Natural Rubber and Reclaimed Rubber Composites – A Systematic Review

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Abstract

This paper is a review on the tensile, curing, viscoelastic, morphology and thermal properties of natural fiber reinforced rubber composites and reclaimed rubber. Natural fibers have lately become attractive to researchers, engineers and scientists as another reinforcement for fiber reinforced polymer composites. Owing to their low cost, fairly good mechanical properties, and high specific strength, non-abrasiveness, eco-friendly and bio-degradability characteristics. They are exploited as a replacement for the conventional fibers, such as glass, aramid and carbon. The tensile properties of natural fiber reinforce polymers (both thermoplastics and thermosets) are mainly influenced by the interfacial adhesion between the matrix and the fibers. Several chemical modifications are employed to improve the interfacial matrix–fiber bonding resulting in the enhancement of tensile properties of the composites. In all polymers, natural rubber received a growing attention due to mainly abundance and applications in rubber industries. Given the environmental problems as a results of industrial waste, recent studies seemed to have focused more into reclaimed rubber and recycling thereof, which is dominated by end-of-life-tires. This review would cover the aspects of reclaimed rubber as well, which is the rubber recovered from de-vulcanization of a wasted rubber.

Keywords: Rubber composites; Composite materials; Vulcanizing agent

Introduction

Composite materials are a combination of two or more materials that have different properties, such that the combinations render a product which has intermediatory characteristics of the components. For example; polymeric composites normally yield composites which are light yet strong due to filler in-cooperated. Even-though some materials require a chemical treatment to gain strength. Rubber composites are typical examples since curing is a recipe of chemicals for modification of rubber elasticity and strength. This is dependent on a number of factors including type of vulcanizing agent, accelerator (s), activator (s), reinforcing filler, anti-oxidant, heat retardant, mixing/mastication procedure and processing temperatures [1-4]. Generally properties of composite materials are influenced by the two materials involved as well as the method of processing [5]. The primary objective in composite formation is to obtain a good orientation of the reinforcement and an efficient interfacial adhesion by combining the matrix and the reinforcing material [6]. The reinforcing material provides strength and stiffness and also acts as a load transferring medium. The matrix material acts as an adhesive holding the reinforcing material's particles together. Strong interfacial bond between these two materials is very crucial for superior composite properties. The interest in modern composite materials has increased because of their high strength, low density and ease of manufacturing [5]. The material properties of composites can be tailored to meet requirements of a specific application. Selecting an appropriate combination of matrix and reinforcement material would permit production of a new material that meets the requirements of a particular application. Composites find various applications in transport; electrical/electronics; building construction; infrastructure; aerospace/defence; consumer/recreation; medical products and sport equipment. These products have environmental and a technical demand because they are renewable, recyclable, require less maintenance and they also provide desired flexibility. They can be moulded into different complex shapes [5,6].

Composites may be classified according to type of matrix phase; this would include polymer matrix composites; metal matrix composites and ceramic matrix composites. Polymer matrix composites made the most largest and diverse use of composites due to ease of manufacturing; low cost; and good

properties. Rubber is one of commercially used polymeric matrix mainly due to good energy absorbing properties. It can undergo much more elastic deformations under stress than other materials and still return to its original shape without permanent deformation after the stress is released [7]. This unique property gives rubber an extensive variety of applications [8]. Previous researchers have studied a lot of different types of rubbers which include natural rubber (NR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), isobutylene isoprene rubber (IIR) and poly (styrene-butadiene-styrene, SBS) rubber primary due to their domestic applicability. For example, natural rubber is widely used in production of tyres, gloves and condoms. It finds all these applications because it is a biomaterial and it has superior mechanical properties. However it does have a few disadvantages like low thermal resistance and low organic solvent resistance. That makes it require chemical modifications, such as incorporation of additives or blending with other polymers [9]. In most applications it is applied after vulcanization because of the three dimensional network structures which form to allegedly transfer a stress virtually evenly amongst the rubber chains. However, this in the long run, could lead to environmental pollution as recycling of vulcanized rubber get complicated after vulcanization [10]. Reclaiming is a process where vulcanized rubber is coerced to devulcanized using thermal, chemical and mechanical techniques to break the vulcanized structure. In most cases, reclaimed rubber has the plasticity practically equivalent to a virgin rubber, but a reduced molecular weight and mechanical properties compared to virgin rubber [11]. Given that, studies had recommended a use of reclaimed rubber for improving properties of rubber composites [12]. This appeared as a breakthrough in improving the effective use of reclaimed rubber as an additive for virgin rubber, which in turn would save expenses as well as preservation of natural resources and the environment [13-15].
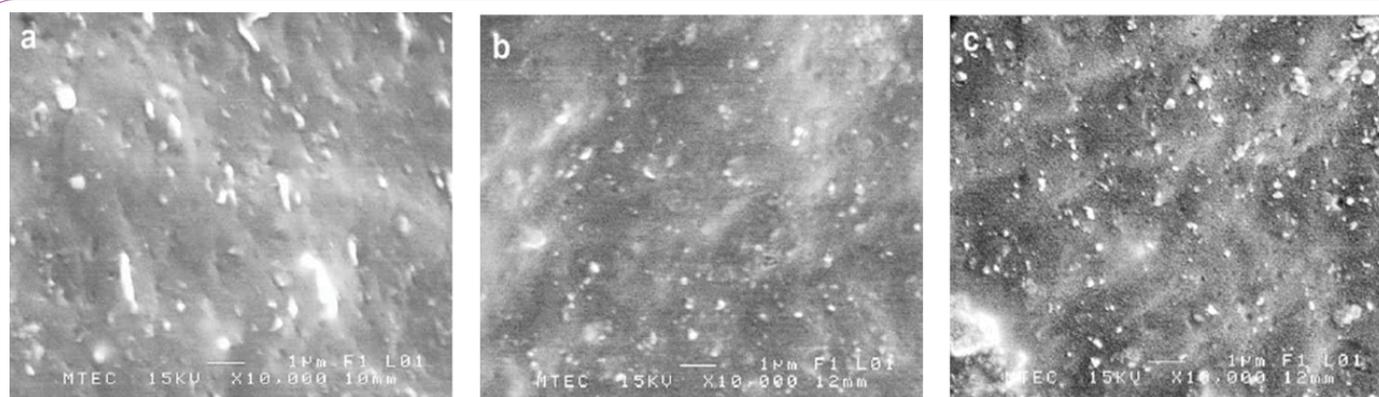
Like most polymers, the effectiveness of rubber depends on its strength and stiffness and the properties cannot be improved by solely using chemical modifications. It may be reinforced by using a filler which is stronger and stiffer to compensate for its intrinsic low strength and modulus [7,8]. Fillers are used as reinforcement materials in rubber composite production to improve properties; develop flexibilities in product design and reduce cost of cured rubber [6,16-18]. The interfacial bond between filler and matrix is one of the most critical aspects to performance of composites [18], poor interfacial bond is associated with relatively poor overall properties compared with strong interfacial bond [19,20].

Composites may also be classified according to type of filler/reinforcing material. These may include continuous fiber composites; short fiber composites and particle filled composites. Each type of filler has different property requirements for an optimal reinforcement. The properties for particle based composites depend on particle size, surface area, surface activity and aggregate structure; filler dispersion and concentration and filler-matrix interactions [21,22]. As for fibrous fillers the properties also depend on fiber aspect ratio, concentration, dispersion and orientation and fiber- matrix interaction [20]. Carbon black; silicates and fibers are the most commonly used reinforcing materials in polymer composites. Silica allegedly provides a unique combination of tear strength; aging resistance and good adhesion properties [23]. Whereas carbon black is used

as reinforcement in rubber to enhance its thermal and structural properties [24], however it is known for environmental effluence and inflict of a black colour [25]. When the fillers were compounded to natural rubber morphology and mechanical properties improved [8,26]. However, a compatibility at an interface limited somehow a stress transfer [8]. In order to produce approximately flawless composites that show desirable properties, the filler and the matrix should portray at least a good compatibility [6,16]. Reinforcing efficiency of natural rubber by silica; carbon black and clay have been compared by Rattanasom, et al. [26]. The carbon black indicated outstanding mechanical properties (hardness, 300% modulus, tensile strength and tear strength) than silica, this behaviour was attributed to better dispersion of carbon black in the matrix as revealed by morphological analysis in **Figure 1**. The carbon black filled composites (**Figure 1a**) revealed smoother surface with well dispersed filler particles than silica filled composites (**Figure 1c**). On the other hand, a higher content of silica was required to reach the same level of hardness as clay and carbon black filled compounds. Clay reached the competitive attractive properties at lower content compared to silica and the carbon black.

On the other hand natural fibers reportedly enhanced mechanical properties of natural rubber composites resulting to high modulus, reduced elongation at failure, increased hardness and improved tear, puncture and cut resistance [27]. Those are some of the factors that elevated interest in production of bio-sustainable composites from natural reinforcing fillers [19,28]. The other added advantages of using natural fibers include low cost; ease of processing, low density, biodegradability and good mechanical properties [20,29]. Synthetic fibers on the other hand (glass, carbon and aramid) have also been used as reinforcement materials in production of rubber composites. These fibers have allegedly high strength and high surface-to-volume ratio which provides high surface area and enhanced interfacial adhesion [30,31]. However there are high costs and environmental concerns involved, which further motivate for utilization of natural fillers. A number of short natural fibers have been incorporated in natural rubber and the properties achieved were relatively poor compared to carbon black and silica reinforcements. This was mostly attributed to poor interfacial adhesion resulting from poor compatibility between rubber matrix and reinforcement. Surface modifications using bonding agents; alkali treatments; acetylation and mercerization have shown a capability to enhance interfacial adhesion and consequently mechanical properties of fiber reinforced rubber composites [19,30]. Modified short natural fiber reinforced rubber composites have been used successfully in production of v-belts; hoses; tire treads and complex-shaped mechanical goods [20].

Chemical treatments of fibers have gained prominence in production of composites with attractive properties [30,31]. Alkali (NaOH) treatments and acetylation of fibers resulted in a decrease in diameter and weight. This has led to production of composites that show improved mechanical properties; thermal stability; better wetting and dispersion into the matrix as well as enhanced reinforcement. Generally, poor compatibility is observed for composites filled with untreated fibers compared to treated counterparts [31-33]. John and Anandjiwala [32] reported acetylation as one of the most attractive and effective treatment in reducing the hydrophobicity of fibers [8].

Figure 1 SEM micrographs of natural rubber composites filled with 6 phr of (a) clay, (b) carbon black and (c) silica [26].

Some coupling agents promote crosslinking of elastomeric materials, which also reported to improve mechanical and thermal properties of composites by enhancing interfacial adhesion between the matrices and reinforcing filler [33-35]. Common coupling agents are silanes, isocynanates, maleated polymers and titanate-based compounds [30]. An ideal coupling agent would be bi-functional to establish covalent bonding between the polymer matrix and fiber [30,36]. One of which would bond with the hydroxyl group (O-H) on the fiber surface and the other would bond with the matrix [34-36]. Researchers have reported the efficiency of silane coupling agents on modification of fillers. IR spectroscopy has shown that formation of Si-O and C-H bonds improves processing characteristics of composites. Fillers treated with silane coupling agents were observed to have more dispersed particles; low agglomeration, improved mechanical properties and better interfacial interaction than unmodified counterparts when in cooperated in polymeric matrices [37,38]. Silane coupling agents provide advantages such as commercial availability on a large scale, alkoxysilane groups which can bond with O-H rich fiber surface and a large number of reactive functional groups which can bond to the matrix. This permits the establishment of a covalent bond between the fiber and the rubber matrix [36]. Silane coupling agents have been reported to improve interaction between silica and rubber matrix because they react with both silica and rubber matrix. Sae-Oui et al. [38] compared the effects of silane coupling agent on silica/natural rubber and rice husk ash/natural rubber composites. They discovered that silanes improved interfacial interaction in silica filled natural rubber, however no significant improvements were observed for rice husk ash composites. They attributed this to the fact that the ash did not have reactive silanol groups on the surface which would chemically react with the organosilane and result to improved interaction and filler dispersion. The current study will focus on composites of natural rubber and reclaimed rubber (rubber collected after the end use). Much attention would be on curing characteristics; mechanical properties; thermal degradation, thermomechanical and morphology. The primary objective is to study the effects of various filler materials on properties of natural rubber and reclaimed rubber composites.

Natural Rubber Composites Properties and Applications

Natural rubber (NR) is a biopolymer based on cis- 1,4-polyisoprene which has good elastic properties, resilience and damping behaviour but poor chemical resistance and processing ability [37]. It is obtained from the milky secretion (latex) of various plants, but the only important commercial source of natural rubber (sometimes called Pará rubber) is the tree Hevea brasiliensis. The only other plant under cultivation as a commercial rubber source is guayule (Parthenium argentatum). Well known applications of natural rubber include tyres; machinery components; gloves; toys; shoe soles; elastic bands; flippers; erasers and sport equipment. It is generally used for applications requiring abrasion/wear resistance; elastic resistance and damping or shock absorbing properties [38]. Oil is one of the required substituent in production of synthetics rubber. Due to expensiveness of oil, NR enjoyed increasing market share and has become an attractive substitute for synthetic rubber [37]. Because natural rubber shows better properties compared to other rubber produced synthetically, rubber industries normally use it to improve properties and expand applications of other rubber materials by blending [39]. It has also been reported to have a very low level of adherence to other materials [40-44]. Hayeemasae et al. [44] reported properties of natural rubber blended with virgin and recycled ethylene-propylene-diene monomer (EPDM). The curing rate of natural rubber vulcanizates was reduced with addition of these elastomers. That was attributed to cure incompatibility of these materials with natural rubber. However maximum torque was increased with addition of both virgin and recycled EPDM and was even higher for the recycled material. This was attributed to higher crosslinking density introduced by EPDM. Blends of natural rubber with styrene butadiene rubber (SBR) have been studied by Fernandez [45] and Goyanes [46]. Addition of SBR in NR shifted the glass transition temperature of natural rubber towards higher temperatures, since SBR has a higher glass transition temperature than natural rubber [46].

Curing properties

Rheology provides information about minimum and maximum torque, scorching time, curing time as well as curing rate of a particular formulation. Maximum torque is related to the stiffness, crosslinking density and viscosity of the compound under testing.

Minimum torque indicates the processability of the material; the higher it is the lower the material's processability. Scorch and cure times measure the time taken to begin and end vulcanization, respectively [44]. Evaluation of curing characteristics is a method used to observe the rate of rubber vulcanization reaction. There are a number of techniques which have been used to evaluate curing characteristics of rubber compounds, but Rheometer is the most widely used instrument in industry and research institutions [47]. Effects of compound variations on curing characteristics are significant in rubber compounding. Rheological studies are necessary to determine curing characteristics per particular compound composition. A number of studies have been done on rheology of natural rubber composites. Khalil et al. [8]; Soltani et al. [20] and Fidelis et al. [31] investigated the curing characteristics of filled and unfilled natural rubber. They observed that addition of fillers leads to an increase in minimum and maximum torque and a decrease in scotch time and cure time with increasing filler loading. In a study by Thomas et al. [33] the change in torque as a function of time for sisal/oil palm hybrid fiber reinforced natural rubber composites was investigated (**Figure 2**). The torque values decreased at first and started to increase after a certain time and remained almost constant with time. The initial decrease was attributed to the softening of rubber at the beginning of curing and the increase was associated to an increasing cross linking sites. They also reported that addition of bonding agent might have contributed to the increased torque. According to Khalil et al. [8] and Aleksandra et al. [43] an increase in torque indicates strong filler-matrix interactions and therefore stronger composites. According to Rattanasom et al. [48] an increase in minimum with increasing content of filler is an indication of increasing viscosity.
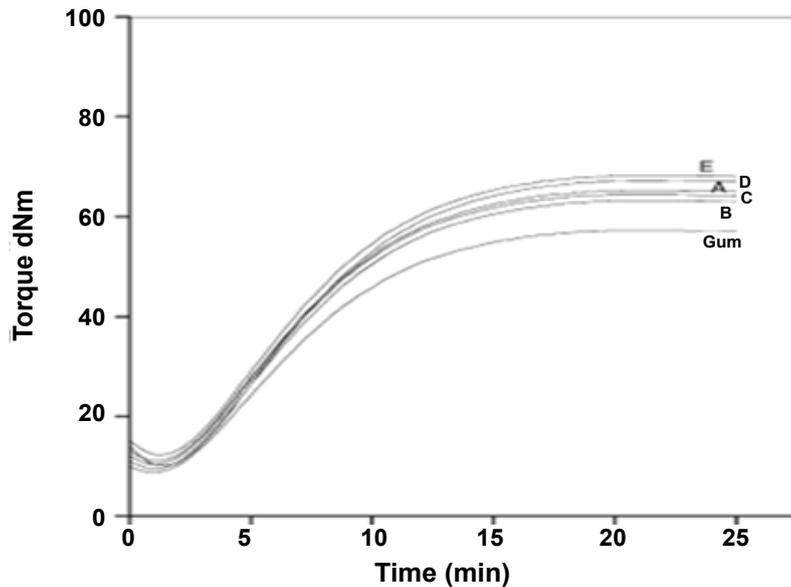
Incorporation of clay filler into the rubber matrix increased cure rate (promotes the vulcanization reaction) which reduced cure time values. A decrease in scorch time values indicated a better heat distribution in the matrix due to incorporation of filler [49]. **Figures 3** represented cure and scotch times, respectively and resulting elongation at break obtained by Fidelis et al. [31]. The incorporation of fillers reduced cure time, but it is worth noting that the chemically treated fibres showed a higher cure time as compared to untreated fibres. That behaviour was allegedly due to the higher moisture content of untreated fibres. Chemical treatments reduce the hydrophilicity of the fibres and therefore resulting to fibres that have lesser water content. It was also reported that cure rate dependent on humidity and water content of the rubber compound, where higher water content would result to lower curing time. Ismail et al. [6] ascribed the decrease in scotch and cure times, with increasing fibre loading to possible increase in mixing times. That caused more head build-up which then results into a decrease in cure time. They also investigated effect of adding bonding agent, which was improved adhesion between filler and matrix and hence causing a further decrease in scotch and cure time. Arroyo et al. [28] added unmodified and modified clay in natural rubber as a substitute of carbon black. Due to poor compatibility, unmodified clay had no significant effect on curing behaviour of natural rubber. However, a modified clay proved to be a good accelerator for vulcanization. That was evidenced by a reduction in both scorch time and optimum cure time on addition of modified clay to natural rubber. On comparison to carbon black, the extent of decrease in scorch and optimum cure time was lesser for carbon black filled rubber than modified clay filled rubber. Sae-oui et al. [38] compared reinforcing effects of rice husk ash; carbon black and silica in natural rubber vulcanizates. Both scorch time and optimum cure time decreased with addition of carbon black. Cure time was observed to increase slightly at very high silica content. That was ascribed to a possible reduction of accelerator (zinc complex) in the rubber matrix which might be trapped inside silica surface. Rice husk ash was regarded as an inert filler as it had no effect on curing behaviour of natural rubber vulcanizates.
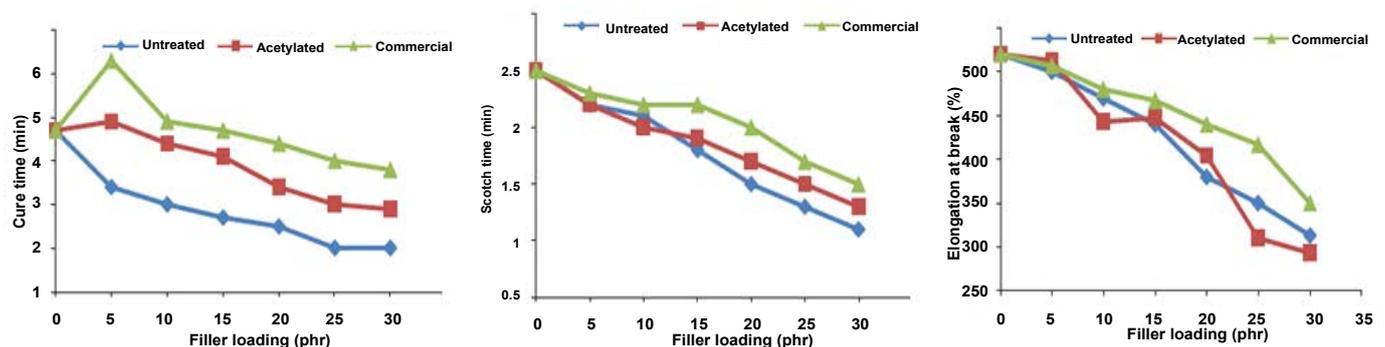
Mechanical properties

Different rubber materials have various mechanical properties to meet specific applications. Mechanical analysis is an evaluation of a material's physical strength including tensile strength; tear strength; hardness; tensile modulus and elongation at break. Generally a material has tensile strength if it is strong when pulled/stretched, this is a force required to break a material under stretch. Tear strength indicates fatigue, abrasion and growth of cut when a material is exposed to sudden stress. Tensile modulus is a measure of a material's resistance to deformation under stress, it is basically related to the stiffness of the material. Elongation at break is the ability of a material to stretch several times its original length; this is one of the most important properties of rubber.

In the studies by Khalil et al. [8], Ezema et al. [34] and Aleksandra et al. [49] it was observed that tensile strength, tear strength, hardness and modulus of filled natural rubber composites increased with increasing filler content and decreasing filler particle size. Those mechanical properties were also observed to be enhanced compared to those of unfilled natural rubber. Arroyo et al. [28] compared the reinforcing efficiency of organo-montmorrillonite and carbon black. Those fillers enhanced the mechanical properties of rubber vulcanizates. However they noticed that, unlike carbon black, organo-montmorrillonite retained the elasticity of natural rubber. Fidelis et al. [31] revealed that at low filler loadings the filled composites showed lower tensile strength compared to unfilled natural rubber. An increase in tensile strength was observed at high filler loadings, but tensile strength started to decrease at very high filler contents. Ismail et al. [6] incorporated bamboo fiber in natural rubber, in their study both tensile and tear strength were reduced with addition of fibers. They attributed the behaviour to irregular shape, size and length of fibers which lead to ineffective stress transfer and poor adhesion and therefore poor mechanical properties. They then added a bonding agent which improved the properties by allegedly betterment of interfacial adhesion. The above studies [8,34,31,49] reported that the elongation at break of filled composites was lower compared to that of unfilled natural rubber and it decreased gradually with increasing filler loading. The smaller filler particles were more compatible with the rubber matrix compared to the larger particles leading to better filler-matrix interfacial adhesion. That was reportedly due to increased surface area resulting from enhanced filler particle distribution. The behaviour was evidenced by the enhancement of tensile properties with incorporation of smaller filler particles into the rubber matrix [8]. When composites are subjected to load, stress is transferred from the matrix along the filler particles leading to effective and uniform stress distribution, which improves mechanical properties. However stress distribution is dependent on concentration and orientation of filler. At low filler content,

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Figure 2 Torque -time curves of natural rubber composites at different fibre loadings. Fibre loading increases in order B<C<A<D<E [33].

Figure 3 Change in cure time, scotch time and elongation at break of maize stalk fibre reinforced natural rubber composites with increasing filler content [26].
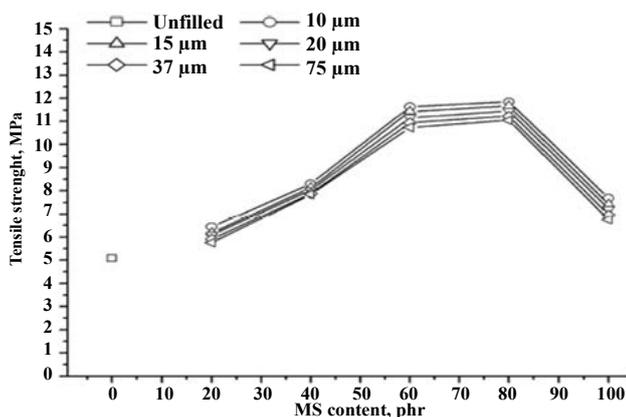
with poor orientation; effective load transfer is difficult to achieve, stress accumulates at certain parts leading to low tensile strength [31,33]. Natural rubber allegedly possess a strain-induced crystallization, this crystallization is disrupted on incorporation of filler leading to a decrease in tensile strength. Hence at low filler loadings, composites showed tensile strength which was lower than that of natural rubber [31,33]. At very high filler loadings, filler agglomeration occured due to strong filler-filler interaction. The matrix phase continuity is disturbed; stress transfer was blocked and consequently led to weaker composites with low tensile strength [8,31,33]. Optimal mechanical properties (modulus, tensile and tear strength) of composites were obtained at moderate or rather lower filler loadings, and further enhanced with addition of bonding agent [5]. Effective stress transfer and filler orientation occurred leading to effective motion of rubber chains [8]; effective fiber-matrix interfacial interaction [8,31] and effective energy dissipating capacity [49]. The increase in hardness of reinforced natural rubber was related to reduction of plasticity and elasticity of natural rubber caused by incorporation of filler leading to more rigid and stiff composites [6,8].

Elongation at break was reduced (**Figure 3**) due to the stiffening of composites introduced by the incorporation of filler to the rubber matrix [31] resulting to high rigidity, low ductility and resistance to stretch under strain [8,31,33]. John et al. [29] reported mechanical properties of natural rubber composites reinforced with lignin from caryota fiber. Tensile modulus increased with filler loading up to 25 phr and started to decrease at loadings above 35 phr. However elongation at break decreased gradually with increasing filler loading, whilst hardness increased. **Figure 4** displayed tensile strength behaviour with both filler content and filler particle size. The tensile strength of the compounds appeared not to depend solely on filler loading and filler particle size, but on filler orientation as well. Where high fiber orientation yields high tensile strength. Fiber orientation has also shown to somehow depend on fiber loading as indicated in **Figure 5**, from which a high loading displayed aggregates which decreased the orientation [33,34]. Similar effects could reflect on modulus and tear strength of natural rubber composite as shown in **Figures 6 and 7**. In a study by Lui et al. [50] mechanical properties of chemically modified starch reinforced natural rubber composites were reported. They discovered that starch acts as an inert
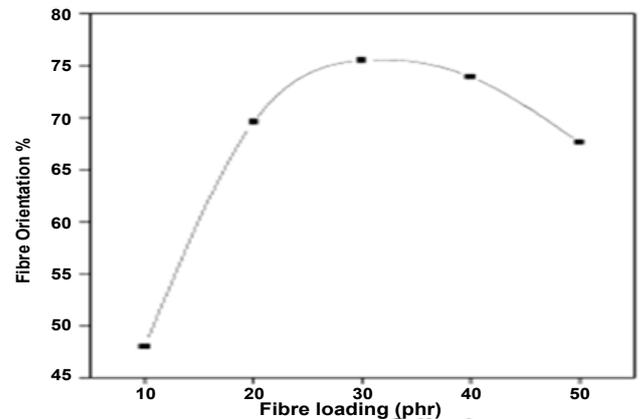
filler, resulting to a monotone decrease in tensile strength and elongation at break of natural rubber when added from $0-30$ phr. On addition of chemically modified starch, mechanical properties were improved and this behaviour was attributed to enhanced adhesion. Optimal mechanical properties (tensile strength; tear strength; elongation at break; 300% modulus) were obtained with starch content of 15 phr, no significant changes were observed for the hardness. Soltani, [20] incorporated short nylon fiber into natural rubber/styrene-butadiene rubber. They discovered that nylon cannot effectively reinforce the rubber matrix in the absence of a suitable bonding agent. This was evidenced by relatively poor tensile properties in absence of bonding agent; but all properties were improved with addition of bonding agents (silica and hexamine). They indicated that synthetic fibers like nylon; glass; polyester and rayon mostly have smooth surfaces which affect bonding between fibers and the rubber matrix [20]. In a study by Sae-Oui et al. [38] the reinforcing effects of carbon black, silica and rice husk were compared; where rice husk was regarded as an inert filler and the others as reinforcing fillers. They reported that regardless of filler type; hardness of natural rubber vulcanizates increased with increasing filler loading due to reduced elasticity and consequently formation of rigid compounds. That effect was more enhanced with reinforcing fillers. They also noticed that silica gave harder compounds than carbon black at higher filler loadings because of the so called stronger filler network.

Another prevalently studied analysis is dynamic mechanical to determine the viscoelastic behaviour of the material. It can be measured by cooling a sample of rubber down to below glass transition temperature and applying a sinusoidal load whilst heating it up to above softening point. This allows for the determination of the material's energy dissipating capacity which is important in a design of structures and mechanical devices. Dynamic mechanical analysis provides information about loss and storage moduli of a material, as well as damping factor (tan delta) which is related to a glass transition temperature. Loss modulus corresponds to the maximum heat dissipation per unit deformation and storage modulus is related to the degree of elasticity/rigidity and crosslinking density [51].
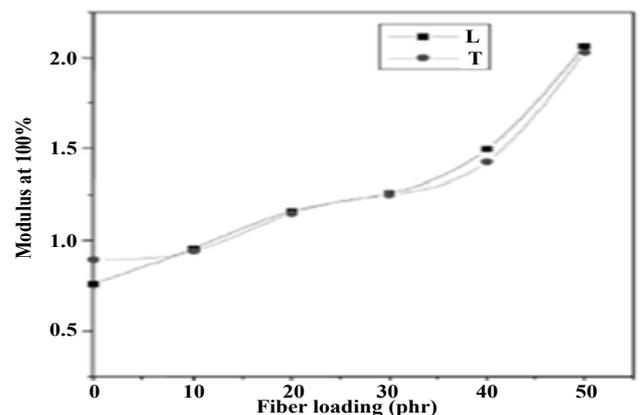
Shirazi et al. [22] reported viscoelastic properties of short aramid fibers reinforced natural rubber and evaluated the properties
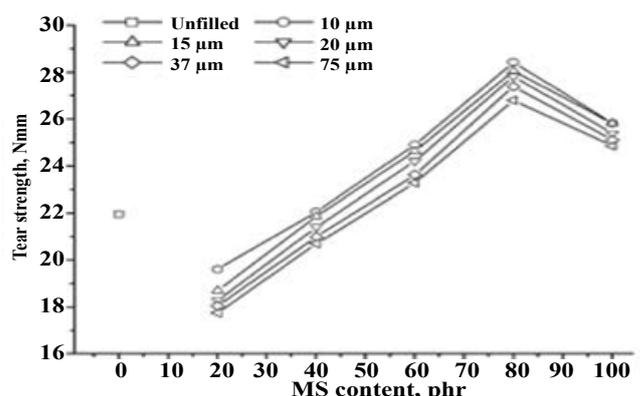
Figure 5 Dependence of filler orientation on filler loading [28].

Figure 6 Change in modulus of natural rubber composites with inreasing filler loading [28].

Figure 7 Change in tear strength of natural rubber composites with inreasing filler loading [3].

in temperature; strain and frequency sweep modes. Storage modulus increased with addition of filler in both strain and temperature sweep modes. No significant changes were observed in frequency sweep mode; hence they concluded that degree of crosslinking is more sensitive to strain than frequency. Aleksandra et al. [49] also reported on frequency dependence of the damping factor, storage and loss moduli. The damping factor increased

Figure 4 Tensile strength of natural rubber composite material with varying filler content and filler particle size [3].

with increasing frequency of loading. Storage modulus was constant within the frequency range under investigation, and the loss modulus showed a slight increase with increasing frequency. Anuchit [52] reported dynamic mechanical properties of natural rubber composites filled with cobalt ferrite, in temperature sweep mode. Storage modulus showed no significant change with increase in temperature. However it increased slowly with addition of filler from 0-15 phr, and then increased significantly at 25 phr. It then decreased at 35 and 45 phr. In another study by Angkana and Rathanawan [53] it was reported that both storage and loss moduli of natural rubber composites decrease with increasing temperature. They also observed that storage modulus was enhanced with increasing filler content. Chonkaew et al. [54] reported temperature dependence of storage modulus with increasing content of silica (**Figure 8**). The similar study was also conducted by Prasertsri and Rattanasom (**Figure 9**) [55]. At low temperatures there was no evidence of reinforcement as the addition of silica allegedly caused a reduction in storage modulus of natural rubber. Reinforcement started occurring at temperatures above the glass transition temperature of the material. This is evidenced by enhancement in storage modulus. **Figure 9** displayed temperature dependence of tan delta obtained for natural rubber composites filled with silica. The height of the tan delta peak decreased significantly and was attributed to both restriction in mobility of rubber segments and crosslinking density.

In the study by Soltani et al. [20] the effects of adding bonding agents in natural rubber composites were investigated and it was discovered that the increase in storage modulus was even higher in the presence of a bonding agent; accompanied by an increase in viscosity. Angkana and Rathanawan [53] also reported the effect of temperature and filler loading on tan delta of natural rubber. This property increased slightly with increase in temperature as well as with increasing filler loading. The glass transition temperature was reduced with addition of filler and further reduced slightly with variation of filler loading. All dynamic properties were enhanced for filled composites compared with natural rubber. Enhancement in damping properties has been attributed to enhancement of chain relaxation from local motions at the interface between filler and rubber matrix [52,53]. This was also related to an increase in stiffness of the material [53]. Energy dissipation of filled composites under cyclic loading resulted from breaking of filler network. High filler content led to an increased energy dissipation on breaking of filler network which led to more energy per cycle required to deform the material that contained high amounts of filler [49].
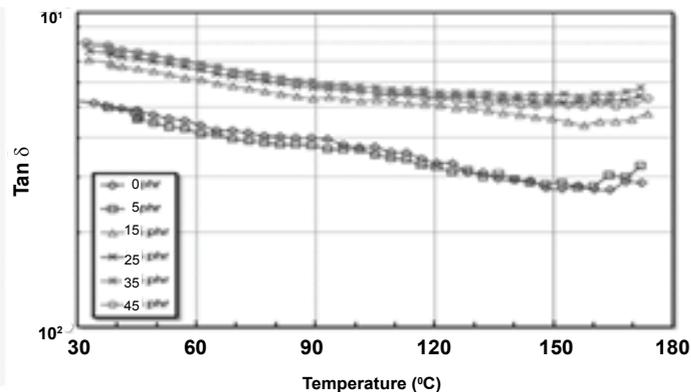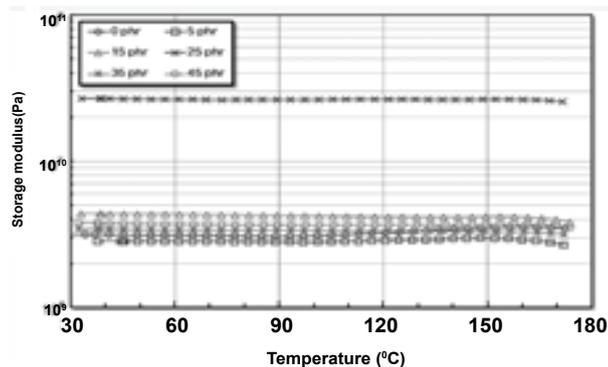
Thermal properties

Thermal analysis studies involve accelerated decomposition of compounds by using heat and the transitions materials undergo when subjected to heating. The molecular chains in natural rubber contain double bonds which allow chain degradation when exposed to heat [53]. Generally, degradation of natural rubber could be due to many environmental factors including humidity; impurities; mechanical load; irradiation and chemicals [42]. Thermogravimetric Analysis (TGA) is the most widely used technique for studying polymer decompositions and evaluating thermal stability of polymer materials. When used with appropriate calibration curves, TGA derivative (DTGA) profiles can be used to distinguish different formulations in a mixture/

blend of elastomers [42,45]. Differential Scanning Calorimeter (DSC) is another thermal analysis technique which may be used to investigate thermal transitions occurring in a compound. It has been used to determine the glass transition temperature of elastomers, which may allow for determination of miscibility between two polymers in a blend [56]. It has also been used in determination of crosslinking density and curing efficiency in natural rubber vulcanizates [25].
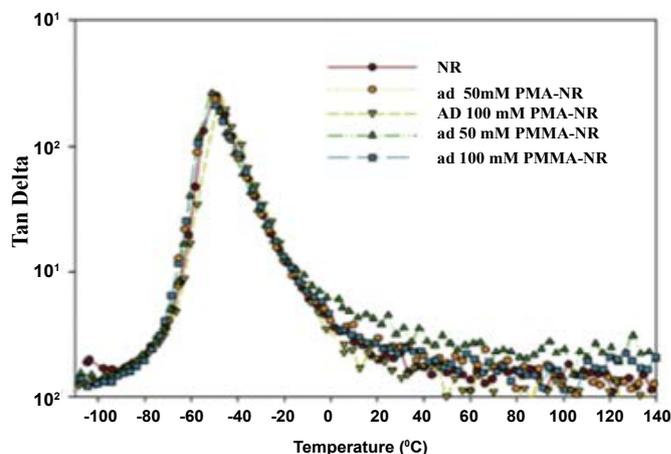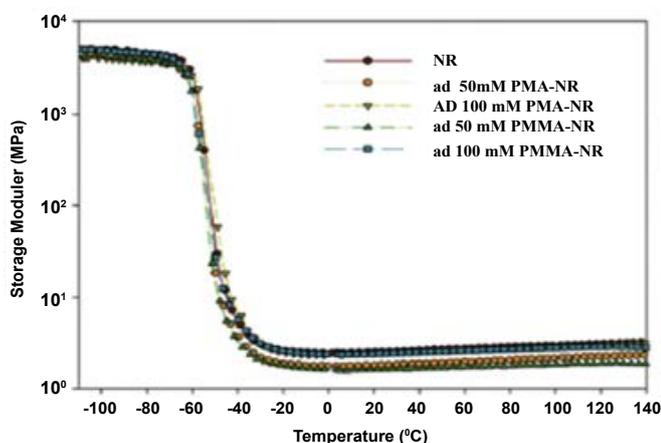
Li [57] and Angakana and Rathanawan [53] reported that TGA and DTA curves of filled and unfilled natural rubber show a single decomposition step. But the curves of the filled rubber are shifted slightly to higher temperatures, which implied enhanced thermal resistance. They also reported thermal degradation kinetics at multiple heating rates where the activation energy of decomposition was determined and was found to be higher for filled natural rubber compared to unfilled rubber, which then implied that the composites had enhanced thermal stability. Aleksandra et al. [49] reported that differences in decomposition behaviour between natural rubber and composites are only observed at higher temperatures (above 50% weight loss), where the composites start to show a slower rate of decomposition than natural rubber. The decrease in decomposition rate was attributed to the probable elevated thermal degradation of an amine-organic modifier which was used in the filler. **Figure 10** showed that a change in decomposition behaviour of the composites is observed around 350 °C where 50% mass loss has already occurred. However it is worth noting that the decomposition profile of the composites is more similar to that of the natural rubber matrix. They also observed that high filler content leads to even slower rate of decomposition and consequently higher decomposition temperature [49]. Hi-Res TGA has been used by Fernandez et al. [45] in quantification of elastomer composition of NR/SBR in tyre formulation. In their study it was observed that NR decomposes at approximately 350 °C. However, Lee et al. [58] reported a thermal degradation peak at 403 °C. Salgueiro et al. [56] and Goyanes et al. [46] used DSC to determine the glass transition temperature in vulcanized natural rubber. A natural rubber sample was heated from 195-298 K at a scan rate of 9 K/min in nitrogen atmosphere. The glass transition temperature of natural rubber was 213 K. It was reported that the glass transition temperature of natural rubber increased with increasing crosslink density due to free volume effects [46]. Arroyo et al. [28] used DSC to determine degree of curing in clay filled natural rubber composites (**Figure 11**). After isothermal vulcanization at 160 °C in DSC they observed that crosslinking was enhanced with addition of modified/unmodified clay and carbon black. This was evidenced by an increase in heat of formation in the presence of these fillers. A more prominent increase was observed for modified clay filled composites as compared to carbon black filled composites, this implied a higher degree of curing/ crosslinking with incorporation of clay.

Morphology

Studying morphology of a material allows for determination of the compatibility and dispersion of fillers in composites. It may be done through observation of a fractured surface or distribution of particulates throughout the matrix and it allows for prediction of the material's behaviour under mechanical loading. Generally

Figure 8 Effect of filler content on storage modulus and damping factor (tan delta) of natural rubber composites [44].

Figure 9 Storage modulus and damping factor (tan delta) of natural rubber/ PMMA blend composites at different filler contents [45].

fractured surface morphology of both composites and polymers predict thermal, mechanical and viscoelastic properties [24].

In a study done by Anuchit et al. [52] the SEM micrographs showed that unfilled natural rubber has smooth surface whilst filled natural rubber has a rougher surface due to allegedly discontinuity in the molecular chains. The effect of filler content was also observed and it was observed from the SEM micrographs that at high filler loadings formation of agglomerates are evident with a rougher surface compared to the lower filler containing counterparts. Micro-scale clusters were also observed. Angkana and Rathanawan [53] reported on topography of filled natural rubber by SEM and TEM. The TEM micrographs (**Figure 12a-12c**) show that unfilled natural rubber (14 a) has a very smooth surface. The filled natural rubber surface was rougher and looked thicker (14 b). At very high filler loading (14 c) aggregates occurred and these are clearly visible on the TEM micrographs. It was evident that at low filler contents filler dispersion was better and can spread more smoothly than at high loadings.

A chemical treatment seemed to be a factor that influenced morphology of the composites [52,53]. Soltani et al. [20] reported that addition of bonding agent in short nylon fiber reinforced NR/ SBR system changes the morphology of the fracture surfaces. That was evident through the presence of short broken fibers (**Figure 13b**) on the surface indicating stronger adhesion between filler

and matrix. The system revealed poor interfacial adhesion in the absence of bonding agent (**Figure 13a**) evidenced by dark holes after fracture and long de-bonded fibers when fibers are pulled out of the matrix. Lui et al. [50] reported surface morphology of chemically modified starch reinforced natural rubber composites. A more dispersed distribution of filler particles in matrix; as well as enhanced filler-matrix interfacial interaction was observed on incorporation of chemically modified starch compared to unmodified starch.

FTIR is a useful technique in determining vibrational energy levels of different molecules. It identifies chemical bonds; detects functional groups and characterize covalent bond formation in a compound. It has been used successfully in analysis and characterization of natural rubber in composite formulations. Gunasekaran et al. [59] and Angakana and Rathanawan [53] reported FTIR observations of natural rubber in filled and unfilled form. The spectra obtained were almost identical, showing that the polymeric units in both elastomers are the same except for small differences (**Figure 14**). From the spectra of unfilled natural rubber two absorption peaks occurred in the region between 2900 and 3000 cm^{-1} and were assigned to symmetrical and asymmetrical stretching mode of C-H bonds in methyl group. However Lee et al. [58] observed an absorption peak at 1375 cm^{-1} in an FTIR spectrum of natural rubber. This peak was assigned
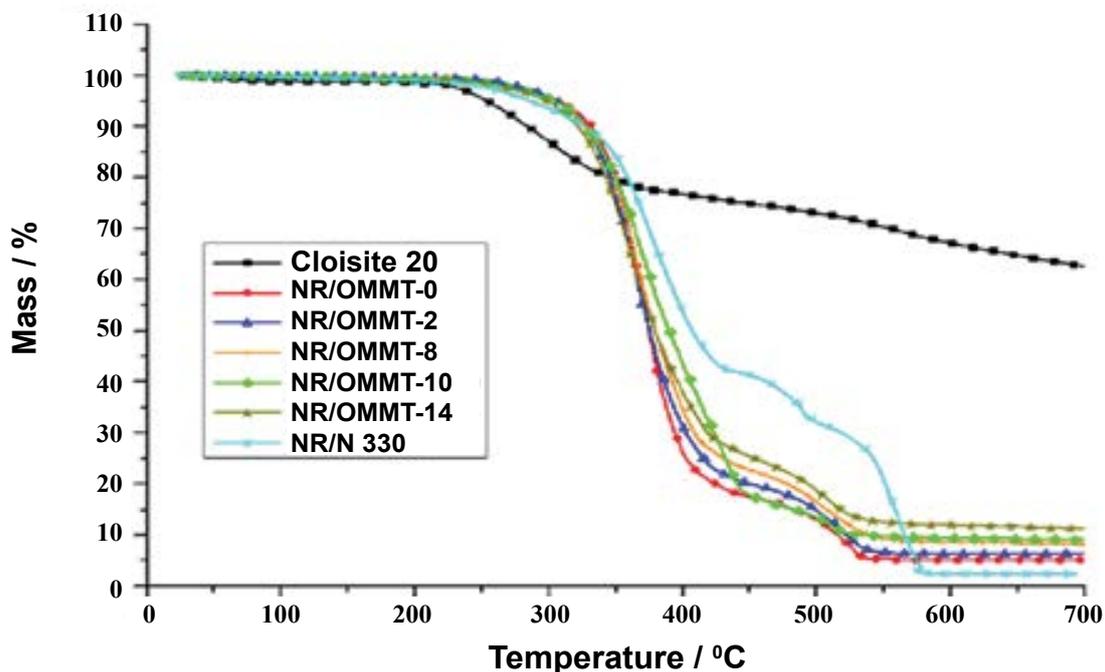
Figure 10 TGA thermo-grams of natural rubber and natural rubber composites [40].
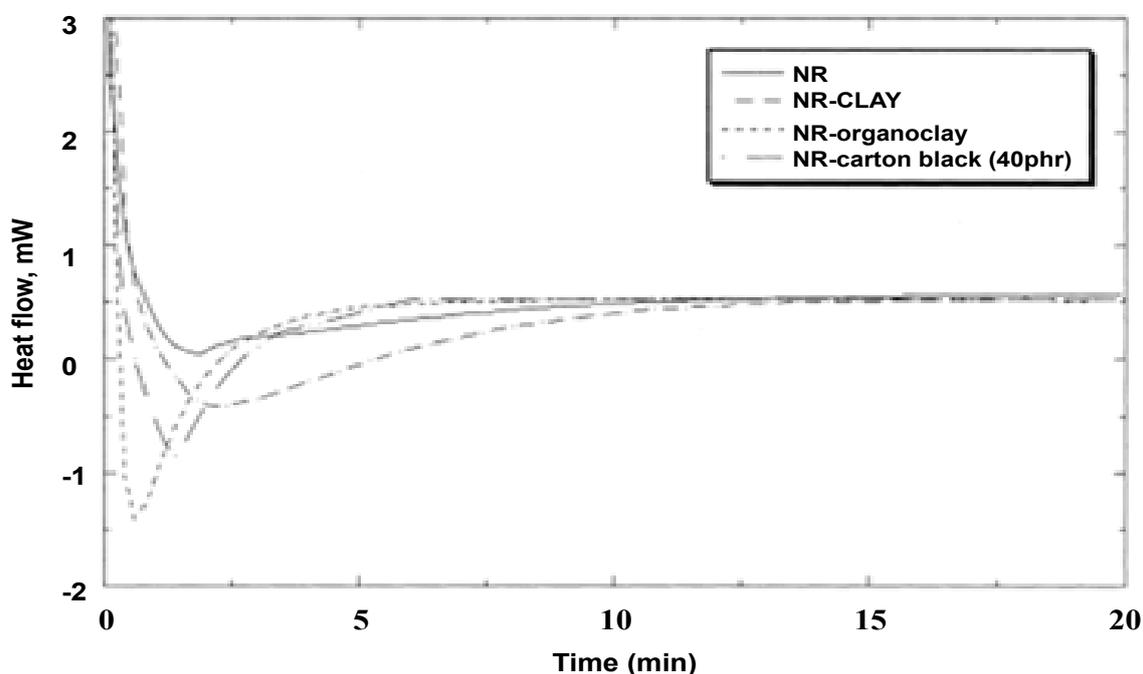

Figure 11 Isothermal DSC thermo-grams of natural rubber composites at 160°C [22].

to methyl group symmetrical vibrations. In the same study by Gunasekaran et al. [59] both filled and unfilled rubber materials showed an absorption peak at 1076 cm^{-1} and it was assigned to Carbon-Sulfur-Carbon group stretching vibrations introduced by Carbon-Sulfur bonds during sulphur vulcanization. This absorption wa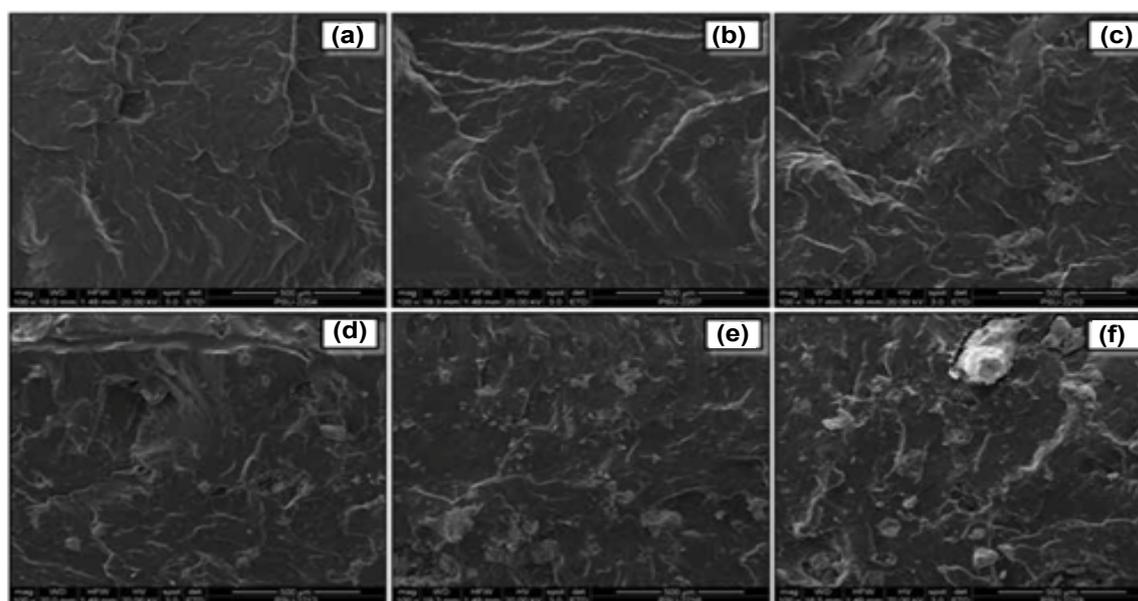s observed to be higher for the reinforced material compared with the unfilled material. They concluded that the only difference between the spectral properties of filled and unfilled natural rubber was the rate of absorption which was higher for reinforced material compared to natural rubber. The increase in absorption was related to the clustering and entanglement of filler particles into the long chain.

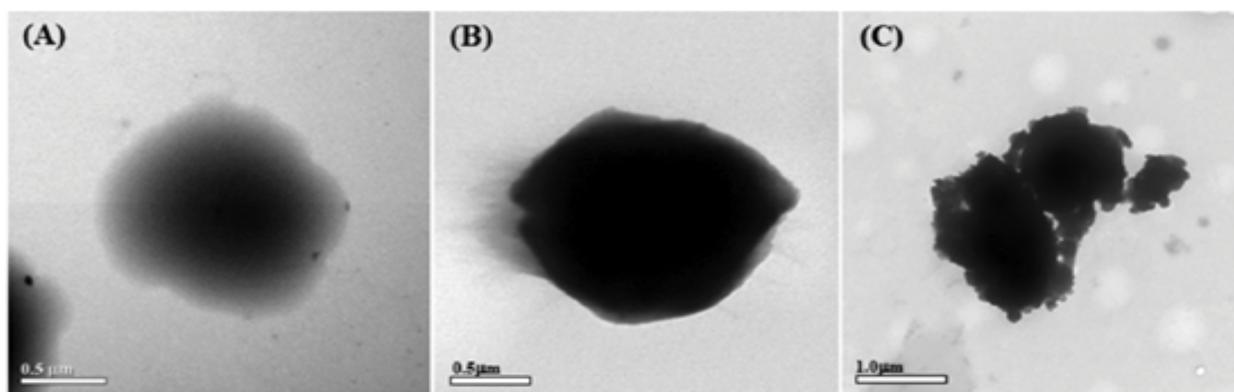# Reclaimed Rubber Composites Properties and Applications

The main source of waste rubber is discarded rubber products such as rubber hoses; belts; shoes and tires [13]. Various methods of rubber recycling have been investigated, including reclaiming; re-treading; landfilling; incineration; pyrolysis; ultrasonic devulcanization; applications in road pavement by asphalt modifications and re-use as filler in plastics and rubber compounds [60-62]. End-of-life-tires make the largest contribution to the amount of rubber waste. They usually constitute of two or more polymers, including natural and synthetic rubbers; additives and plasticizers [59]. These tires can be ground at temperatures below the glass transition temperature of all the polymers in the material to form ground tire rubber (GTR). This process reduces the dimensions of the rubber matrix particles. GTR with dimensions less than 2mm can be reused as filler in other applications. Due to incompatibility, it is also not possible to incorporate GTR in virgin rubber because of the sulphur crosslink network. However compatibility can be improved by reclamation process [60]. Reclaiming converts vulcanized rubber to rubber compounds that can be reprocessed; re-cross-linked and reshaped [19]. It breaks the crosslinking sites, resulting to relatively low molecular weight rubber [61]. Reinforcement of virgin rubber with reclaimed rubber contributes towards product quality and production costs. However good compatibility between reclaimed rubber and virgin rubber should be attained in order to improve a material [15]. Incorporation of reclaimed rubber in rubber formulations is practiced industrially for a number of advantages. These include improved processing, uniformity, low heat development, low thermo-plasticity, low swelling and shrinkage, high curing rate, good shape retention and improved tack [13,14,62-66]. Reclaimed rubber is normally used for extending virgin rubber compounds; cost reduction of rubber compounds and minimizing virgin rubber elastomer requirements [62]. Some example include adhesives; automotive

floor mats; mechanical goods and tread of passenger car, light truck and off-road tires [14]. However, there is still a limited industrial application of reclaimed rubber reinforced rubber materials due to relatively poor impact strength and brittleness [63].
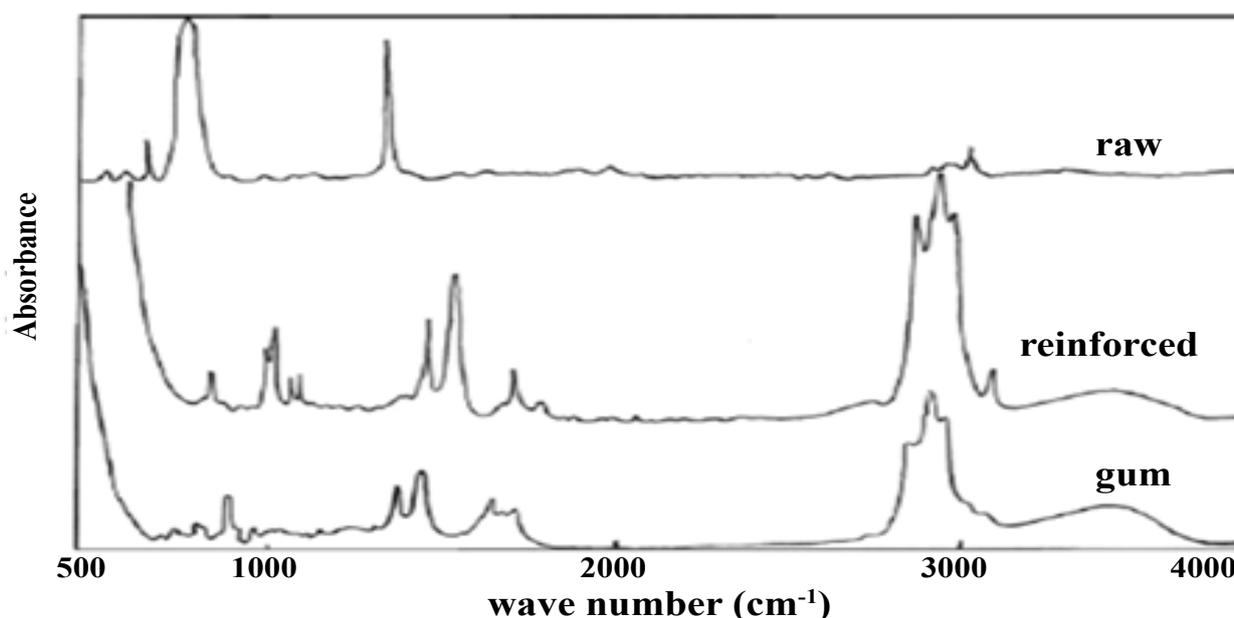
Reclaimed rubber was found suitable for pressure sensitive applications because its tack showed very little variation with changes in weather. Unlike natural/virgin rubber which was tacky in hot conditions and dry in cold conditions. During reclamation, rubber was plasticised due to the large amount of mechanical work which led to reduction of mixing times to almost half that of virgin rubber during rubber formulation [13,64]. Different types of reclaim exist in the market and good quality of reclaim permits relatively higher quantities of reclaimed rubber to be incorporated into new rubber with little compromise in properties [66]. Quality of reclaimed rubber was affected by the type of curing system and vulcanizing conditions which influenced crosslinking density and consequently affecting thermal and mechanical properties [65]. In the case of mechano-chemical reclaiming, shear force applied on the rubber particles influenced the degree of reclaiming [59]. During the reclaiming process, not all crosslinks were destroyed in the rubber material. This resulted to high crosslink density after re-vulcanization of the reclaim. Because of the high crosslinking in reclaimed rubber, molecules were tightly bound and did not have enough freedom to entangle and interact with matrix, leading to poor interfacial adhesion [63]. Therefore waste rubber seemed to favour treatment with coupling agents before mixing in order to promote good compatibility [63,66,67]. It may be concluded that composition and processing of waste rubber influenced the overall properties of the composites. Generally mechanical properties like modulus; tear strength; tensile strength; storage modulus and others were by concentrations of reclaimed rubber in virgin rubber [13]. Antioxidants were normally required in rubber formulations to protect rubber materials from thermo-oxidation and guard it against aging of the vulcanized material. The aging process may start because

Figure 12 SEM micrographs of (a) natural rubber, (b) natural rubber composites with 5phr filler, (c) 15phr (d) 25 phr, (e) 35phr, (f) 45 phr [44].

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Figure 13 TEM micrographs of (A) natural rubber, (B) natural rubber composites with low filler loadings, (C) natural rubber composites with higher filler loading [53].

Figure 14 FTIR spectra of natural rubber in unvulcanised (raw), vulcanized (gum) and filled (reinforced) forms [59].

of atmospheric conditions [43]. However reclaimed rubber has been reported to have an anti-aging property, this becomes an advantage when reclaimed rubber is incorporated in virgin rubber as little or no anti-oxidants may be required. Method of processing may have effects on the final properties of composites. Krzysztof et al. [63] used TGA to characterize ground-tire rubber (GTR), they reported that GTR contained approximately 50% elastomer (NR and SBR); 30 % carbon black and 15% additives. Mangili et al. [64] also characterized GTR by TGA and reported that approximately 53% of GTR is elastomers, with 70% being natural rubber. Zhang et al. [21] compared properties of waste tire fiber reinforced reclaimed rubber composites prepared by conventional two-roll mixer with composites prepared by pan milling. Tensile properties of composites prepared conventionally were deteriorated with increasing fiber content. Whilst the pan composites showed maximum tensile properties with 5% fiber loading. Krzysztof et al. [63] also reported that reclaimed rubber of high degree of reclamation obtained under high shear

force results to deterioration in tensile properties; hardness; resilience and abrasion resistance. Mangili et al. [64] compared mechanical properties of natural rubber/GTR and natural rubber/ devulcanized GTR blends. Mechanical properties of NR/GTR blends were poor compared to mechanical properties of natural rubber alone. However addition of devulcanized GTR to natural rubber resulted to improvements in tensile strength; 100% and 300% moduli and elongation at break.

Curing properties

A study of incorporation of reclaimed rubber into styrene butadiene rubber was done by Debapriya and Debabish [17]. They reported an increase in cure rate, a decrease in cure time and insignificant changes in scorch time on addition of reclaimed rubber. However, Sombatsompop and Kumnuantip [65] incorporated reclaimed rubber into natural rubber and observed an increase in cure rate, decrease in scorch time and little change in cure time. Khaled [68] reported a decrease in

maximum torque and an increase in minimum torque, scorch time and curing rate with incorporation of reclaimed rubber into virgin rubber. It can be said that cure rate is enhanced on incorporation of reclaimed rubber into virgin rubber. This curing rate behaviour has been related to active crosslinking sites and untreated curatives present in reclaimed rubber which could accelerate rate of crosslink formation [17,65-70]. Farahani [71] also reported on cure characteristics (**Figures 15**) of natural rubber/reclaimed rubber blends, where they observed that addition of reclaimed rubber up to 50 phr resulted to a decrease in cure time and scorch time and an increase in cure rate. Above 50 phr cure rate decreased, scorch time increased and cure time showed no considerable change. They attributed this trend to the different concentrations of sulphur present above and below 50 phr. Ravichandran and Natchimuthu [62] reported a reduction in maximum torque on addition of reclaimed rubber (500 phr) to a mixture of natural rubber(100 phr) and leather protein fiber (100 phr). But minimum torque values were increased. The increase in minimum torque was attributed to physical stiffening effect of reclaimed rubber on natural rubber matrix before vulcanization. They attributed the decrease in maximum torque to dilution effect of high quantity reclaimed rubber compared to the amount of curatives present.
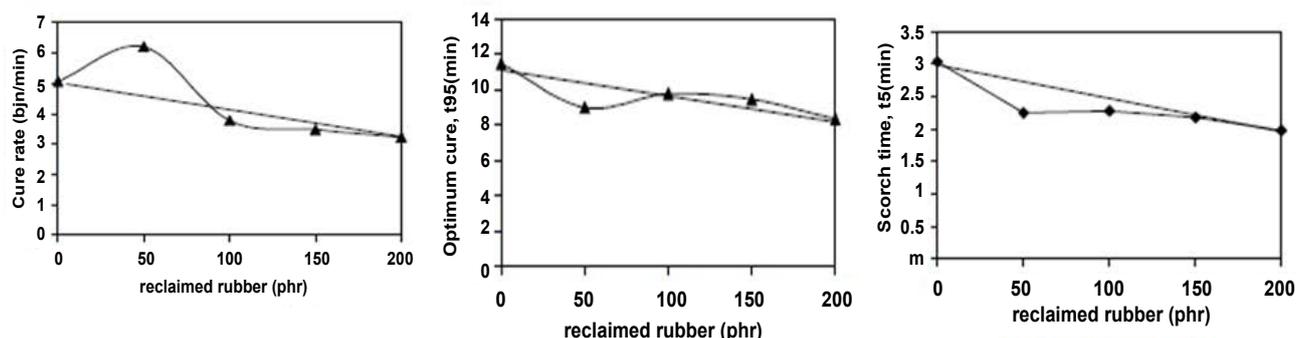
Mechanical properties

Mechanical properties still seem to be more likely to determine a future of application of composites. In a study by Vorga [14] they have investigated modification of properties of rubber through introduction of reclaimed rubber into virgin rubber. They observed that tensile strength and elongation at break of virgin rubber were higher compared to that of the mixture of virgin and reclaimed rubber. Addition of different compatibilizers improved those properties relative to the unmodified mixture. However Khaled [68] reported an increase in elongation at break and a decrease in tensile strength on incorporation of reclaimed rubber in virgin rubber. In another study by Debapriya and Debabish [17] it was reported that incorporation of reclaimed rubber into styrene butadiene rubber increased tensile strength, modulus, elongation at break and hardness with increasing content of reclaimed rubber. The increase in tensile strength and modulus was allegedly due to the presence of carbon black and high crosslink density in reclaimed rubber (**Figure 16**) [12,17]. Increase in elongation at break of composites was attributed to an extent of adhesion between virgin rubber and reclaimed rubber [17]. A study by Adhikari et al. [15] reported a deterioration in
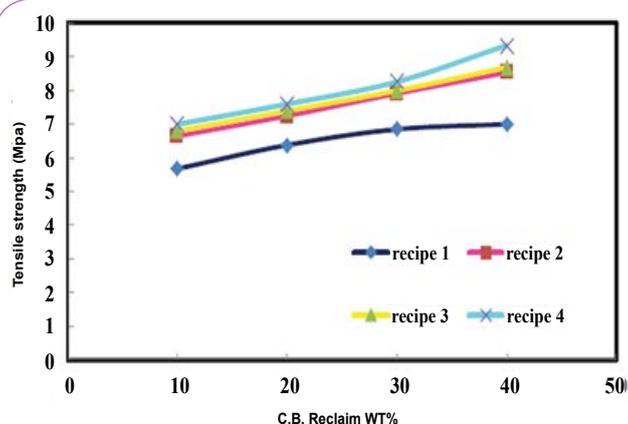
mechanical properties as more of reclaimed rubber is added to virgin rubber. Xiaoou [71] reported that incorporation of filler into reclaimed rubber increased tensile strength and decreased elongation at break with increasing amount of filler. This indicated a considerable enhancement in strength and rigidity of the composites. Sombatsompop and Kumnuantip [63] explained the changes in mechanical properties by lesser homogeneity compared to natural rubber. The lesser homogeneity is said to have caused defects resulting to decrease in tensile strength and elongation at break. Khaled [68] reported that use of reclaimed rubber as an alternative for virgin rubber would somehow result in a reduction in elasticity and a 10-15% deterioration in physical properties which may be due to reduction in average length of rubber polymer chains caused by addition of reclaim, leading to reduction on tensile strength (**Figure 17**). Nesrawy reported that mechanical properties of NR/SBR blends were improved on addition of a mixture of reclaimed rubber and carbon black, and they were enhanced with a further increase of the mixture. They observed an increase in hardness, tensile strength, tear resistance and modulus, but a decrease in elongation at break [72,73].

However a slightly different trend was reported by Farahani [71] where hardness and modulus both increased while tensile strength and elongation at break both decreased with an increase in amount of reclaimed rubber incorporated into natural rubber. Also Debapriya reported that tensile strength increased with increasing reclaim content but it was less for the natural rubber/reclaim rubber blends than for virgin rubber only formulations. Hardness showed no significant changes at low reclaim content but showed a considerable increase at very high reclaim contents [74-80].
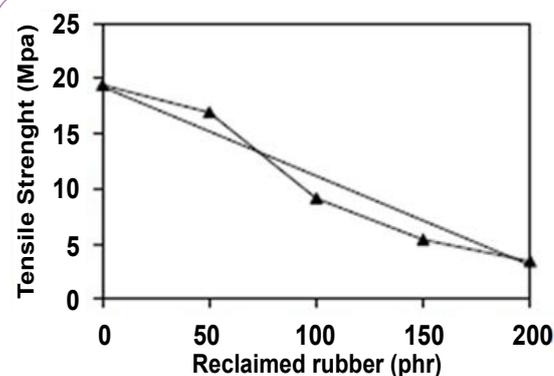
The damping factor (tan delta) is a very important parameter in determination of damping properties and energy dissipating capacity of composites materials. Damping properties are affected mainly by the matrix. Composites consume energy based on mechanism of stress transfer between matrix and filler. Hence in most cases filled composites showed better damping behaviour than the unfilled matrix [72]. A dynamical mechanical analysis study done by Xiaoou [72] reported damping factor (tan delta); storage and loss moduli of filled reclaimed rubber composites. Increased amount of the filler decreased the damping factor and slightly increased storage and loss moduli. It was deduced that filler content has very little effect on loss and storage moduli of filled reclaimed rubber and the composites display enhanced energy dissipating capacity. Viscoelastic behaviour (**Figure 18**)

Figure 15 Changes in cure rate, optimum cure time and scorch time of natural rubber/reclaimed rubber blends with increasing reclaim content [59].

Figure 16 Relation between tensile strength and content carbon black and reclaimed rubber in virgin rubber/reclaimed rubber blends [61].

Figure 17 Relation between tensile strength and content of reclaimed rubber in virgin rubber/reclaimed rubber blends [59].

was reported by Debapriya [78], they observed that storage and loss moduli increased continuously with increasing content of the reclaim rubber, but tan delta decreased. Their results implied that the viscoelastic characteristics of the rubber formulations were enhanced on addition of reclaimed rubber. Nabil et al. [51] incorporated reclaimed EPDM in natural rubber and they observed an increase in storage modulus and glass transition temperature of natural rubber vulcanizates with addition of recycled EPDM. Increasing storage modulus was reportedly due to high crosslink density in reclaimed EPDM as it is believed to have a crosslinked precursor. Increase in glass transition temperature was ascribed to a possible restriction in molecular movement caused by high crosslinking density.

Thermal properties

Degradation state of rubber is best studied by evaluating the percentage retention of properties after ageing [43]. Reclaimed rubber has been reported to have better aging properties compared to virgin rubber [13,66,78]. The improvement in thermal aging behaviour was attributed to the stabilization of the hydrocarbon chains during reclamation through heating, digestion and mechanical shearing [13]. Because of this enhancement in aging properties utilization of anti-oxidants may not be necessary

if reclaimed rubber is used in rubber compounding. A thermal aging analysis of reclaimed rubber reinforced composites was reported in the study by Debapriya and Debasish [17]. They reported that percentage retentions of tensile strength and elongation at break were reduced with progress of thermal aging, however percentage retention of tensile strength increased with increasing reclaimed rubber content whilst percentage retention of elongation at break was reduced significantly. Percentage retentions of hardness and 300% modulus showed an increase with progress of thermal aging (**Figure 19**). However Debapriya et al. [78] reported that percentage retentions of tensile strength and elongation at break were higher for natural rubber/reclaimed rubber blends compared to those of natural rubber. Nabil et al. [51] reported ageing properties reclaimed EPDM/natural rubber vulcanizates. They observed a reduction in tensile properties of the compounds after aging which was attributed to chain scission caused by polymer oxidation, resulting to entanglement and therefore reduced tensile strength. Nonetheless, the retained property percentage showed that the thermal stability of the compounds increased with addition of reclaimed EPDM and was attributed to formation of additional crosslinks. Debapriya and Debabish [17] also reported on thermal-gravimetric analysis (**Figure 20**); which indicated that thermal stability of the rubber formulations was enhanced with increasing content of reclaimed rubber. The analysis was in agreement with their thermal ageing study. Krzysztof et al. [63], Mangili et al. [64] and Nadal et al. [79] investigated the decomposition profile of a tire derived reclaimed rubber by TGA. Krzysztof et al. [71] reported a three step decomposition profile with decomposition of natural rubber and synthetic rubber occurring at 350°C and 600 °C, respectively. However, Mangili et al. [64] observed decomposition at 385ºC and 439 °C and associated them to natural and synthetic rubbers, respectively. Krzysztof et al. [71] also observed a decomposition between 200 °C and 350 °C and this was assigned to decomposition/ evaporation of plasticizers and low molecular weight additives of the reclaim. Nadal et al. [79] reported that volatile compounds were released at about 200 °C, whilst associated natural rubber and butyl rubber/ styrene butadiene rubber to the decompositions occurring at around 382 °C and 461 °C, respectively.
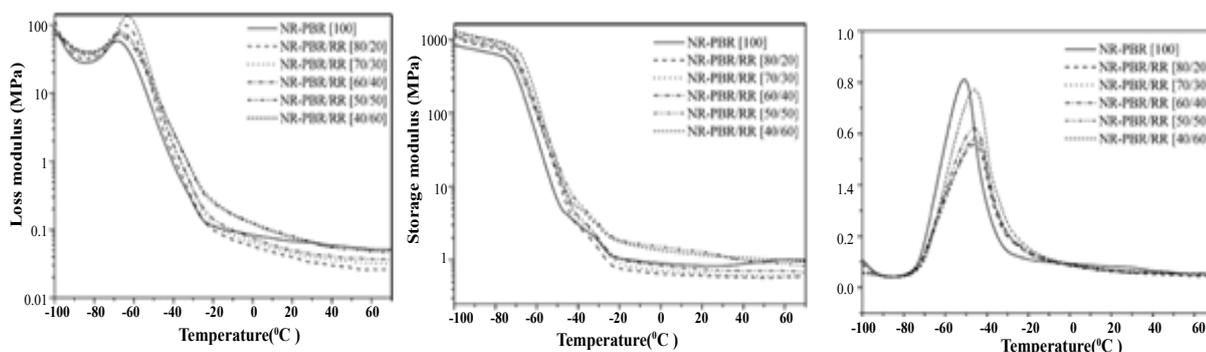
Morphology

SEM studies done by Vorga et al. [14] and Debapriya and Debabish [17] showed that insufficient interaction occurred between virgin rubber and reclaimed rubber. This was evidenced by appearance of several holes and cracks in SEM micrographs of virgin rubber/ reclaimed rubber blends, indicating that the material would be weak under mechanical stress. Tensile fracture surfaces of virgin rubber showed a homogenous morphology. **Figure 21a-21c** displayed SEM micrographs reported by Ahmed et al. [80], which shown that use of a compatibilizer improved the interaction between natural rubber and recycled acrylonitrile butadiene rubber (NBR). Higher tensile strength is indicated by presence of many tearing lines on the surface treated with a compatibilizer (21 b), whereas a broader tearing line is observed for the unmodified blend (21 a). The presence of many tearing lines allegedly indicated that the material received a lot of deformation before breaking; which implied good interaction between the two elastomers. **Figure 21c** displayed the effect of adding higher
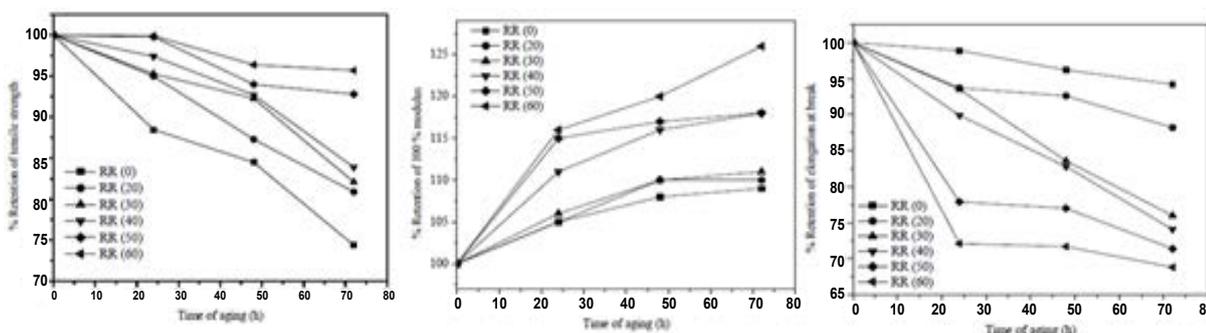
quantities of reclaim. A number of voids on failure surface were indication of weak interaction and explanation of poor tensile strength. SEM micrographic images reported by Xiaoou et al. [72] and Wu [35] showed fiber entanglements in tensile fractured surfaces of fiber reinforced composites. Fiber networks did not form at low fiber contents as compared to higher loading. The observations were evidenced by SEM micrographs on **Figure 22a-22e** where better compatibility is observed at moderate filler quantity (b). A few holes are observed at lower filler quantity (a). However at very high filler quantities (c) processing was difficult due reportedly due to reduced fluidity and viscosity of composites [35]. Farahani, et al. [71] and Debapriya et al. [78] reported that reclaimed rubber has lower viscosity than virgin rubber and also the blend of natural rubber with reclaimed rubber has lower viscosity than individual components. They attributed the behaviour to a possible non-compatibility and non-homogeneity of the two compounds and to the fact that chain scission occurs during reclamation reducing viscosity of the reclaim.

In a study of cryoground tire reclamation done by Mangili et al. [64] they reported FT-IR spectrum (**Figure 23**) of GTR and devulcanized GTR. They observed absorption peaks at 2920 cm^{-1}; 1450 cm^{-1} and 1375 cm^{-1} corresponding to CH; CH_2 and CH_3 deformation in rubber backbone, respectively. The peaks were similar in both GTR and devulcanized GTR. The CH stretching vibration was more prominent in devulcanized GTR. New peaks were observed in spectrum of devulcanized GTR at 730 cm^{-1}; 690 cm^{-1}; 930 cm^{-1} and 1580 cm^{-1}. The peaks were assigned to CH bending in benzene (730 and 690 cm^{-1}); aromatic C=C

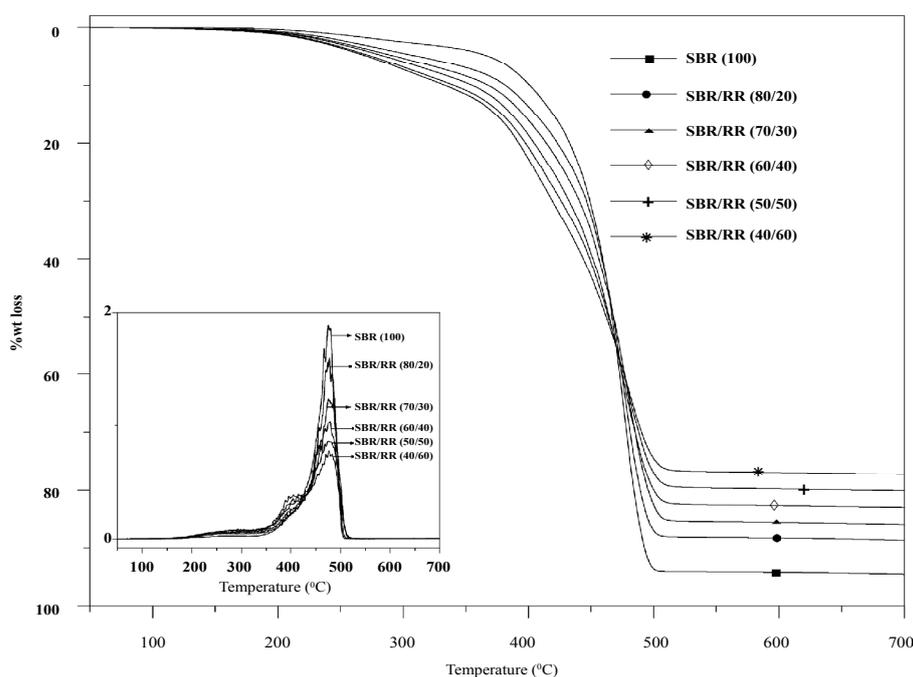stretching vibration and -CH=CH- (trans) bending, respectively. Sutanto, et al. [76] reported FTIR spectra of virgin EPDM and reclaimed (devulcanized) EPDM rubber. From the spectrum of the reclaimed material they observed that there were no peaks above 3000 cm^{-1} which implied avery little or no amount of degradation products that have OH groups. It is believed that degradation of hydrocarbon chains is produced by free radical reaction leading to formation of –C=O and –OH groups. In their virgin rubber spectrum they observed absorption peaks around 1740 cm^{-1}. The peaks were said to be related to –C=O groups from vulcanizing agents. Debapriya et al. [78] investigated the influence of reclaimed rubber on reinforcing effects of silica in styrene butadiene rubber (SBR). An absorption was observed between 1000- 1100 cm^{-1} indicative of $Si – O – Si$ stretching. The absorption was absent in unblended reclaimed rubber. They also observed an absorption at 957 cm^{-1} which was due incomplete reaction of silanol within the matrix (Si–OH). The intensity of this peak was reduced with incorporation of reclaimed rubber and the intensity was further lowered with increase in percentage of reclaimed rubber. The behaviour was related to the presence of reactive sites in reclaimed rubber, and that caused reclaimed rubber to react with more silanol, resulting to less concentration of $Si – OH$. All spectra showed an absorption peak at 2900 cm^{-1} which was said to be due to asymmetric stretching of the hydrocarbon rubber backbone. In a study by Jana and Das [77], FTIR spectrum of re-vulcanized reclaimed natural rubber was reported and compared to that of vulcanized virgin natural rubber. From their findings they deduced that the chemical structure of natural
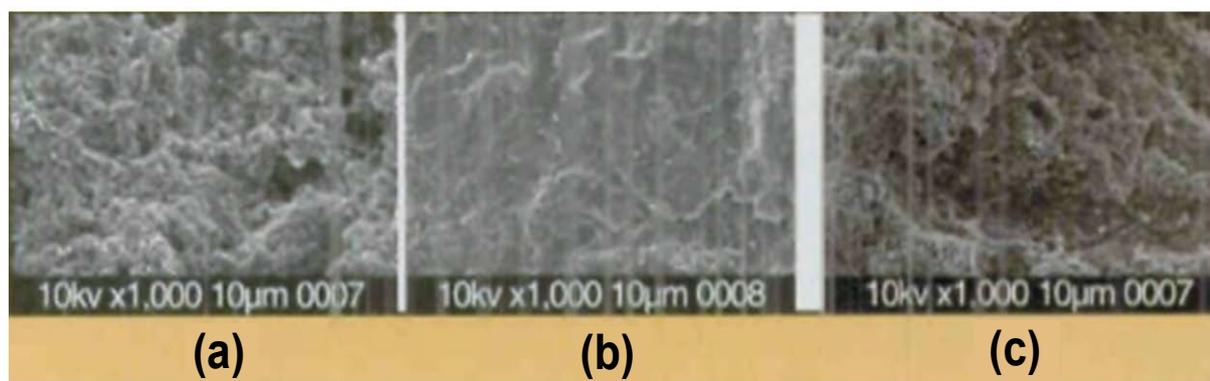

Figure 18   Loss, storage moduli and damping factor of natural rubber /reclaimed rubber blends with variation in reclaim content [62].

Figure 19   % Retention of tensile strength, modulus and elongation at break with increasing reclaimed rubber content and increasing aging periods [12].

Figure 20 TGA thermographs of SBR/reclaimed rubber composites at different amounts of reclaimed rubber [12].
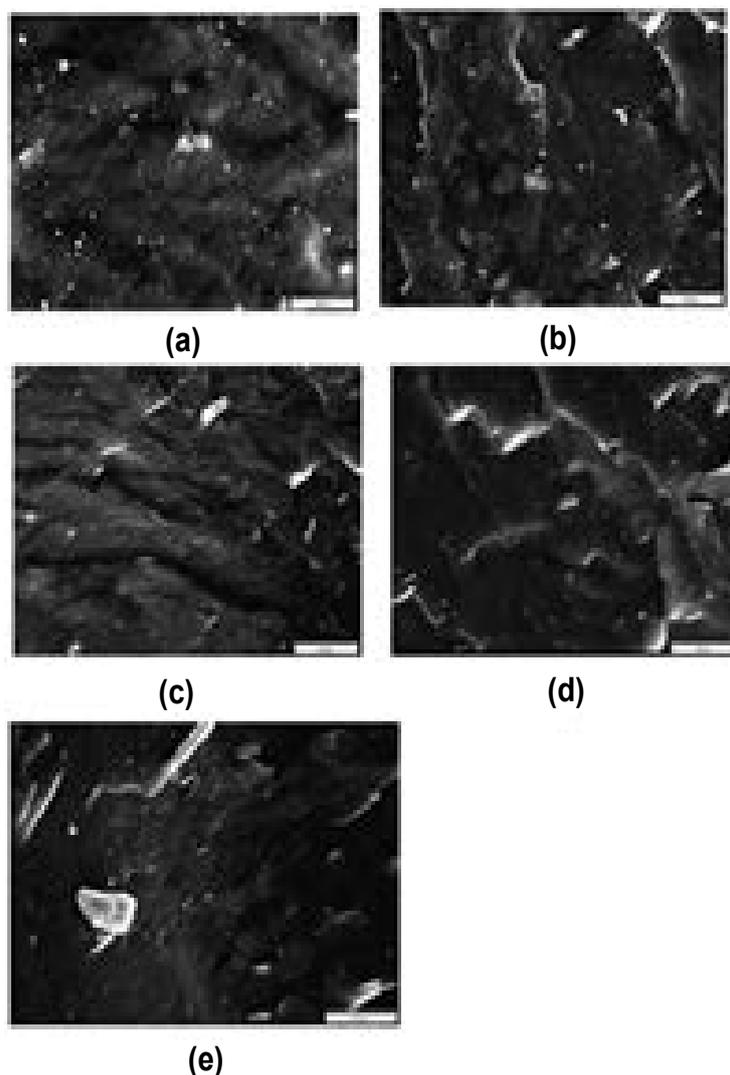

Figure 21 SEM micrographs of tensile fracture surface of reclaimed rubber composites containing (a) 10 phr filler, (b) 25 phr filler and (c) 30 phr filler [30].

rubber does not change after the re-vulcanization process. They also noted that there was no peak indicative of polymer chain degradation at 1730 cm^{-1} (-C=O stretching).
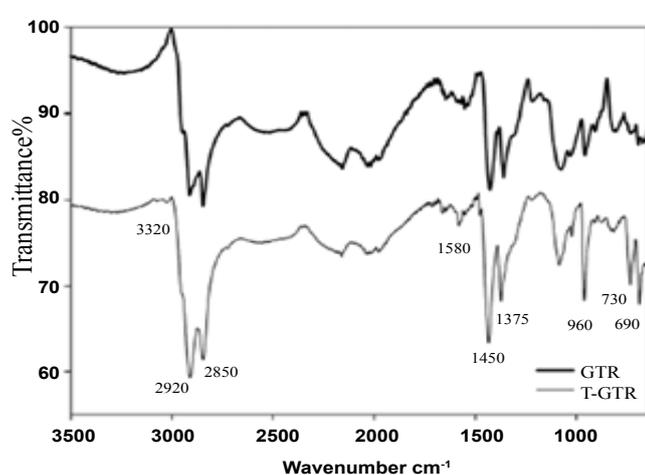
Conclusions

Overall reinforcement of rubber has shown to improve properties like modulus; tensile strength; tear strength and elongation at break [25]. Presence of filler revealed increased maximum torque and reduced scorch and curing time. Generally, two extreme ends of filler content i.e. very low (~3%) and very high filler loadings (~20%) resulted into relatively poor mechanical properties of composites. However maximum/optimal properties are obtainable at relatively moderate filler amounts (~5-10%). Damping properties are generally enhanced by addition of filler and they deteriorate with increasing temperature, however loss modulus was not significantly altered by filler addition. Damping

factor and storage modulus values evidenced that the degree of crosslinking was enhanced by addition of filler and improved further by increasing amount of filler. The decomposition mechanism of natural rubber is not altered by addition of filler but the decomposition temperature increased, which meant that addition of filler enhanced thermal stability of the material. Morphology was affected by incorporation of filler, very high filler loadings showed poor dispersion of filler particles which was evidenced by the presence of agglomerates on SEM micrographs. Reinforcements do not necessarily alter the chemical bonds of natural rubber, the same polymer microstructure seemed to remain as shown clearly in most FT-IR analysis. However, the intensity of absorption has shown a variation. As a matter of principle, filler content affected different properties to different extents. The same applied to elasticity when reclaimed rubber was introduced into virgin rubber. There seemed to be an uncertainty as to what effects are caused by addition of reclaimed rubber into virgin rubber and to which extent. That uncertainty could

Figure 22 micrographs of tensile fractured surfaces of natural rubber/reclaimed rubber blends, (a) 100/0, (b) 75/50, (c) 50/100, (d) 25/50, (e) 0/200 phr. Magnification is 100 [59].

Figure 23 FT-IR spectra of GTR and devulcanized GTR [52].

likely emanated from the type of reclaim rubber. Nonetheless, the quality, composition and processing of the reclaim has a great influence on the overall properties of the composites. That, otherwise should be a course of study for the future. Rubber formulations containing reclaimed rubber showed improved thermal aging properties compared to formulations that did not contain reclaimed rubber. That was an effect of the suspected anti-aging property of reclaimed rubber. The combination of crosslinking and additives seemed to have influenced most changes in properties of rubber formulations.

Going forward it was clear that reclaimed rubber and the utilization of natural fibers, in the form of biomass, was lacking concept in the fraternity of the rubber composites. There was, obviously, number of different methods which can be used to develop the system. Natural fiber reinforced natural rubber/reclaimed rubber composites could in fact respond to the environmental pollution and economy. Therefore, it would be worth pursuing natural fiber reinforced natural rubber/reclaimed rubber composites. In addition to that, it would also be important to investigate a reclaim rubber competent for polymeric blends.

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