opening polymerization and click chemistry [103]. Isothermal crystallization kinetics and melting behavior of polyethylene terephthalate (PET)-attapulgite nanocomposites was studied by Zheng et al. using step-scan DSC. The main effect of AT nanoparticles on the crystallinity of PET was to improve the perfection of PET crystals and weaken its recrystallization behavior [104, 105]. Yao et al. also prepared PET–AT nanocomposites through in situ polymerization of terephthalic acid, ethylene glycol, and AT, which was not premodified [106]. PET–AT nanocomposites were reported by Yuan et al. [107]. Nanocomposites based on biodegradable poly(ϵ -caprolactone)–AT were prepared by solution blending and viscoelastic properties were studied by Liu and coworkers [108, 109]. Drummy et al. filed a patent application for nanocomposites of repeat sequence protein polymers and phyllosilicates which demonstrated improved material properties, for example, improved elasticity, and are useful as suture, tissue scaffolding, and biodegradable composite materials [110]. Waterborne polyurethane-AT nanocomposites were reported by Pan and Chen [111]. Polyamide-6/attapulgite nanocomposites were prepared by different researchers [112-114]. Isothermal crystallization kinetics of poly(butylene terephthalate)-attapulgite nanocomposites was studied by Chen et al. [115].

Attapulgite nanocomposites were prepared with poly(vinyl alcohol) [116, 117], polypropylene [118-123], polyurethane [124, 125], polyacrylamide [126, 127], poly(methyl methacrylate) [128], polycarbonate [129], epoxy [130] by various researchers.

1.7. Scope and objectives

Tire industries use large amount of continuous synthetic fibers mostly nylon 6 (NY) and polyester [Polyethylene terephthalate (PET)] for reinforcement. However, during processing, there is some wastage of fibers which adversely affects the economy of tire production. There is always an effort to use these waste fibers in some form for any value added product/component. These fibers may be used in composites for tire applications such as apex compound. Nylon 6 and PET are taken in the present work as they are the most widely consumed fibers in tire industries. So such waste fibers can be reutilized. These thermoplastic fibers are subjected to heat treatment to improve dimensional stability of the product. To the best of our knowledge, work on heat treated-fiber composite with natural rubber is not available in the open literature.

Some inorganic fibrous material like attapulgite can be used to modify the rubber properties. Because of their nano dimension, these fibrous material can modify the properties at much lower concentration compared to other fillers. As evident from the thorough literature search, very few rubber composites based on this clay are reported till date.

Fibrillar composites give good tear strength which can improve the durability of a tire. The objectives of the present work are as follows.

- To use the process fiber waste to some value added product.
- To study the effect of heat treatment on fiber properties and for understanding of the structural changes in fibers
- Development of fibrous composite to improve the durability of a tire.
- To study the effect of heat treatment on fiber properties and for understanding of the structural changes in fibers.
- To improve the compatibility of the inorganic filler with rubber through organic modification of this filler.

- Preparation of hybrid composites by replacing part of carbon black dosage with fibrillar (macro/nano) fillers. To study the effect of such hybrid composites on relevant properties and to look for some applications of the same.
- To study the effect of hybrid composites on tire rolling resistance through finite element analysis.

1.8. References

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