FABRICATION AND CHARACTERISATION OF MAGNETORHEOLOGICAL ELASTOMERS BASED ON NATURAL RUBBER, CARBONYL IRON AND WASTE NATURAL RUBBER GLOVE POWDER

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LIST OF SYMBOLS

$[X]$	Crosslink density
%	Percent
a	Level in Taguchi orthogonal array
A	Factor in Taguchi orthogonal array
cm3/mol	Cubic centimetre per mol
g	Gram
G′	Storage modulus
G″	Loss modulus
Hz	Hertz
M	Magnetic field
m_{dry}	Dry mass of MREs
min	Minute
mm	Milimetre
MPa	Megapascal
mT	Militesla
m_{wet}	Swollen equilibrium mass of MREs
phr	Part per hundred rubber
S/N	Signal-to-noise
T	Pre-structuring temperature
t	Pre-structuring time
tan δ	Tan delta
µm	Micrometre
ρ_r	Density of natural rubber
ρ_s	Density of solvent

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American Society of Testing and Materials
CBS	N-Cyclohexylbenzothiazole-2-sulfenamide
CIP	Carbonyl iron particle
FTIR	Fourier-transform infrared spectroscopy
IPPD	N-Isopropyl-N'-phenyl-1,4-phenylenediamine
M100	Modulus at 100% elongation
MR	Magnetorheological
MRE	Magnetorheological elastomer
MRFs	Magnetorheological fluid
NR	Natural rubber
OA	Orthogonal array
SEM	Scanning electron microscopy
SMR	Standard Malaysian rubber
TESPT	Bis-(3-triethoxysilylpropyl) tetrasulphane
TGA	Thermogravimetric analysis
WGP	Waste glove powder

FABRIKASI DAN PENCIRIAN ELASTOMER MAGNETOREOLOGI BERDASARKAN GETAH ASLI, BESI KARBONIL DAN SISA SERBUK SARUNG TANGAN GETAH ASLI

ABSTRAK

Elastomer magnetoreologi (EMR) adalah kelas baru komposit elastomer yang terdiri daripada matrik getah dan partikel bermagnet. Dalam kajian ini MREs berasaskan getah asli (GA), sisa serbuk sarung tangan getah asli (SSS) terbuang dan partikel besi karboksil (PBK) telah berjaya dihasilkan. Kaedah Taguchi digunakan untuk mengkaji kesan ketiga-tiga faktor pra-penstrukturan iaitu masa, suhu dan medan magnet kepada tan δ dan sifat tegangan dan meramalkan kombinasi faktor yang optimum. Keputusan menunjukkan bahawa medan magnet mempunyai pengaruh terbesar kepada tan δ untuk julat frekuensi 1 - 100 Hz manakala masa pematangan dan medan magnet mempunyai pengaruh terbesar kepada tan δ untuk julat amplitude terikan 0.1 - 6%. Walau bagaimanapun, tiada faktor yang menunjukkan pengaruh terhadap sifat tegangan. Keadaan pra-penstrukturan yang optimum kemudiannya digunakan untuk menghasilkan EMR dengan penambahan SSS dalam usaha untuk meningkatkan sifat redaman. Analisis mekanikal dinamik menunjukkan penambahan SSS meningkatkan prestasi dinamik EMR. Tan δ tertinggi diperolehi dengan menggunakan 10 phr SSS, dengan peningkatan 10% dalam ujian julat frekuensi dan kenaikan 30% dalam ujian julat amplitud. Walau bagaimanapun, ruang yang jelas diantara PBK dan matrik getah serta partikel tertarik keluar dapat diperhatikan dengan ujian SEM, menunjukkan interaksi diantar PBK dan matrik getah adalah lemah. Oleh itu, bis- (3-trietoxysilylpropyl) tetrasulphane (TESPT) digunakan untuk memperbaiki interaksi antaramuka antara getah dan PBK. Interaksi yang berlaku di antara getah dan

PBK telah dikenalpasti oleh spektrum FTIR, kepadatan sambung silang oleh ujian pembengkakkan dan peratusan cantuman oleh analisis termogravimetrik. Kandungan optimum TESPT didapati pada 4 phr, dengan kenaikan purata tan δ sebanyak 40% untuk julat frekuensi 1 - 100 Hz dan 13% untuk julat amplitude terikan 0.1 - 6%.

FABRICATION AND CHARACTERISATION OF MAGNETORHEOLOGICAL ELASTOMERS BASED ON NATURAL RUBBER, CARBONYL IRON AND WASTE NATURAL RUBBER GLOVE POWDER

ABSTRACT

Magnetorheological elastomers (MREs) are a new class of elastomeric composites consisting of a rubber matrix and magnetic particles. In this work MREs based on natural rubber (NR), waste natural rubber glove powder (WGP) and carbonyl iron particles (CIP) were successfully produced. The Taguchi method was utilised to study the effect of three pre-structuring factors - time, temperature and applied magnetic field on tan δ and tensile properties and predict the optimum combination of factors. Results indicated that magnetic field had the greatest influence on tan δ over 1 – 100 Hz frequency range while pre-curing time and magnetic field had the greatest influence on tan δ over 0.1 – 6% strain amplitude range. However, none of the factors exhibited significant influence on tensile properties. The optimum pre-structuring conditions were then applied to fabricate MREs with the addition of WGP in attempt to enhance damping. Dynamic mechanical analysis showed that addition of WGP improved dynamic performance of MREs. The highest tan δ was obtained with 10 phr WGP, with an increment of 10% in frequency sweep test and a 30% increment in amplitude sweep test. However, obvious gaps and particle pull-out were evidenced by SEM, suggesting weak interfacial bonding between CIP and WGP with the rubber matrix. Consequentially, bis-(3-triethoxysilylpropyl) tetrasulphane (TESPT) was used to improve the interfacial adhesion between rubber and CIP. Coupling occurring between rubber and CIP was identified by FTIR spectra, crosslink density by swelling test and the grafting percentage by thermogravimetric analysis. The optimum content of TESPT was found at 4 phr, with an average increment in tan δ of 40% over a 1 – 100 Hz frequency range and 13% over a 0.1 – 6% strain amplitude.

CHAPTER ONE

INTRODUCTION

Background

Vibration is a common occurrence in our daily lives. Vibration can be desirable, for instance, the motion of watches, musical instruments and microwave ovens. In many cases, however, vibration is undesirable, wasting energy and creating noise, for example, the vibration of engines, motors and structures. Therefore, vibration control is an essential concern in construction and engineering applications. One of the most common and effective methods to help minimise unwanted vibration and noises is the use of dampers, devices designed to counter and reduce vibration. Damping can be achieved through active or passive methods. Active damping consists of a sensor that detect vibration and an actuator to initiate responses to the vibration, which can be adjusted in real time. Passive damping utilises the intrinsic ability of a material to dissipate energy. It is desirable for a damping material to have a high damping capacity while maintaining good mechanical properties. Materials for damping can be categorised into metals, ceramics, polymers or composites (Chung, 2001).

In general, metal has good mechanical properties but low damping performance. Development of two-phase metal matrix composites (MMC) has been proven to improve damping and attain a reconciliation between mechanical properties and damping (Lu et al., 2009). Shape-memory alloys (Chung, 2001; Cimpoeşu et al., 2010; Li et al., 2010; Lu et al., 2009; Prasad and Shoba, 2014), ferromagnetic alloys (Chung, 2001; Emdadi et al., 2015; Mou et al., 2015) and metal laminates (Chung, 2001) are other examples of high damping metal-based materials. High damping metals may be attractive as dampers in certain environments and circumstances where soft materials cannot be used, but their applications have been restricted due to extremely high cost, health hazards and complicated processing.

Ceramic exhibits low damping but high stiffness. Ceramic is widely used in construction due to high strength and heat resistance. Common ceramic materials for construction and damping are concrete, other cement-based composites and asphalt (Chung, 2001, 2002; Leiben et al., 2018; Leung and Grasley, 2012). Silica fume has been used to improve the damping of cement-based materials (Chen and Chung, 2013; Muthusamy et al., 2010). Despite being used extensively in construction, ceramic has very limited applications as damping materials due to its low damping capacity and lack of flexibility.

Elastomer is the most commonly used materials for energy absorption and vibration control. Although rubber has demonstrated its utility in damping, its low stiffness limits its usefulness in practical applications (Chung, 2001; Xia et al., 2018). Many efforts have been carried out to modify elastomers to improve their mechanical properties while maintaining their damping performance. The use of polymer blends (Li et al., 2018; Lu et al., 2014; Mao et al., 2008) and penetrating networks (Lv et al., 2017) have been employed to broaden the damping temperature range and provide more damping by exploiting interface between the polymers in the blend or network (Chung, 2001). Other methods to improve damping and stiffness in polymers involve incorporation of reinforcement materials, such as fibres (Das et al., 1993; Jahed et al., 2016; Joseph et al., 2010; Li et al., 2017; Lv et al., 2006), carbon nanotubes (Li et al., 2015; Prasertsri and Rattanasom, 2011) and inorganic fillers (Boczkowska and Awietjan, 2012; Xu et al., 2017, 2015). In more recent research (Ubaidillah et al., 2014), magnetic particles have been incorporated in rubber, resulting in significant improvement of vibration damping and stiffness. These magnetic rubber composites are termed magnetorheological elastomers (MREs). Rheological properties of MREs can be adjusted by applying a magnetic field during fabrication and/or operation. When MREs undergo shear stress in the presence of an external magnetic field, the particles are dislocated from their original position, causing deformation to the matrix, resulting in an increased stiffness of the material. In the case of anisotropic MREs with chain-like structures of magnetic particles caused by the magnetic field during fabrication, when the particle chains are displaced, due to the tendency of the chains to return to their original minimum energy stat, more work is required to shear the material and as a result the shear modulus of MREs is increased (Boczkowska and Awietjan, 2012; Jolly et al., 1996).

MREs can be produced without or with a magnetic field. The absence of a magnetic field during fabrication results in isotropic MREs, while applying a magnetic field produces anisotropic MREs. Isotropic MREs is distinguished by a homogeneous distribution of magnetic particle in the rubber matrix. In anisotropic MREs, magnetic particles are arranged into column-like structures in the matrix as a result of curing the material under an applied magnetic field (Chen et al., 2007; Fuchs et al., 2007; Li et al., 2013). This process is called the pre-structuring process. In this stage, uncured MREs samples are placed for a period of time at elevated temperature under an applied magnetic field (Li et al., 2008). The field induces magnetic dipole in each particle in the direction of the field. The north pole of a particle is attracted to the south pole of its neighbouring particle, resulting in the alignment of particles into columns inside the matrix. Eventually, when the material is cured, the particles are sealed and fixed in the matrix (Raa Khimi et al., 2015). It has been revealed that anisotropic MREs possess higher stiffness and improved damping compared to isotropic MRE or conventional rubber composites. Here damping is mainly promoted by energy absorption by friction between the molecule chains in the rubber matrix and damping provided by matrix-filler interface as with conventional rubber composites, but inclusion of magnetic particles in rubber enables additional damping through magnetism-induced damping (Kaleta et al., 2011; Li and Nakano, 2013).

Problem statement

Common matrix materials for MREs are natural and synthetic rubbers, such as butadiene rubber, butyl rubber, synthetic polyisoprene, etc. due to their intrinsic good damping capability. Selective thermoplastics and polymer blends can also be used as matrix. Carbonyl iron is the typical choice for magnetic particle because of its high permeability, low remanence, and high magnetic saturation (Ubaidillah et al., 2014). Less commonly used magnetic particles are nickel (Ausanio et al., 2007), hard magnetic particles (Koo et al., 2012) and different types of ferrites (Makled et al., 2005; Zaborski et al., 2009). However, the performance of MREs is influenced not only by the selection of matrix materials and magnetic particles, but also by manufacturing conditions. Formation of chain-like structures in MREs are greatly influenced by the pre-structuring process during curing. Therefore, it is substantial to understand the effect of the factors involved in this process. Several works have been carried out to investigate separated effect of factors influencing pre-structuring process of MREs. This includes the influence of pre-structuring time, pre-structuring temperature and applied magnetic field. Bokzkowska and Awietjan (2006) studied the influence of magnetic particles loading, magnetic field strength and direction during fabrication on mechanical properties of urethane-based MREs. Li et al. (2008) investigated the influence of time, temperature and magnetic field during the pre-structure or pre-cure process in manufacturing of MREs based on silicone rubber. In Chen et al.’s work (2007), the impact on NR-based MREs of matrix type, magnetic field, temperature, plasticiser and iron particles content was examined. Qiao et al.’s work (2015) studied the effect of magnetic particle content, pre-structure time, temperature and magnetic field on the properties of MREs based on poly(styrene-b-ethylene-co-butylene-b-styrene). The aforementioned researches recorded individual effect of each factor during preparation of MREs, however, no available work has been carried out to study the combination influence of pre-struturing time, temperature and magnetic field.

The promising potential of MREs has prompted its considerable growth in research and applications in the past decade (Ahamed et al., 2018; Ubaidillah et al., 2014). The increasing use of rubber in research and development of MREs has perpetually raised awareness in environmental concerns. Moreover, regarding another aspect of the rubber industry, the generation of waste latex gloves has increased as a consequence of continuously elevated awareness of infection prevention in medicine and personal protection in scientific and technological fields. In addition, while there are meticulous specifications for latex gloves, defects such as pinholes and tears can relatively easily be caused during manufacturing of latex gloves.As a result, considerable amounts of defective latex gloves (up to 15%) are rejected as scraps during manufacture due to defects (Alakrach et al., 2018; Rajan et al., 2006) and, together with the disposal of used gloves, lead to overflow in waste latex gloves. A common reclamation approach is incorporation of waste latex gloves in rubber blends (Afiratul et al., 2014; Dahham et al., 2015). Utilisation of waste latex gloves in fabrication of MREs to enhance damping is a pertinent direction due to the improvement of damping provided by the matrix. However, the incompatibility between carbonyl iron and rubber-latex glove matrix can cause poor matrix-filler adhesion as well as insufficient wetting of the fillers, therefore, modification of the filler surface is plausible to achieve better interfacial damping, which depends greatly on the adhesion between matrix and fillers.

Objective

The objective of this research was to optimise the damping capability of MREs based on natural rubber (NR) and carbonyl iron. The specific research objectives are:

i. To inspect the effect of pre-cure time, pre-cure temperature and magnetic field during curing on the properties of magnetorheological elastomer and determine the optimum values for these three parameters utilising the Taguchi method.
ii. To enhance the damping performance of magnetorheological elastomer with waste natural rubber glove powder.
iii. To assess the effect of silane coupling agent in improving the interfacial bonding between the rubber matrix and carbonyl iron particles.

Outline of the thesis

This thesis is divided into five chapters, each with their own purpose as follows:

Chapter 1 provides an introduction to materials for vibration damping, including metals, ceramic and elastomers, as well as a brief overview of MREs, identifying a gap in research and the objectives of the study.

Chapter 2 discusses the fundamentals of rubber, MREs and the Taguchi method, and also reviews the literature on fabrication and characterisation of MREs.

Chapter 3 gives a detailed description of the materials, equipment and experimental procedures involved this research.

Chapter 4 discusses the test results on the optimisation of the pre-structuring process of MREs, the effect of waste glove powder and the effect of silane coupling agent on properties of MREs.

Chapter 5 presents the conclusions on the current work and recommendations for future work.

CHAPTER TWO

LITERATURE REVIEW

Magnetorheological (MR) materials

Despite rubber being the most common material for damping, the potential of rubber is restricted due to its low stiffness and toughness. Attempts to improve mechanical properties of rubber for damping have given way to a new class of materials known as magnetorheological (MR) materials (Ahamed et al., 2018). MR materials are composed of magnetically permeable particles dispersed in a non-magnetic carrier, typically a fluid or an elastomer. In MR materials, energy dissipation occurs due to viscous flow of the carrier material, as well as interfacial damping and magnetic interaction between the particles. MR materials can operate in passive or active mode. In an active state, the application and variation of a magnetic field allows for rapid and reversible changes of rheological characteristics of the material. MR materials can be divided into magnetorheological fluids (MRFs) and magnetorheological elastomers (MREs). Other forms of mediums to contain magnetic particles include foam, polymer gel and thermoplastic (Ahamed et al., 2018).

Magnetorheological fluids (MRFs)

MRFs were first developed by Rabinow in 1948 and have since widely been made commercially available for many applications. MRFs comprise of magnetic particle suspended in a fluid. Typical fluids used in MRFs include silicone oil, mineral oils, synthetic and semisynthetic oils, polyesters and polyethers, lubricating oils, and other polar organic liquids (de Vicente et al., 2011; Wang and Gordaninejad, 2008). Carbonyl iron is commonly used as magnetic particles because of its high magnetisation saturation. Additives, such as thickening agents are usually required to prevent sedimentation of the particles.

The enhancement of damping in MRFs is promoted by the increase in viscoelasticity of the fluid induced by the magnetic field. Without the presence of a magnetic field, MRFs exhibits the characteristics of a Newtonian fluid and has low viscosity. When a magnetic field is applied, the particles are magnetised, attracted to each other and arrange into columnar structures along the direction of the field. As a result, the viscosity of the fluid is increased due to the obstruction of its flow caused by these particle chains. This rheological change causes MRFs to behave similarly to a solid and increases the yield stress of the material, promoting additional damping as more energy is now required to overcome the yield stress and make the fluid flow (de Vicente et al., 2011).

Since their discovery, MRFs have been utilised in many applications, including dampers, breaks, clutches, polishing devices, seals, and hydraulic valves (Wang and Meng, 1948; Wang and Gordaninejad, 2008). However, despite their commercial popularity, MRFs still have certain shortcomings that eventually interfere with their efficiency in practical applications. The difference in density between the fluid and the magnetic particles leads to sedimentation and aggregation over time, causing problems in re-dispersion of the particles and ultimately diminishing the MR effect.

Magnetorheological elastomers (MREs)

The development of MREs has evolved to overcome the disadvantages of MRFs. The most obvious drawbacks of MRFs are sedimentation of the particles and risk of leakage, which can be resolved when an elastomer matrix replaces the fluid as the carrier of the magnetic particles. MREs also offer more flexible choices in application as they can work in an active mode, which takes advantage of the MR effect, or in a passive mode, which does not require the use of a magnetic field.

MREs comprise of magnetic particles dispersed in an elastomeric matrix. Natural rubber is commonly employed as matrix in MREs. Other applicable elastomers involve synthetic rubbers such as silicone rubber, polyurethane, butadiene rubber and other elastomers. Carbonyl iron is frequently over other types of magnetic particles in fabrication of MREs, not only because of its high permeability, low magnetic remnant, and high saturated magnetization, but also because of its commercial availability and reasonable cost. Nickel, cobalt, and various types of ferrites are some of the less conventional magnetic particles (Ubaidillah et al., 2014).

Because of their structure, MREs operate in different modes from MRFs. As the matrix for the magnetic particles is a solid, MREs work in the viscoelastic deformation region, as opposed to the post-yield state in which MRFs operate. MREs can be fabricated either without or with a magnetic field. The former results in isotropic MREs, while the latter results in anisotropic MREs. Isotropic MREs can be characterised by a uniform magnetic particle distribution in the matrix. Anisotropic MREs have a special chain-like columnar structure of magnetic particles in the matrix as a result of curing the materials under an applied magnetic field. Figure 2.1 demonstrates particle distribution in isotropic and anisotropic MREs.

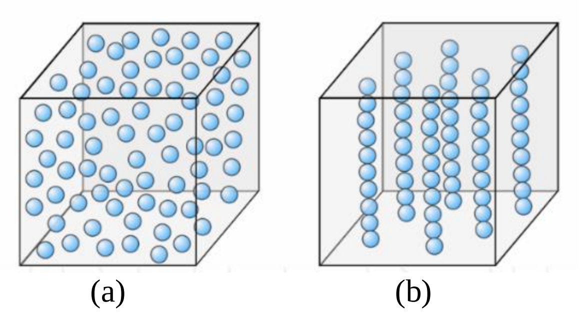

(a) (b)

Figure 2.1 Microstructure of (a) isotropic MREs and (b) anisotropic MREs (Boczkowska and Awietjan, 2012)

Damping mechanisms in magnetorheological elastomers

Damping in MREs relies on three damping mechanisms, which are viscoelastic damping, interfacial damping and magnetism-induced damping (Yang et al., 2012). Viscoelastic damping comes from the viscoelasticity of the rubber matrix, which displays both elastic and viscous characteristics when undergoing deformation. The elastic component of rubber behaves according to Hooke's law and allows the material to store energy during deformation and return to its original shape after the stress is removed, and thus does not contribute to damping in rubber. In contrast, the viscous component of rubber follows Newton's law and allows energy dissipation during deformation. When a stress is applied, the long, entangled molecular chains in rubber uncoil and rearrange to adapt to the stress, a phenomenon known as creep. Internal friction caused by movement of rubber chains allows kinetic energy to be converted into heat, which is the source that causes damping in rubber. The viscous stress lags behind the elastic stress by a 90° angle. Ratio of stress modulus and elastic modulus is called the loss tangent, denoted by tan δ and represents the damping capacity of the material.

Interfacial damping is contributed by damping at weakly bonded interface and strongly bonded interface between the matrix and the filler. At weakly bonded interface, damping occurs due to friction between the matrix and the filler particle surface. Damping at strongly bonded interface is induced by the viscous flow of the matrix, now more restrained because of matrix-filler bonding. At high strain amplitude, the breakdown of matrix-filler bonding allows more energy absorption due to stress release. Moreover, when the content of filler increases, agglomeration occurs in which the particles surround and restrict the movement of some rubber portions. Figure 2.2 demonstrates trapped rubber being confined by an agglomerate of fillers. At high strain amplitude, the agglomerates are broken and trapped rubber is freed to take part in damping. In addition, when strongly bonded interface is destroyed, it becomes weakly bonded interface and converts energy into heat by interfacial friction.

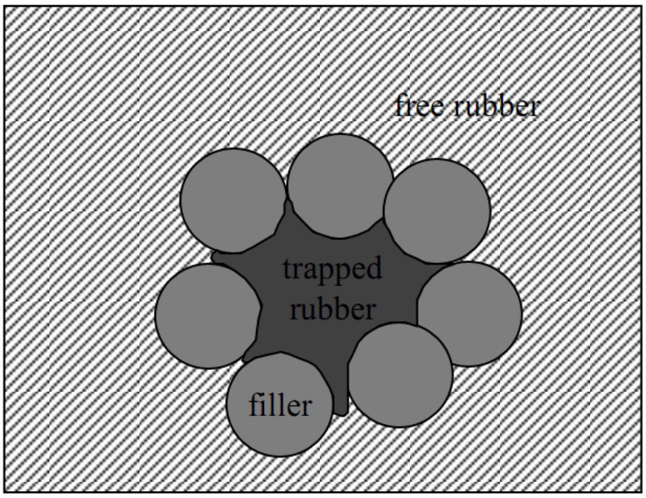
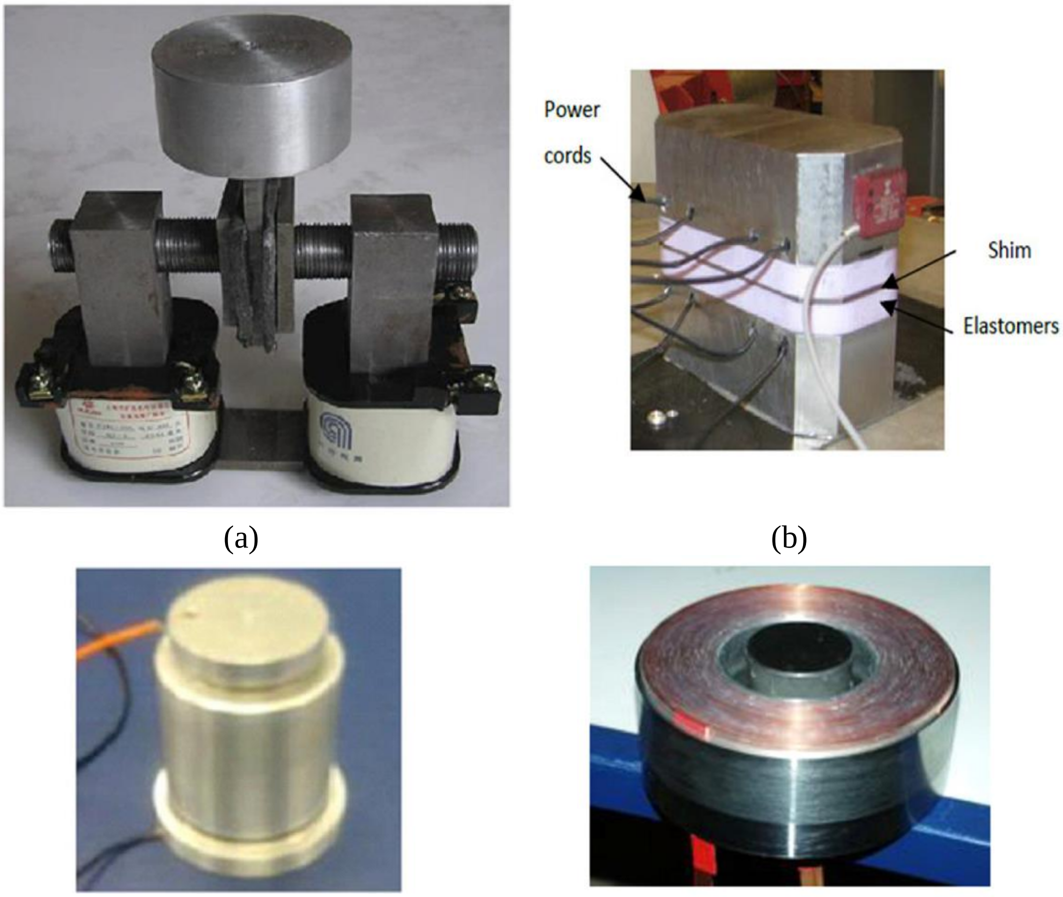


Figure 2.2 Constrained and free rubber in an agglomerate (Raa Khimi, 2015)

The third damping mechanism in MREs is induced by the magnetic interaction between magnetic particles. When a magnetic field is applied, the neighbouring magnetic particles are magnetised and become magnetic dipoles. The north pole of one particle is attracted to the south pole of the one next to it. Such magnetic attraction causes the particles to form chain-like structures in the matrix. Magnetism-induced damping is mainly ascribed to additional energy required to overcome magnetic interaction between magnetic particles. When a shear stress is applied perpendicularly to the direction of the particle chains, the chain diverges from its direction. The adjoining particles, as a result, are pulled apart as the chain is stretched. Magnetic interaction tends to cause the particles to return to their original low energy state; this allows more energy to be absorbed and thus enhances damping in MREs. Obviously, magnetism-induced damping is dependent upon the structure of particle chains, which in turn is influenced largely by the pre-structuring process, as it is in this stage – before curing of the matrix – that the particles are able to move and form columnar structures.

Magnetorheological elastomer applications

MREs have found applications mainly in vibration absorption and vibration isolation devices. In mechanical engineering, MREs are utilised in fabrication of active absorbers employed in various applications in machinery and automotive. These devices operate by altering the stiffness of the MRE component by applying a variable magnetic field, usually generated by an electromagnet. MREs have been extensively used in engine mounts, automotive bushings and seat vibration absorbers. The stiffness of MREs are adaptively changed by a control unit that responds to the signals sent by a sensor that measures vibrations. The tuneable stiffness in MREs has also been exploited to produce spring elements with adjustable stiffness for application in automobile vehicles. MRE can be incorporated into the spring system assembly or fabricated into an MRE spring that replaces the conventional spring. MRE has also been used in air springs. The stiffness of the spring is varied using an electromagnet in the system that is capable of generating a wide range of magnetic field strength. An MRE tire pressure control was also proposed with an MRE component installed inside the wheel chamber. A sensor recognises changes in the tire pressure and sends signal to a control module that regulates the magnetic field produced by an electromagnet. Under the influence of the magnetic field, the stiffness and shape of the MRE component is altered, resulting a change in air cavity in the wheel chamber. MREs have also been utilised in seismic isolators to protect civil structures. The variable rheological properties of MREs allow for adaptive damping in a wide range of earthquake frequencies (Ahamed et al., 2018; Ubaidillah et al., 2014). Plate 2.1 shows several proposed applications of MREs in vibration absorption and isolation systems, a force sensor and a tuneable spring element.



(a) (b)

(c) (d)

Plate 2.1 Prototype of (a) tuned vibration absorption system using MRE, (b) MRE isolator with variable stiffness and damping, (c) MRE-based force sensor and (d) tuneable spring element (Ahamed et al., 2018)

Magnetorheological elastomer components

Matrix material

Materials for MREs matrix are mainly natural and synthetic rubbers. Among the most commonly used are natural rubber (Chen et al., 2007; Raa Khimi et al., 2015) and silicone rubber (Li et al., 2008). Other matrices include epoxidised natural rubber, polyurethane rubber (Boczkowska and Awietjan, 2008), chloroprene rubber (Chen et al., 2008), butadiene rubber (Sun et al., 2008), bromobuthyl rubber (Zhu et al., 2014) and nitrile rubber (Masłowski and Zaborski, 2012). Selected thermoplastic copolymers

(Li et al., 2012; Qiao et al., 2015) and polymer blends have also been used. As an approach in rubber recycling, Ubaidillah et al. (2016) utilised scrap tyre rubber as matrix for MRE in their work. NR has been broadly selected for its excellent mechanical properties and simple mixing process. Table 2.1 compares the physical properties of different types of rubber. Evidently, NR exhibits superior mechanical properties over synthetic rubbers, giving it a wider potential range of applications. A higher stiffness also makes NR a more advisable candidate in structural vibration control.

Table 2.1 Physical properties of common types of rubber (reproduced from (Schaefer, 2002))

ASTM designation	Natural rubber	Butadiene rubber	Styrene butadiene rubber	Butyl rubber	EPM EPDM	Chloroprene rubber	Nitrile rubber	Silicone rubber
Durometer range	30-90	40-90	40-80	40-90	40-90	30-95	40-95	30-90
Tensile max, psi	4500	3000	3500	3000	2500	4000	4000	1500
Elongation max, %	650	650	600	850	600	600	650	900
Compression set	E	G	G	G	G-E	G	G	G-E
Creep	E	G	G	G	F-G	G	G	F-E
Resilience	High	High	Med	Low	Med	High	Med-low	High-low
Abrasion resistance	E	E	E	F	G	E	E	G
Tear resistance	E	G	F	G	F	G	G	F-G

E = excellent, G = good, F = fair

Natural rubber

Since the momentous discovery of vulcanisation in 1839, rubber has gradually found extensive use in both day-to-day life and various engineering and technological fields due to its distinctive properties, especially its elasticity and capability to endure high deformation. The development of synthetic rubber has only broadened the spectrum of rubber utilisation. Today, NR is still irreplaceable in most of its applications and its potential continues to grow.

Natural rubber is a unique elastomer in that it comes from nature. The main source of NR is the sap of the tree *Hevea brasiliensis*, indigenous to the Amazon rainforest. Although archaeology has recorded the use of NR in scarce and simple applications by several cultures where it originated, it was not until the late eighteenth century that rubber became an interest in science. Since the introduction of *Hevea brasiliensis* into Asia in 1876, Southeast Asia has become a major rubber-producing part of the world, along with Sri Lanka and India. Rubber tree is also cultivated in Nigeria, Ivory Coast and several other African countries, and parts of South America with less plantation area and yield (De and White, 2001).

The *Hevea brasiliensis* sap, or latex, contains water, poly(*cis*-1,4-isoprene) as shown in Figure 2.3, and a small percentage of other components such as proteins, fatty acids and inorganic materials (De and White, 2001). The chemical composition of fresh latex is given in Table 2.2.

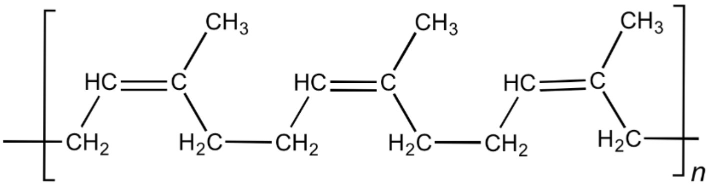


Figure 2.3 Structure of linear poly(*cis*-1,4-isoprene) (De and White, 2001)

Table 2.2 Chemical composition of fresh latex (De and White, 2001)

Constituent	Percentage
Rubber	30 – 40
Proteins	1 – 1.5
Resins	1.5 – 3.0
Minerals	0.7 – 0.9
Carbohydrates	0.8 – 1.0
Water	55 - 60

Because fresh field latex is vulnerable to bacterial attack and degradation, it requires to be processed into more stable and marketable forms of rubber. Preserved latex and concentrated latex are supplied for direct manufacturing for a number of products, such as gloves, foam, balloons, rubber bands, mattresses, elastic threads, and adhesives. Other commercial forms of raw NR include ribbed smoked sheet (RSS) and air dried sheet (ADS), pale latex crepe (PLC), and estate brown crepe (EBC), field coagulum crepe, and block rubber or TSR (technically specified rubber) (De and White, 2001).

TSR is one of the most important forms of raw NR products because of the standardised affirmation and consistency of quality that comes with its systematically specified technical parameters. In addition, its clean, economical packing that consumes less storage space and allows easier handling also makes TSR industrially attractive. TSR is produced in cubic bales weighing 33 – 35kg and wrapped in polyethylene films in corresponding colour codes specifying the rubber grades. TSR grades are designated by ASTM-specified upper limit for parameters such as dirt, ash, volatile matters, etc. Some rubber grades are given in Table 2.3.

Table 2.3 Specifications for NR grades (ASTM D2227-96) (De and White, 2001)

Property	Rubber grade				
	L	CV	5	10	20
Dirt retained on 45-micron sieve, max, %	0.05	0.05	0.05	0.10	0.20
Ash, max, %	0.60	0.60	0.60	0.75	1.00
Nitrogen, max, %	0.60	0.60	0.60	0.60	0.60
Volatile matter, max, %	0.80	0.80	0.80	0.80	0.80
Initial plasticity, P_0, min	30	-	30	30	30
Plasticity retention index, PRI, min, %	60	60	60	50	40
Colour, Lovibond scale, max	6.0	-	-	-	-
Mooney viscosity, ML (1 + 4), 100°C	-	60 ± 5	-	-	-

L: light colour; CV: constant viscosity;
The number 5, 10, 20 indicate the maximum permissible dirt content in the grade

Depending on commercial requirements, NR and NR latex can be modified physically and chemically to suit manufacturing demands for specific properties. Figure

2.4 outlines different types of physical and chemical modifications of NR.

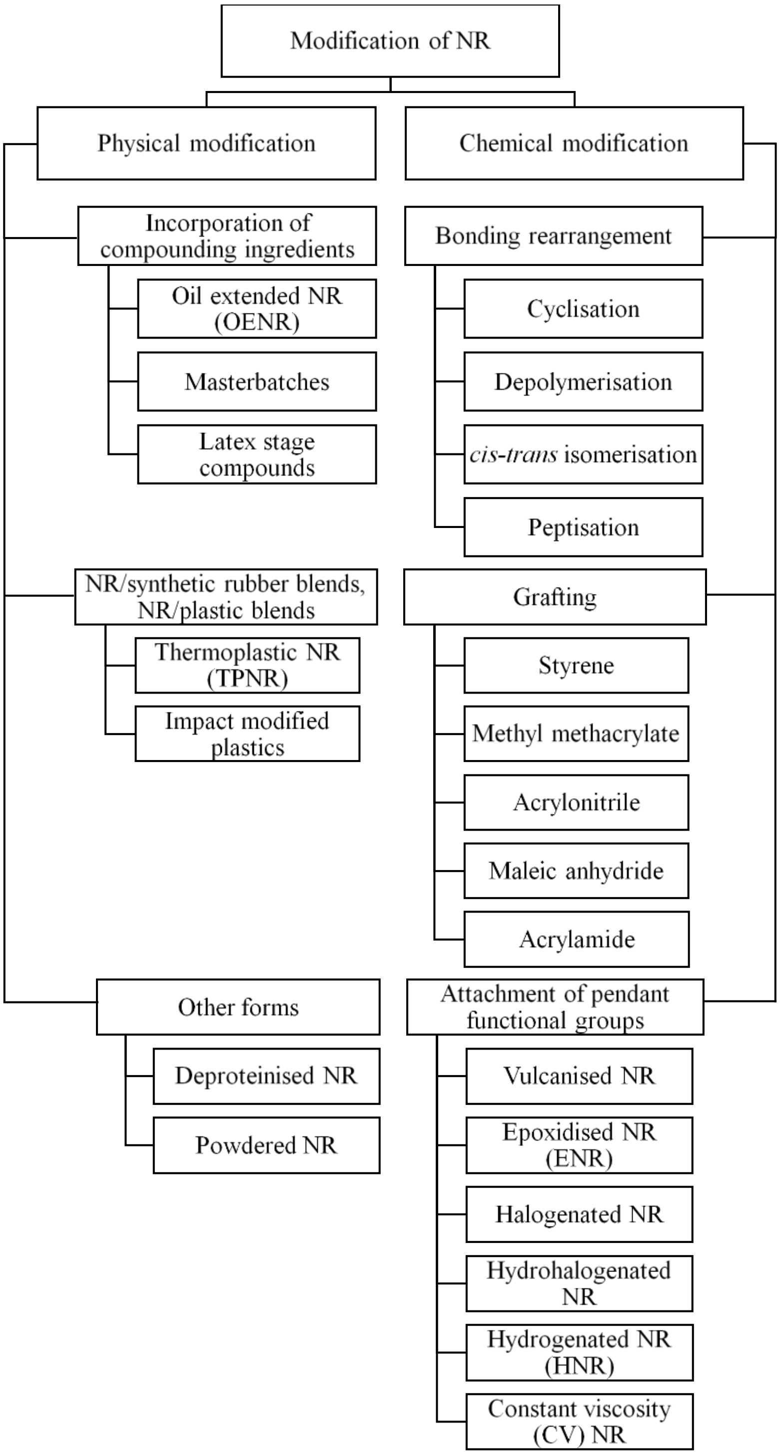


Figure 2.4 Modification methods for natural rubber (reproduced from (De and White, 2001))

Physical modification involves processes and additives that do not alter the chemical composition of rubber. Incorporation of aromatic or naphthenic oil (20 to 25 phr) into NR latex or dry NR produces oil extended natural rubber (OENR), which has good skid resistance for use in tyre tread on wet surfaces (De and White, 2001). Rubber masterbatches are made commercially available by mixing rubber, fillers, additives, insoluble sulphur and pigments at a high concentration optimised for specific final product requirements. Compounding can also be carried out on NR in latex form to make it more stable by adding appropriate ingredients according to end product specification (Hill, 2018). To customise raw rubber for specific target properties, NR are blended with other elastomers such as styrene-butadiene rubber (SBR) and butadiene rubber (BR), or with thermoplastics such as polyethylene and polypropylene. The properties of the outcome rubber blend is determined by the ratio between the components. NR latex can be deproteinised with an enzyme treatment to reduce the content of proteins and hydrophilic constituents in NR. Deproteinisation helps minimise latex allergy and moisture absorption caused by proteins and mineral components which subsequently has a negative impact on several properties like modulus, creep, stress relaxation and electrical resistance (De and White, 2001).

Chemical modification of NR induces changes in the chemical makeup of rubber through rearrangement of chemical bonds in NR, grafting of other polymers onto the rubber molecules, or incorporation of functional groups that react with NR. Cyclisation, depolymerisation and *cis-trans* isomerisation are examples of chemical modification by bonding rearrangement. These methods alter the chemical structure of NR without the incorporation of foreign atoms or molecules. A remarkable product from bonding rearrangement of NR is liquid natural rubber (LNR), resulted from depolymerisation of NR using various approaches such as mechanical scission, oxidative or photochemical depolymerisation. LNR produced via chemical approaches has a lower viscosity that allows easier processing and also possesses functional groups attached at the end of the chain during the chemical depolymerisation procedure, allowing for various applications such as viscosity modifier, adhesive, tackifier, sealing agent, plastisizer and compatibiliser in blending NR and other elastomers (Hashim and Ong, 2017). Modification by grafting involves polymerisation of one or two foreign monomers onto the allylic carbon of NR (the carbon next to the C=C bond) in latex, solid or solution form. The grafting percent decide the properties of the outcome copolymer (De and White, 2001; Hashim and Ong, 2017). Modification by attachment of functional groups has yielded some of the most important forms of chemically modified NR, including constant viscosity (CV) rubber and epoxidised natural rubber (ENR). CV rubber is produced from latex that has undergone treatment with hydroxylamine salts to help achieve a steady viscosity of the rubber throughout storage and processing. ENR is obtained by transforming the double carbon bond in NR structure into oxirane using peracid or through *in situ* epoxidation using an acid and hydrogen peroxide. Compared to NR, ENR has better damping performance, air permeability and wet grip (De and White, 2001; Hashim and Ong, 2017). Vulcanisation, further explained in 0, is the most common method of chemical modification of NR.

Raw NR is a linear polymer with long molecule chains of various lengths and average molecular weight ranging from 30,000 to 10 million, and has been found to have a glass transition temperature around -70°C. To be manufactured into end products, raw rubber requires compounding and vulcanisation, and its high tack and green strength of allow an easy compounding process. Vulcanisation improves elasticity, tensile strength, tear strength and toughness of NR (Coran, 2013). Natural rubber is outstanding in its in strength when compared to most synthetic rubbers. The maximum tensile strength of rubber is over 30 MPa, exceeding most synthetic elastomers (De and White, 2001; Long, 1985; Schaefer, 2002). Another remarkable feature of NR is its high elasticity which spans a broad range of temperature from -60°C to about 100°C. Due to the strain-induced crystallisation phenomenon, NR is able to undergo high strain. This results in low creep and low relaxation, and a long fatigue life and thus makes NR an attractive nominee in most engineering applications (De and White, 2001).Natural rubber latex gloves

Waste natural rubber latex gloves

Latex gloves are one of the most important natural rubber latex products and are often produced by the straight dipping process, in which hand-shaped positive moulds (the formers) are submerged into latex compound so that the latex can form a film attached to the formers. The formers are then dried in a heating tunnel and the upper edge of the gloves are rolled down to create a thickened and strengthened rim (beading). After that, the products are vulcanised, dipped in warm water (leaching) to loosen them for easier removal (stripping).

A large number of defects in latex gloves can occur due to the instability of the latex compounds or the faults in the manufacturing line. Mechanical damages, such as tears and rubs – areas of built up latex, can be caused by the glove formers knocking and rubbing against each other due to misalignment in close proximity, or by sharp protrusions and edges in the equipment scratching the latex film. Foreign bodies such as dirt particles or fibres, and bubbles in the latex compound can also produce defects like pinholes and blisters. Ineffective stripping can cause "flats" or "stickies", where the latex film sticks to itself. Overheating can result in many types of bead defects, such as uneven thickness of the bead (knotted bead) or roughness of the bead surface (Hill, 2018). The high quantity of defected latex gloves rejected from factories due to strict quality requirements have contributed considerably to the total amount of waste latex products (Alakrach et al., 2018; Rajan et al., 2006). Waste latex gloves, like natural rubber latex waste in general, maintain a high percentage of good-quality and only slightly crosslinked rubber hydrocarbon, which makes it a suitable source for high-quality reclaimed rubber (Rajan et al., 2006). The focus on waste gloves reclaimation has been on incorporation of waste gloves as fillers in natural rubber and synthetic elastomers as well as elastomer blends. In this approach waste gloves are usually cut by scissors or shredded using a two-roll, ground into powdered form and screened through a sieve to obtain suitable particle size (Afiratul et al., 2014; Alakrach et al., 2018; Dahham et al., 2015). Patarapaiboolchai et al. (2002) used natural rubber waste gloves powder as a filler in alcium carbonate-filled natural rubber and found that as gloves powder loading increased, scorch time and cure time decreased along with tensile strength, modulus M300, elongation at break and abrasion index while tear strength and crack growth percentage increased. Dahham et al. (2015) studied the cure characteristics, tensile and physical properties of acrylonitrile butadiene rubber filled with natural rubber waste gloves powder. They reported a decrease in scorch time and cure time and an increase in hardness with increasing waste glove powder loading. Their results also suggested that fine size of waste glove powder (300 – 700 µm) resulted in better curing characteristics, tensile properties and hardness compared to coarse size, and optimum tensile properties were achieved with 20 phr waste glove powder. Afiratul et al. (2014) found that in epoxidized natural rubber compounds filled with recycled latex glove powder, highest tensile properties were achieved by with 15 phr glove powder and that with fine size (300 – 700 µm), tensile strength and tensile modulus were better enhanced compared to coarse size.

Rubber compounding

Rubber compounding is necessary in improvement of the properties of raw rubber, including mechanical properties, aging and oxidation resistibility, among others. Compounding process involves the mixing of rubber and other chemicals and additives with the appropriate loading. The properties of the rubber compound and the end products are heavily influenced by the chemicals introduced during the compounding process. Selection and dosage of additives are based on many facets of manufacturing, such as application requirements, costs, environmental concerns and health safety. A typical formulation of a rubber compound includes: rubber, activators, plasticiser, fillers, accelerators, and crosslinking agent. The content of each ingredient is measured in parts per hundred rubber (phr), with rubber content measured at 100 phr. Table 2.4 shows some typical types of additives in a rubber compounding formula with their respective function and some examples of chemicals commonly used as compounding additives.

Vulcanisation

Vulcanisation is the process of producing crosslinks between rubber chains, through which the rubber compound from a soft and tacky material becomes strong and elastic due to a three dimensional linked polymer network. Sulphur vulcanisation system is the most commonly used for unsaturated rubbers like NR. The crosslinking process involves a sequence of reactions as illustrated in Figure 2.5. First, the ring structure of sulphur is divided into small portions of reactive polysulphide S_x and react with activator and accelerator to form active sulphurating agents S_x—A, with x usually varying from two to eight. The active sulphurating agents then react with the allylic hydrogens in rubber, which are the hydrogens bonded the carbon next to the C=C bond.

After the allylic hydrogen atom is subtracted from the rubber chain, a polysulphidic rubber-bound intermediate is formed, with the initial crosslinks between the rubber molecule chains. These initial crosslinks may then be shortened dependent of the vulcanisation time and temperature, and the accelerator-to-sulphur ratio. The ratio of accelerator to sulphur also affects the number of crosslinks formed in the rubber network. An efficient vulcanisation (EV) system, with a high accelerator-to-sulphur ratio, results in a final network with more monosulphide crosslinks. In contrast, in a conventional vulcanisation (CV) system with a low accelerator-to-sulphur ratio, more polysulphide crosslinks are produced along with some di- and monosulphide crosslinks (Sethuraj and Mathew, 1992).

Table 2.4 Common additives used in rubber compounding (reproduced from (Raa Khimi, 2015))

Additive	Function	Examples
Crosslinking agents	Form crosslinks between rubber chains	• Sulphur • Peroxides • Dithiomorpholine (DTDM) • Caprolactam disulphide (CLD)
Activators	Improve the crosslinking efficiency of the vulcanisation system	• Zinc oxide or magnesium oxide • Stearic acid
Accelerators	Increase the reaction rate between the crosslinking agent and rubber	• N-cyclohexylbenzothiazole- 2-sulfenamide (CBS) • Tetramethyl thiuram disulphide (TMTD) • 2-mercaptobenzothiazole (MBT)
Antidegradants	Reduce the rate of aging caused by the environment, chemicals, and aging during service	• 2,6-di-t-butyl-p-cresol (BHT) • Hydroquinone derivatives • Tris(nonylphenyl)phosphite (TNP)
Plasticisers	Lower the viscosity of rubber and allow easier processing	• Naphthenic oil • Paraffin oil