STUDY OF NANO – ZINC OXIDE AS RUBBER ADDITIVES

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ABSTRACT

In this research work, application of nano-ZnO as a rubber additive was explored using NR as a model rubber. Comparative study between nano-ZnO and conventional ZnO was carried out. Standard rubber formulas were compounded by using a two – roll mill and shaped into samples by using compression molding technique. Then, several properties of rubber were characterized including were characteristics (i.e., scorch time (t_{s2}), cure time ($t_{c(90)}$), CRI, and M_{HF}), mechanical properties (i.e., tensile strength, % elongation at break, rubber modulus (M100)), aging properties (i.e., QUV testing) and thermal properties (DMTA). In this work, some factors affecting rubber properties were studied, such as, ZnO loading (1-5 phr), effects of silane coating (KBE 603 and KBM 403), etc. It was found that with increasing nano-ZnO loading, the rubber vulcanizates were increased in cure time ($t_{c(90)}$) and scorch time (t_{s2}). Especially, coated nano-ZnO with silane KBM 403 had the most delayed cure characteristics. Mechanical properties of vulcanizates mixed with different ZnO were quite similar. This might be attributed to poor distribution of nano-ZnO in rubber vulcanizates. Since nano-ZnO has very small particle sizes and high surface area, it tends to agglomerate yielding similar results compared to conventional ZnO. In DMTA tests Tg from tan δ peak of the nano-ZnO mixed rubber was found to be similar to that of the conventional ones. However, in QUV aging tests, it was found that nano-ZnO had better UV resistance than conventional ZnO.

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Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Rational and Research Motivation

Nanotechnology is a technology that concerns material synthesis or equipment in atomic levels, molecular levels or small particle sizes covering range between 1 to 100 nanometer [1]. In nanotechnology, nanoparticle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to sizes: In terms of diameter, fine particles cover a range between 100 and 2500 nanometers, while ultrafine and nanoparticles, on the other hand, are sized between 1 and 100 nanometers. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles [2].

Nanocomposites are a new class of composites in which the reinforcing phase dimensions are in the order of nanometers. Because of their nanometer size characteristics nanocomposites possess superior properties than conventional microcomposites, such as, electronic properties, optical properties, magnetic properties, chemical properties, mechanical properties, thermal properties, etc [3].

Nanoadditives are very small additives (nanometer (10^{-9} m) or sub-micron in size), such as nano-clay (organo-clay or modified clay), nano-ZnO, nano-$CaCO_3$, nano-Silica, nano-Silver. They have low percent loading (1-5%) due to large surface area (small in size), increase in mechanical properties (e.g. tensile strength and modulus due to reinforcing effects) and also improved gas and water barrier properties (due to alignment of additives) [3].

In this research work, application of nano-ZnO as a rubber additive was explored using NR as a model rubber. Comparative study between conventional ZnO and nano-ZnO was carried out. Standard rubber formulas were compounded by using a two – roll mill and shaped into samples by using compression molding technique. Then, several properties of the rubbers were characterized including cure characteristics (i.e., scorch time (t_{s2}), cure time (t_{c90}), CRI, and M_{HF}) and mechanical properties (i.e., tensile strength, % elongation at break, rubber modulus (M100)), aging properties (i.e., QUV testing) and thermal properties (DMTA). In this work, some factors affecting rubber properties were studied, such properties as, ZnO loading (1-5 phr), effects of silane coating (KBE 603 and KBM 403), etc.

1.2 Objectives

This research work focused on comparative study between conventional ZnO and nano-ZnO in order to use ZnO as an additive in rubber industries. Some parameters affecting rubber properties were studied, such as, ZnO loading, types of ZnO, effects of coating, etc.

1.3 Scopes of Study

This project can be divided into several sections as following:

1. Literature reviews of theories and publication involved this research
2. Raw materials were compounded using a two-roll mill. The compound samples were tested for:

   - Mooney viscosity (ML1+4 (100°C))

   - Cure characteristics (i.e., scorch time (t_{s2}), cure time ($t_{c(90)}$)), Cure Rate Index (CRI) and plateau modulus (M_{HF}).
3. Rubber vulcanized samples were prepared by using compression molding technique.
4. Several properties of the samples were characterized, such as,

   - Mechanical properties, i.e., tensile strength, % elongation at break, rubber modulus (M100, M200, M300), hardness shore A, etc.

   - Aging properties by QUV Accelerated Weathering Testers

   - Thermal properties by DMTA
5. Some factors affecting rubber properties were studied, such as,

   - ZnO loading (1-5 phr)

   - Types of ZnO

   - Effects of ZnO coating (KBE 603 and KBM 403 silane coating)

1.4 Expected Results

1. To promote domestic nano-ZnO industries in Thailand.

2. Knowledge giving from this work can be applied to others.

Chapter 2

Theory and Literature Reviews

Rubber or elastomers are classified as natural and synthetic rubbers, such as, natural rubber (NR), styrene butadiene rubber (SBR), butadiene rubber (BR), chloroprene or neoprene (CR), nitrile rubber (NBR), butyl rubber (IIR) and etc. By definition, rubbers can be extended very easily after receiving force and then can be returned to their original dimension when the force is not applied. They also have low energy absorption, which can prevent heat buildup. In addition, some types of rubbers exhibit low water and gas permeation. From those properties that make rubbers are very versatile in many industries, such as, rubber tires, automobile part, rubber flooring, and rubber glove.

Usually, natural and synthetic rubbers perform low strength, tackiness, and unstable dimension. They become stiff and brittle at low temperatures and very soft and sticky at high temperatures that make rubber exhibits a limitation of service temperature. Thus the invention of vulcanization overcame these problems and allowed the development of many new uses. The vulcanization is a process for crosslink the polymer chains by the reaction with vulcanization agents to form three-dimensional structures. This reaction transforms soft, weak plastic-like material to strong elastic products. The rubber losses its tackiness and becomes insoluble in solvents. It is more resistant to deterioration by heat, light and aging processes [4].

2.1 Natural Rubber (NR) [5]

Natural rubber was first used by the indigenous peoples of the Amazon basin for a variety of purposes. The best source of latex, the milky fluid from which natural rubber products were made, is *Hevea brasiliensis*, which grew predominantly in the Brazilian Amazon. Natural rubber trees are shown in Figure 2.1.

Figure 2.1 Natural rubber trees [5]

Natural rubber (NR) is a polymer called "cis-1, 4 polyisoprene" that has very high molecule weight, broad molecule weight distribution and also low glass transition temperature (Tg about -73°C). Chemical structure of natural rubber is shown in Figure 2.2 [6].

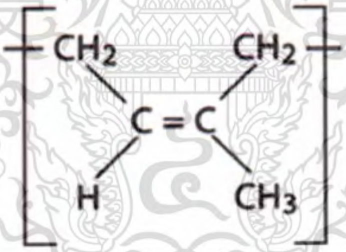


Figure 2.2 Chemical structure of natural rubber [6]

The properties of natural rubber are high green strength, excellent mechanical strength under severe deformation, high resilience, susceptible to mechano-chemical degradation upon shearing, poor weather resistance and etc [7]. To support data in this Tables 2.1 and 2.2; showing trend in export, products and processing of rubber in Thailand in 2006-2009 [8].

Table 2.1 Export and rubber products of Thailand in 2006-2009 [8]

Table	2006	2007	2008	%increase/decrease(-)	
				2007	2008
Rubber	205,483	194,339	223,628	-5.42	15.07
Rubber products	117,270	125,961	149,914	7.41	19.02
Rubber wood products	28,274	28,650	29,404	1.33	1.36
Total	351,027	348,950	402,528	-0.59	15.37

Source: Update from information and communication technology center ministry of commerce Thailand.

Table 2.2 Production of natural rubber in 2006-2008 [8]

Country	2006	2007	2008	%increase/decrease(-)	
				2007	2008
Thailand*	3137.0	3056.0	3089.8	-2.58	1.11
Indonesia	2637.0	2755.2	2824.0	4.48	2.50
Malaysia	1283.6	1199.6	1077.9	-6.54	-10.15
India	853.3	811.1	879.8	-4.95	8.47
Vietnam	555.4	601.7	662.9	8.34	10.17
China	533.0	600.0	638.0	12.57	6.33
Côte d'Ivoire	178.3	188.5	194.5	5.72	3.18
Liberia	100.3	105.5	81.0	4.98	-23.22
Sri Lanka	109.2	117.5	125.7	7.60	6.89
Others	313.7	290.9	368.4	-7.27	26.64
Total	9701.0	9726.0	9942.0	0.26	2.22

Source: IRSG rubber statistical bulletin, Jan-Mar 2009

2.2 Zinc Oxide [9]

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the earth crust as a mineral zincite. However, most ZnO used commercially is produced synthetically.

2.2.1 Chemical and Physical Properties of Zinc Oxide [10]

Zinc oxide (ZnO) occurs as white powder known as zinc white or as the mineral zincite. The mineral usually contains a certain amount of manganese and other elements and is of yellow to red color. Crystalline ZnO is thermo chromic, changing from white to yellow when heated and in air reverting to white on cooling.

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rock salt. The wurtzite structure is most stable at ambient conditions and thus most common. Wurtzite structure is shown in Figure 2.3. Typical properties of ZnO are given in Table 2.3.

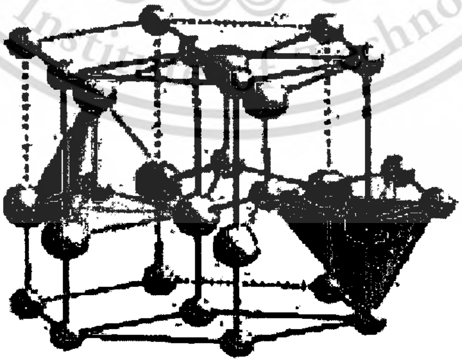


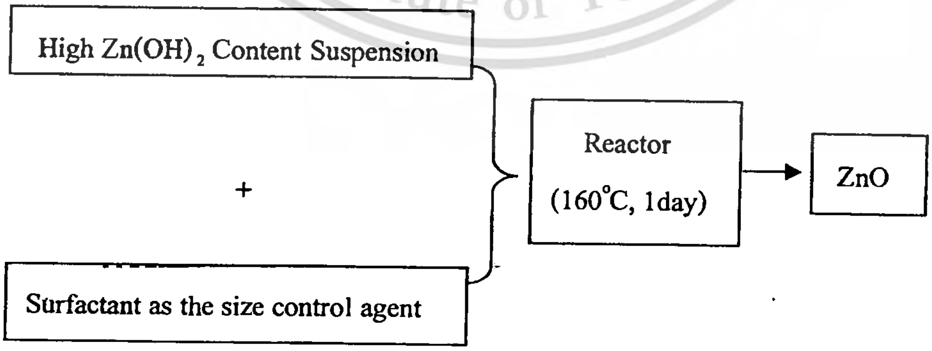
Figure 2.3 Wurtzite structure [10]

Table 2.3 Typical properties of ZnO [10]

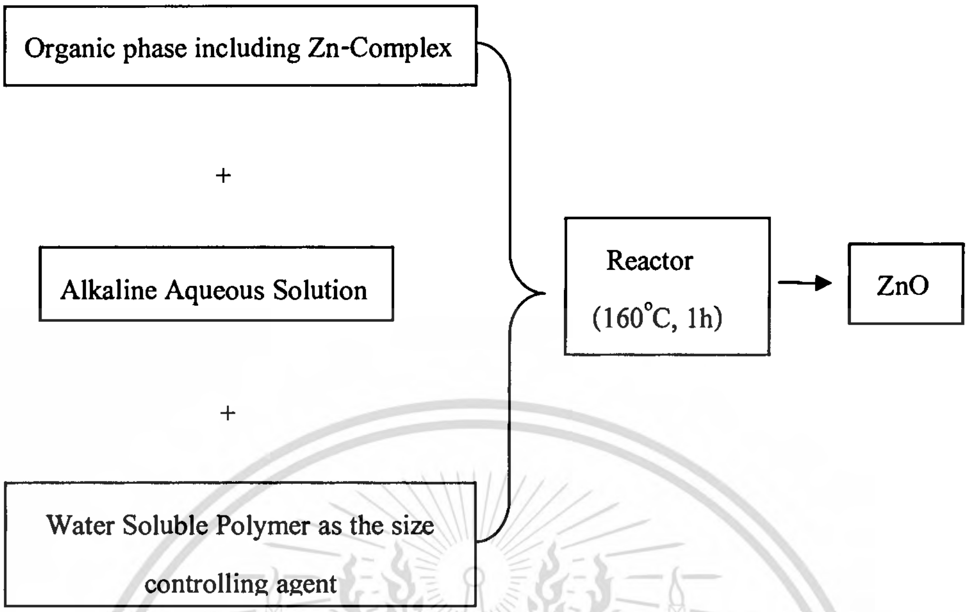
Properties	
Molecular formula	ZnO
Molar mass	81.408 g/mol
Appearance	White solid
Odor	Odorless
Density	5.606 g/cm^3
Melting point	1975 °C (decomposes)
Boiling point	2360 °C
Solubility in water	0.16 mg/100 mL (30 °C)
Refractive index (n_D)	2.0041

2.2.2 Preparation Method of Zinc Oxide Particles [11]

1) Method 1 Gel-Sol Process.



2) Method 2 Solvent Extraction-Hydrothermal Process.



Method 1

ZnO particles of narrow size distribution could be obtained with high yield.

Size of the particles could be controlled by the amount of surfactants.

Method 2

ZnO particles (20nm～100nm) of narrow size distribution could be obtained.

Size of the particles could be controlled with the amount of polymeric additives.

Figure 2.4 Different size distributions of ZnO particles [11]

2.2.3 Applications of Zinc Oxide [12]

The applications of ZnO powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, ZnO has high refractive index, good thermal, binding, antibacterial and UV-protection properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc.

For rubber manufacture about 50% of ZnO use is in rubber industry. ZnO along with stearic acid activates vulcanization, which otherwise may not occur at all. ZnO and stearic acid are ingredients in the commercial manufacture of rubber goods. A mixture of these two compounds allows a quicker and more controllable rubber cure. ZnO is also an important additive to the rubber of car tires. Vulcanization catalysts are derived from ZnO, and it considerably improves the thermal conductivity, which is crucial to dissipate the heat produced by the deformation when the tyre rolls. ZnO additives also protect rubber from fungi and UV light.

2.3 Nanotechnology [13]

Nano is a prefix of a Greek word representing one-billionth of something. Nanometer means one billionth of a meter that corresponds to 1/50,000 of the diameter of a human hair. Nanotechnology today is growing very rapidly and has infinite applications in almost everything. Nanocomposites generally include one or several types of nanoscale particles dispersed within a polymer matrix. The benefits of nanoparticles are derived from the surface area interactions of the nanoparticles with the polymer matrix. The nature of this interaction allows for beneficial property improvements, sometimes using fillers at very low loading levels, often as low as about 1 to 10 weight percent. The possibility of using lower loading levels reduces concerns relative to a reduction of tack often resulting from the addition of filler to the adhesive or coating. The lower loading levels also increase the potential for homogeneous dispersion of the filler within the composite matrix.

2.4 Nano-Zinc Oxide [14]

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has drawn increasing attention in recent years due to its many significant physical and chemical properties, such as chemical stability, low dielectric constant, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide, intensive ultra-violet (UV) and infrared (IR) absorption. Therefore, nano-ZnO can be potentially applied to catalysts, gas sensors, semi-conductors, varistors, piezoelectric devices, antibacterial and bactericide. The introduction of nano-ZnO into polymers could improve the mechanical and physical properties of polymer owing to their small size, large specific area and a strong interfacial interaction between the organic polymer and inorganic nanoparticles, respectively. Consequently, these nanocomposites could be widely applied in coatings, rubbers, plastics, sealant, fibers and other applications. Nano-ZnO dispersion is shown in Figure 2.5 [15]. Physical and chemical properties of nano-ZnO are given in Table 2.4 [16].

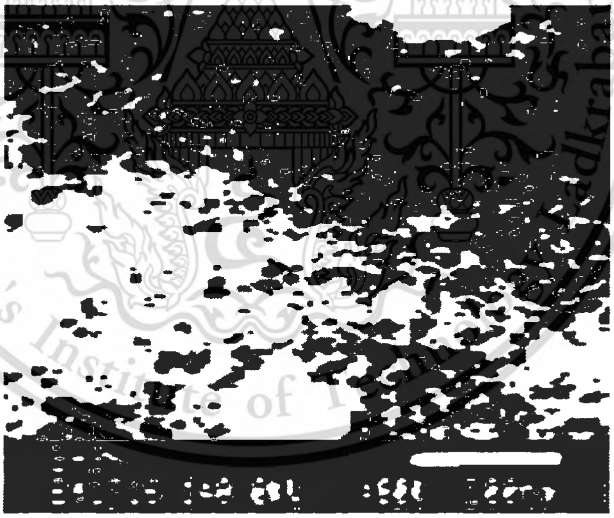


Figure 2.5 Nano-ZnO dispersion [15]

Table2.4 Physical and chemical properties of nano-ZnO [16]

Product Name	ZoNoP (Zinc Oxide Nanoparticles)	
Molecular Formula	ZnO	-
Molecular Weight	81.39	g/mol
Appearance	White powder	-
Crystal Phase	Zincite (Hexagonal)	-
Purity	99.5	%
Average Particles Size	20 – 40	Nm
Specific Surface Area	26.22	m^2/g
Bulk Density	0.14	g/cc
True Density	5.6	g/cc
P.H	7.8	-
Boiling Point	-	°C
Melting Point	1,975	°C

2.4.1 Applications of Nano-Zinc Oxide [17]

Nano-ZnO is currently being used to make nano-textiles (self-cleaning, anti-germ, UV-protected), photo catalysts (kill germs), light sub states, cosmetics, UV sunscreens, copy toners and specialty polymers/rubbers. Micron-sized ZnO is the traditional ZnO that is heavily used in rubber, varistors, talcum powder, ferrites, paint pigments, ceramics and animal food. For industrial application as below [18];

- Animal feedstuffs and drugs: The feedstuffs that contain nano-ZnO deliver much better effect than those with micronized ZnO do, along with other benefits, such as higher absorption rate and less required dosage.
- Rubber industry: Nano-ZnO is the most effective inorganic surfactant and sulfurizing accelerator, featuring faster sulfurizing and wider temperature ranges, which will lead to faster transformation into zinc sulfide and thus more efficient production of anti-abrasion rubber.
- Ceramics industry: Ceramic industry is widely using ZnO as white dyestuff. With nano-ZnO, ceramic ware sintering temperature can lower to 400~600°C, yet surface is burned as polishing as a mirror.

- Textile industry and commodity chemical industry: Producing deodorant, antibacterial, FIR and UV-blocking fiber.
- Painting Industry: Nano-ZnO is a new-type of anti-static agent. Putting semi-conductive nano-ZnO into resin can result in better static shielding.

2.5 Silanes [19]

Organofuction silanes are the best known coupling agents, and their effect is based on their special structures: X-$(CH2)_n$-Si $(OR)_3$, where X represents an organofunctional groups (e.g., amino, vinyl, epoxy, methacryl) that is responsible for the compatibility to the polymer matrix. The OR-group mostly based on their methoxy or an ethoxy group, which is hydrolyzeable and provides chemical (condensation) or physical bonding (hydrogen bonds) to the filler surface. Structure of silane is shown in Figure 2.6.

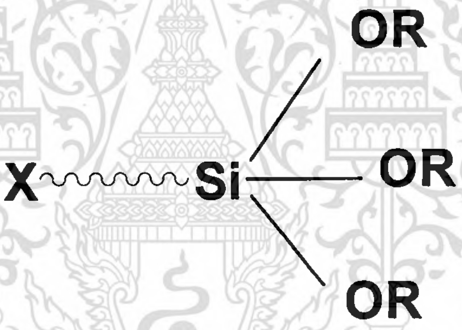


Figure 2.6 Structure of silane coupling agent [20]

Silanes are especially applicable for glass fibers, metal hydroxides, silica, and silicates. However, to cover the optimum performance much more than a monolayer is required because the coating in practice consist of a mixture of physisorbed and chemisorbed material and/or self-condensed polymeric layers. While the effectiveness of silanes in thermosets, rubbers, and polar thermoplastic is quite high, there is almost no interaction with unreactive polymers likes polyolefins. However, in some cases, silanes - treated fillers used in PP and PE to improve dispersion or to reduce water adsorption. The most common silanes and their applications are listed in Table 2.5.

Table 2.5 Silanes and their applications. [19]

FUNCTIONAL GROUP	THERMOSETS	THERMOPLASTICS	RUBBERS
AMINO	MF, PF, PU, EP	PVC, PE, PP, PS, PA, PC, PBT, PPO, PPS, PSU	SILICONE RUBBER
EPOXY	EP, PU, MF, PF	ABS, PET, PS, PVAC	NBR, EPDM, BR
VINYL	UP	PS, EVA, PE, PP	EPDM
METHACRYL	UP, DAP, ACRYLICS	PS, ABS, PE, PP	BR

Silane coupling agents contain at least two different reactive groups within their molecules. One of these functional groups forms chemical bonds with inorganic materials, and the other forms chemical bonds with organic materials. This property enables silane coupling agents to function as intermediaries in bonding organic materials to inorganic materials, which normally tend not to bond with each other.

Silane coupling agents are usually diluted with water to a concentration of approximately 0.1 to 2.0 %. With silane coupling agents that have low solubility in water, a combination of 0.1 to 0.2 % of acetic acid in water or water-alcohol (acetic acid, water, and alcohol together) is recommended. Acetic acid is used to increase the hydrolysis rate improve the stability of the silanols. Depending on the resin or on the filler treatment method, silane coupling agents are sometimes not prepared as solutions [21].

1) Preparation Method for Silane Coupling Agent Solutions

(1) Prepare water solution containing 0.1 to 2.0 % acetic acid.

The concentration of the acetic acid can be reduced if the silane coupling agent has good solubility with water. There is no need to add acetic acid in the case of aminosilanes.

(2) Mix the acetic acid solution thoroughly while dropping the silane coupling agent.

The usual concentration of silane coupling agent is between 0.1 and 2.0%. The mixing should be done as fast as possible without splashing. If the coupling agent is dropped too quickly, it will not disperse adequately in the solution and larger amounts of gel will form.

(3) After the coupling agent has been added, continue attiring for 30 to 60 minutes.

The hydrolysis of the silane is complete when the solution has become nearly transparent.

(4) Filter the solution if necessary.

Filtration is recommended if there are noticeable insoluble materials or suspended solids in the solution. If the silane solution is to be used continuously, then circulating filtration by using a cartridge with a pore size.

2) Method for Treating Powders

(1) Dry Method

A high speed mixer is used to disperse the silane coupling agent into the organic materials. The silane is applied either neat or as a concentrated solution.

Although uniform treatment is more difficult with this method, it is widely used in industry because it enables the treatment of a large amount of filler in a relatively short time. Dry method is shown in Figure 2.7.

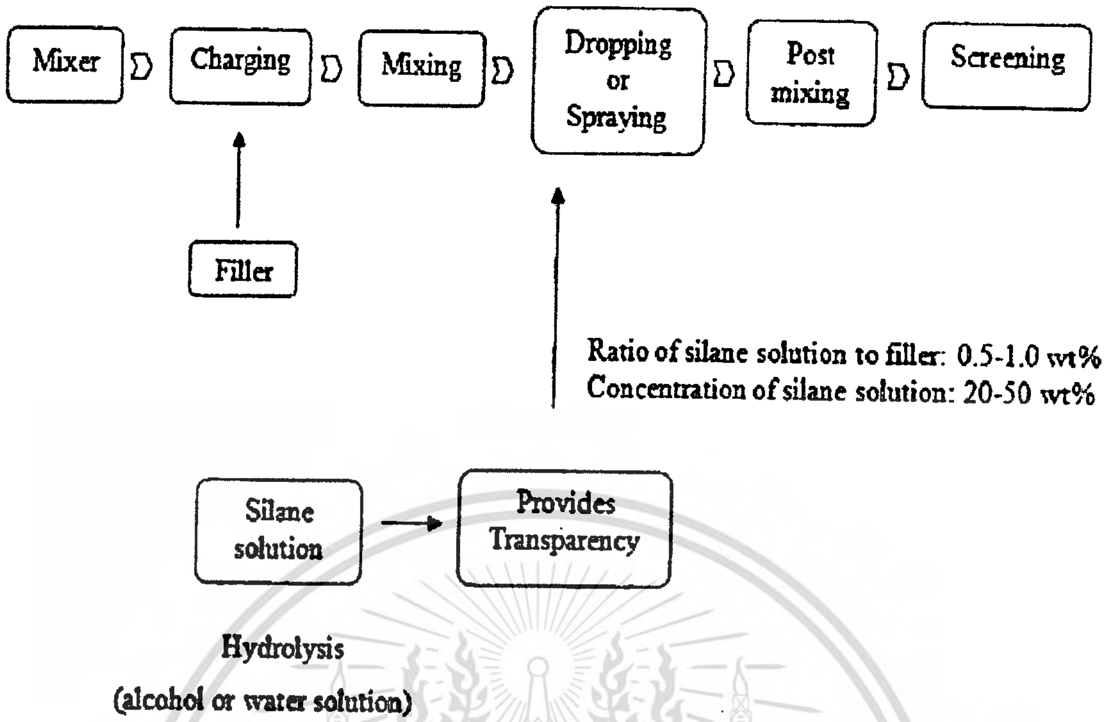


Figure 2.7 Dry method for silane coupling agent solutions [21]

(2) Wet Method

The surface of the material can be treated very uniformly and precisely by mixing a slurry of the inorganic material in a dilute solution of the silane coupling agent or by immersing the material directly into the solution. Wet method is shown in Figure 2.8.

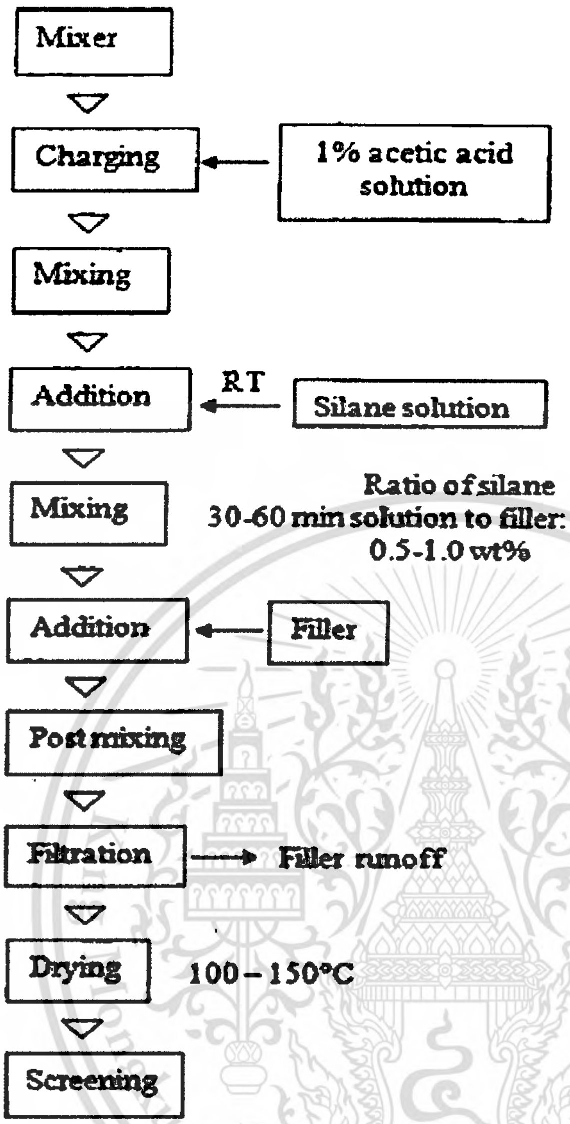


Figure 2.8 Wet method for silane coupling agent solutions [21]

3) Solubility with Water

When the alkoxysilyl group in silane coupling agents dissolves in water, it forms a silanol group that is not stable and will condense over time to form a gel-like siloxane structure.

A silanol group is usually unstable in the presence of water, but it is more stable in weakly acidic solutions. Aminosilanes are an exception because the amino group helps to stabilize the silane in water solution.

The storage stability of the solution can be improved by adjusting the pH to between 4 and 5, by adding alcohol, and by storing the solution below room temperature.

2.5.1 Coated Nano-Zinc Oxide with Different Types of Silane [19]

Typical properties of silane coupling agents are given in Tables 2.6-2.7.

Table 2.6 Typical properties of silane (KBM 403) coupling agents [19]

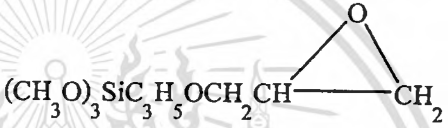
Typical properties	Detail
Functional Group	Epoxy
Product Name	KBM 403
Chemical Name	3-glycidoxypropyl trimethoxysilane
Structure Formula	
Molecular Weight	236.3
Specific Gravity (25°C)	1.07
Refractive Index (25°C)	1.427
Flash Point (°C)	149
Boiling Point (°C)	290
Minimum covering Area,m^2/g	330
UN Hazardous Classification	NONE
Existing Substances No.	2-2071
CAS No.	2530-83-8

Table 2.7 Typical properties of silane (KBE 603) coupling agents [19]

Typical properties	**Detail**
Functional Group	Amino
Product Name	KBE 603
Chemical Name	N-2(aminoethyl)3-aminopropyl triethoxysilane
Structure Formula	$(C_2H_6O)_3SiC_3H_5NHC_2H_4NH_2$
Molecular Weight	264.5
Specific Gravity (25°C)	0.97
Refractive Index (25°C)	1.438
Flash Point (°C)	123
Boiling Point (°C)	135/5mmHg
Minimum covering Area,m^2/g	295
UN Hazardous Classification	NONE
Existing Substances No.	2-2059
CAS No.	5089-72-5

2.6 Rubber Compounding and Vulcanization [22]

In order to develop the utilization of rubber normally, the compounding of rubber is required. The various ingredients to be used are complied into a recipe. Every recipe contains a number of components, which have a specific function in the processing. Typical rubber recipe usually consists of the following chemicals:

1. Elastomers are in forms raw rubbers, Natural rubber (NR) – Rib smoke sheet (RSS3), etc.
2. Vulcanizing agent is used to react with rubber in order to change rubber from linear chain (thermoplastics) into 3-D network (Thermosets) e.g., sulfur (S_8), peroxide, metal oxide, etc.
3. Accelerators are used to act as catalysts to increase efficiency of curing reaction, i.e., rate of vulcanization and control scorch time (t_{s2}) and cure time (t_{c90}) (or vulcanization time), e.g., Tetramethyl thiuram disulfide (TMTD), Mercaptobenzothiazole disulfide (MBTS), CBS, etc.
4. Activators are used to work together with accelerators and so called accelerator – activators in vulcanization reaction to increase cross-linking efficiency. The most popular activators are "ZnO + Stearic acid".
5. Fillers are used to reduce to cost (fillers are cheaper than rubbers). Some fillers can increase strength of rubber so called reinforcement, e.g., carbon black (CB), silica, etc.
6. Processing aids are used to help processability, e.g., naphthanic oil, etc.
7. Antidegradants or Age – resistors are antioxidants, antiozonants and other materials used to reduce aging processes in vulcanizates.
8. Plasticizers or softeners are used in hard rubbers to increase flexibility and softness of rubbers, e.g., polyethylene glycol (PEG), etc.
9. Lubricants are used to reduce friction between machines and rubbers, e.g., polyethylene glycol (PEG), etc.
10. Miscellaneous ingredients e.g.
    - Retarders – to reduce premature vulcanization, longer storage time of uncured compounds
    - Colorants
    - Blowing agents – to create cellular structure (rubber foam)
    - Odorants - to reduce unpleasant odors
    - Tackifiers - to increase tackiness at rubber surfaces

2.6.1. Rubber Mixers [22]

Rubber Mixers: to mix rubber and its additives homogenously, so as known as "Two – roll mill". This mixer needs high shear stress to get good dispersion and good distribution, but disadvantage of two-roll mill machine such as open machine (due to high dispersion for mixer), high human action to cut and fold. Two-roll mill is shown in Figure 2.9.

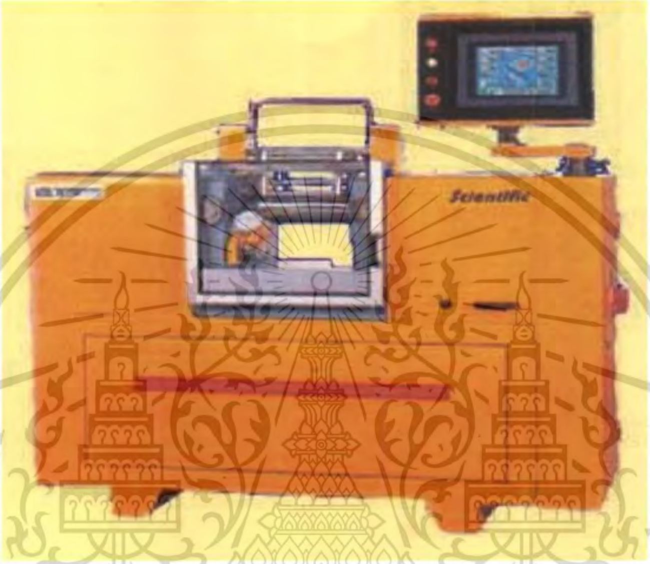


Figure 2.9 Two-roll mill machine [23]

2.6.2 Mooney Viscometer [24]

Mooney Viscometer is used for measuring viscosity and relaxation of base rubber, raw rubber stock or rubber mass pre-vulcanization properties, it is also used for measuring viscosity in Mooney value for compounded or uncompounded unvulcanized natural, synthetic or regenerated rubber. Mooney viscosity (MV) is dimensionless in a range of 0 – 200. Therefore MV is normally used for "quality control (QC)" to monitor materials, e.g., incoming raw rubbers and in - process compounds. For Mooney Viscosity (MV) is similar to ODR or MDR, but the disc is "rotored" at 2 Hz (2 rpm) and measure the torque (convert to Mooney Viscosity) Measurement of viscosity by using mooney viscometer is shown in Figure 2.10.

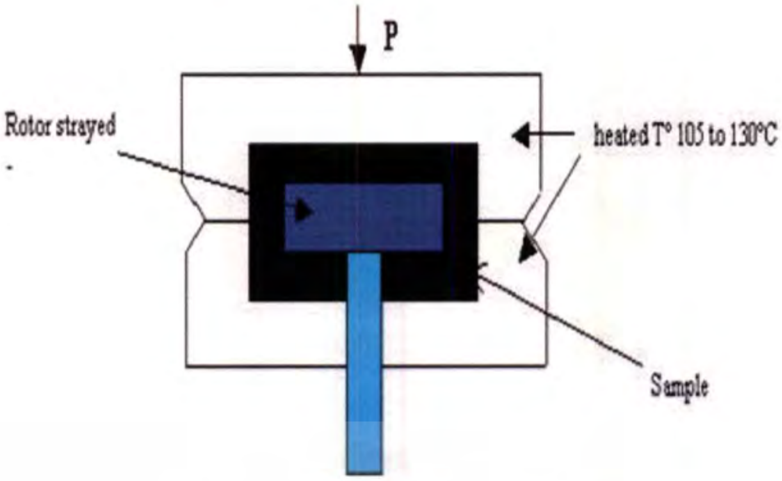


Figure 2.10 Measurement of viscosity by using Mooney Viscometer [24]

2.6.3 Curemeter for Rubber Compounds [22]

1). Oscillating Disc Rheometer (ODR)

ODR disc is covered by compound inside the cavity and heated at curing temperature (150 – 170 °C). The disc is oscillated at 1, 3, or 5 degree. The torque required to oscillate is monitored with time to get the "cure curve" Oscillating disc rheometer is shown in Figure 2.11. Cure curve from Curemeter (ODR) is shown in Figure 2.12.

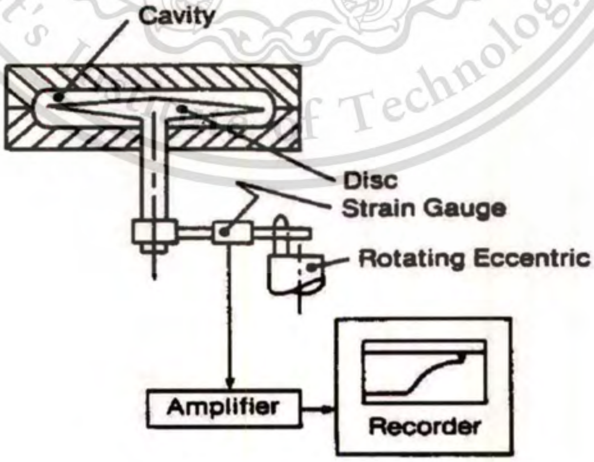


Figure 2.11 Oscillating Disc Rheometer machine [22]

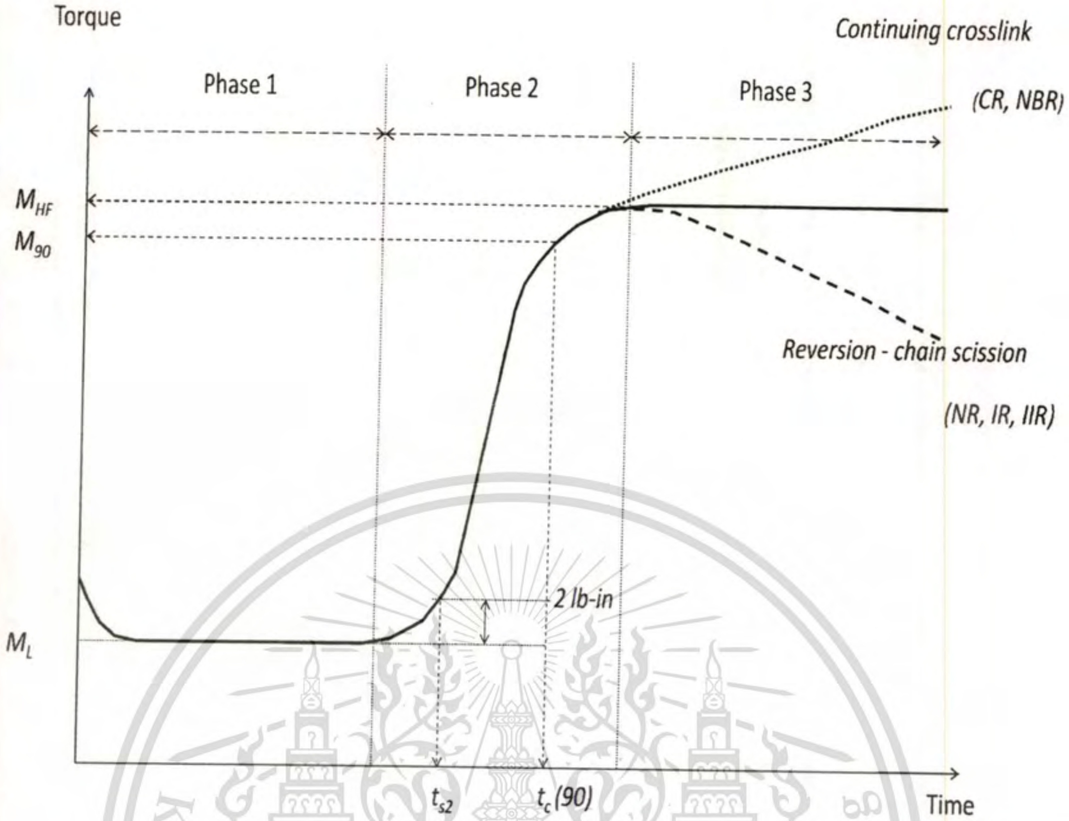


Figure 2.12 Cure curve from Curemeter (ODR) [22]

The ASTM definition of indicated values are as followed;

M_L = minimum torque

M_{HF} = plateau torque (plateau modulus)

t_{s2} = scorch time (time for torque rise 2 torque unit (lb-in, N.m, kgf.cm) above minimum torque)

$t_{c\ (90)}$ = time to reach M90 (optimum cure time (by Monsanto)).

$$M_{90} = M_L + 0.9\,(M_{HF} - M_L)$$

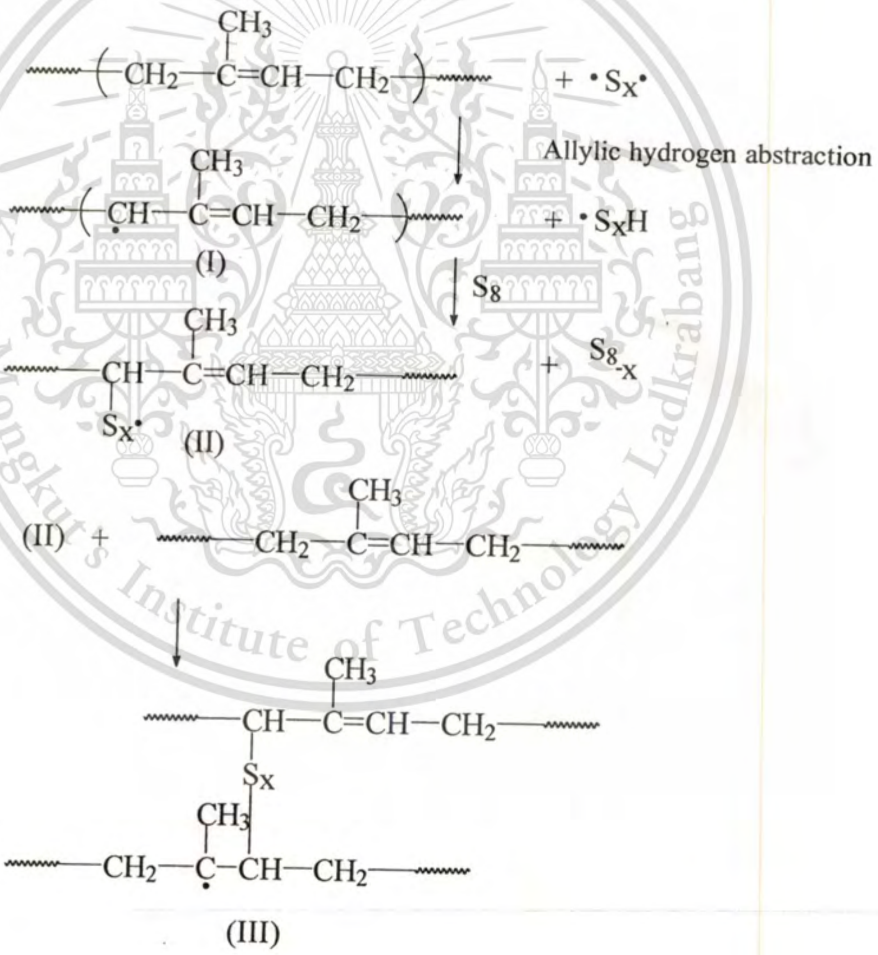
$$\text{Cure rate index (CRI)} = 100 / (t_{c(90)} - t_{s2})$$

2.6.4 Vulcanization [22]

Vulcanization transforms elastomer from a high MW liquid into an elastic solid by chemically linking elastomer chains to form an "infinite" network, resulting in modulus increase, elasticity increases, strength increases, hysteresis decreases, permanent set decreases, etc.

1). Crosslinking Mechanism

Sulfur ring $\longrightarrow$ $\cdot S_x\cdot$ is free radical mechanism



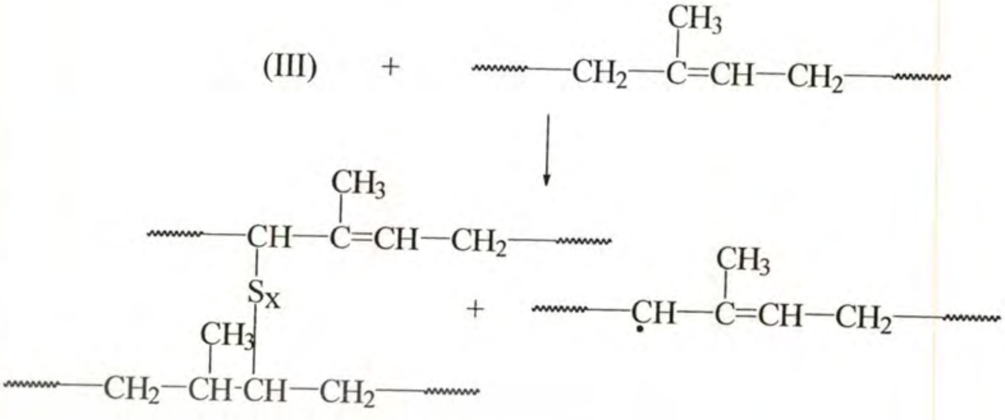


Figure 2.13 Crosslink mechanism of sulfur curing agent [22]

2) Crosslinking Mechanism of S curing with S and Accelerator / Activator

In crosslinking mechanism by using sulfur/accelerator/activator, ZnO reacts with stearic acid to get zinc stearate (a form of soluble Zn^{2+} ions in rubber) that acts as an activator to help breaking sulfur-accelerator bonds is shown in Figure 2.14.

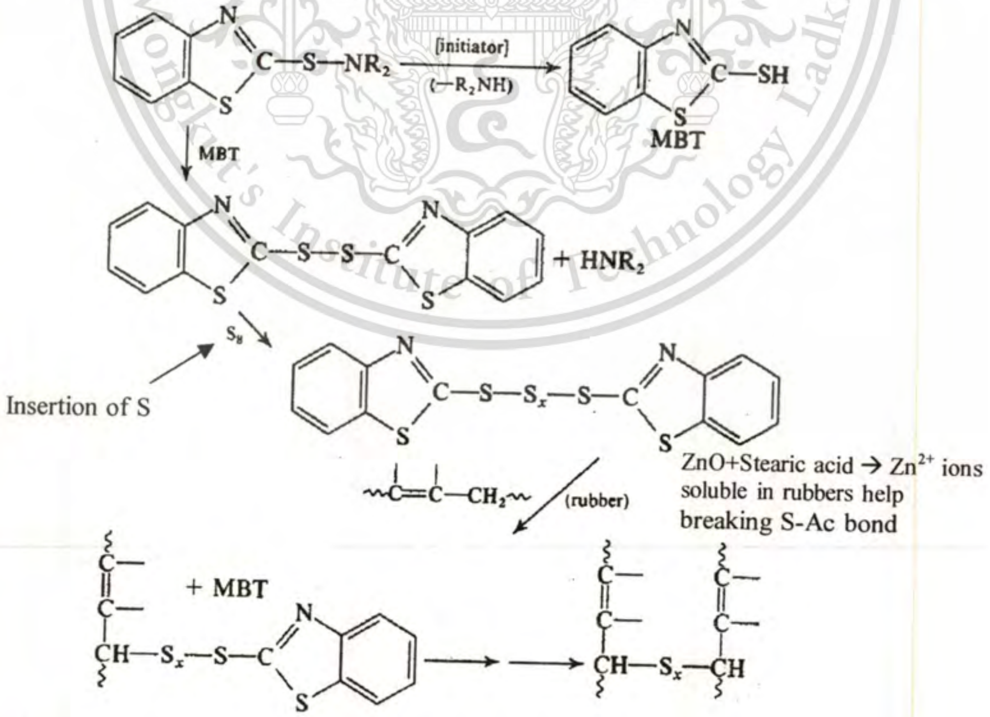


Figure 2.14 Crosslink mechanism of S curing with S and accelerator/activator. [22]

2.6.5 QUV Accelerated Weathering Tester [26]

QUV Accelerated Weathering Tester reproduces the damage caused by sunlight, rain and dew. The QUV tests materials by exposing them to alternating cycles of light and moisture at controlled, elevated temperatures. The QUV simulates the effect of sunlight with fluorescent ultraviolet (UV) lamps. It simulates dew and rain with condensing humidity and water sprays. Exposure conditions can be varied to simulate various end-use environments.

In a few days or weeks, the QUV reproduces the damage that occurs over months or years outdoors. Types of damage include color change, gloss loss, chalking, cracking, hazing, embrittlement, and strength loss. QUV test data can help in the existing materials or the evaluation of changes in formulations [26]. QUV accelerated weathering is shown in Figure 2.15.

Figure 2.15 QUV accelerated weathering [25]

2.6.6 Dynamic Mechanical Analysis (DMA) [27]

The dynamic behavior of filled rubber is of key importance in the performance of rubber engineering products or structural components, such as tyre treads, tank pads, building mounts, automotive suspensions, and engine mounts [27]. The dynamic properties can be expressed in terms of complex modulus (E*) which consists of storage modulus (E') and loss modulus (E"). E' or in – phase component represents the immediate response to the application of force. E" or out – of – phase component energy dissipated as heat. The ratio of E" to E' is in a material is a measure of the energy tan δ, generally known as “hysteresis factor”, “loss tangent” or "loss factor" [29]. The hysteresis factor dissipated by various processes, such as, molecular mobility, breakdown and reformation of the filler particles or slippage of rubber molecules under high strain amplitudes [30]. In addition, a good correlation has been found between loss factor and some properties that are a classical for designing engineering products, namely the noise, damping and acoustic behaviors.

Rubber is commonly used in engineering applications because of its specific properties, such as flexibility, cushioning and damping properties. Normally, rubber as an engineering material is used for applications, in which it undergoes rapid dynamic deformation. These properties are, in general, evaluated by dynamic mechanical analysis (DMA), as functions of temperature, frequency and strain imposed on a sample. With regards to tyre applications, it is known that temperature and frequency are the main factors affecting the service performance of the products during the dynamic applications. Rolling resistance, for example, is related to the movement of the whole tyre corresponding to deformation at a frequency of 10 – 100 Hz and temperatures of $50^{\circ}C$. In the case of wet grip, the stress is generated by resistance of the road surface to the movement of the rubber at the surface, or near the surface of the tyre tread. The frequency of this movement should be very high, probably around $10^4 - 10^7$ Hz at room temperature [28].

As shown in Figure 2.16, Wang [30] studied the influences of frequency and temperature on the tyre performance by applying the time – temperature equivalence principle (or WLF Temperature – Frequency Conversion). It has been proposed that high performance tyre should have a low tan δ value at a temperature of $50\text{-}80^{\circ}C$ in order to reduce rolling resistance and save fuel consumption. Moreover, the ideal material should also give high hysteresis at low temperatures, beside transition zone (Tg), in order to obtain high skid resistance and wet grid.

In addition, many results have been revealed that filler are known to cause a considerable change in dynamic properties [30]. It is therefore of great importance to give some introduction on dynamic properties of rubber in this section. Dynamic mechanical analysis is shown in Figure 2.17 [25].

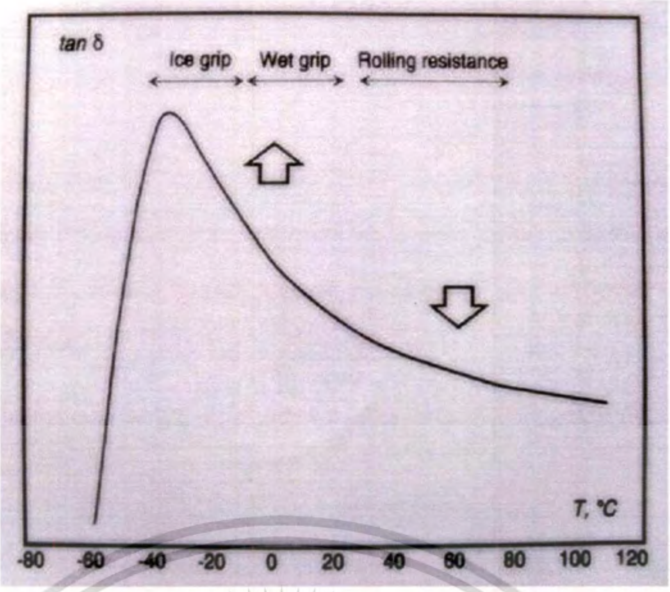


Figure 2.16 Different tyre performances over a wide temperature range at 1 Hz [30]

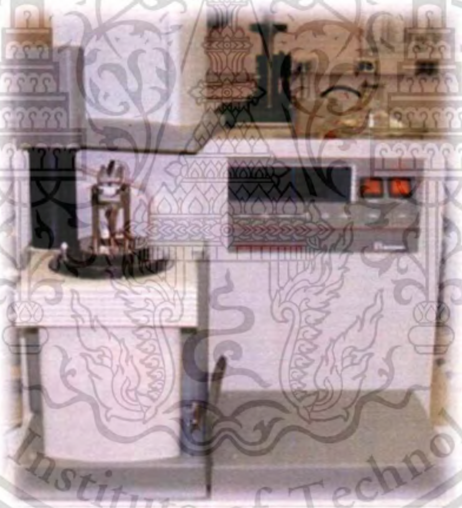


Figure 2.17 Dynamic mechanical analysis (DMA) [25]

2.7 Literature Reviews

L.R. Toib, K. Zohar, M. Alagem and Y. Tsur [31] studied stabilized nanoparticles of zinc peroxide prepared by novel and simple techniques. The technique was based on oxidation hydrolysis – precipitation procedure, using zinc acetate as a precursor, with polyethylene glycol 200 as a surface modifier. ZnO was identified and studied by a variety technique, including DLX, XRD, DSC and TEM. The temperature of reduction of zinc peroxide to zinc oxide nanoparticles by heat treatment. The temperature was found to be 233°C by DSC.

E. Tang, G. Cheng, X. Pang, X. Ma and F. Xing [32] studied nano-ZnO/poly(methyl methocrylate) (PMMA) composite latex microspheres synthesized by in-site emulsion polymerization and nano-ZnO was encapsulated in PMMA phase. TEM and FT-IR confirmed that nano-ZnO particles reacted with MPTMS and copolymer with MMA. ZnO nanoparticles showed that spherical morphology and a homogeneous dispersion of nanoparticles with a mean size from 20 to 70 nm. The absorbance spectrum of the nano-composite polymer show that increased nano-ZnO in composite particles presented perfect UV-shielding properties of the polymer. Nano-ZnO / PMMA composites could limit aggregation of nano-ZnO and improve the compatibility with organic polymer.

Y. Liang, Y. Wang, Y. Wu, Y. Lu, H. Zhang and L. Zhang [33] studied about modification of clay nanocomposites from isobutylene-isoprene rubber/organic that was prepared by solution or melt intercalation. Dispersion states of clay layers in these nanocomposites by using transmission electron microscopy (TEM) and X-ray diffraction (XRD). The TEM image showed both exfoliated and intercalated nanoscale clay layers co-exist in these nanocomposites, and the aspect ratio of clay layers in M-IIRCN was considerably smaller than S-IIRCN. And XRD image showed increasing the basal spacing of clay from 2.2 nm for the original organically modified silicates to 4.2 nm for those dispersed in the composites, and also showed the intercalation of some rubber macromolecules into the galleries of clay layers. They compared between corresponding micro-composites and pure IIR vulcanizate, the preparation nanocomposites showed distinguished mechanical performance and improved gas barrier properties, which are likely good properties to the nanoscale dispersion and high aspect ratio of clay layers. The properties of nanocomposites prepared by solution intercalation were greater than nanocomposites by melt intercalation.

T.H. Mahato, G.K. Prasad., B. Singh., J. Acharya., A.R. Srivastava and R. Vijayaghavan, [34] studied nanocrystalline ZnO materials was studied successfully synthesized by as sol-gel method. Formation of ZnO material of zincite phase with an average crystalline size of ~55 nm was studied by X-ray diffraction, scanning electron microcopy, thermogravimetry, nitrogen adsorption and infrared spectroscopy techniques. Decontamination reactions of sarin were studied on the surface of ZnO nanomaterials and the data were compared with that of bulk ZnO. Nanomaterial hydrolytically decontaminated sarin by resulting non-toxic products such as isopropyl methyl phosphonic acid and methyl phosphonic acid, whereas, the reactions follow pseudo-first order behavior thereby promising the interesting CW decontamination properties of nanocrystalline ZnO.

J.H. Li , R.Y. Hong , M.Y. Li , H.Z. Li , Y. Zheng, J. Ding [35] studied effects of ZnO nanoparticles on the mechanical and antibacterial properties of polyurethane coatings. ZnO nanoparticles were synthesized from $Zn(Ac)_2.2H_2O$ and $(NH_4)_2CO_3$. Polyurethane coating were prepared by hydroxyl-acrylic resin (HAR) - trimer of hexamethylene-1,6-Diisocyanate (HDI trimer) reaction. Polyurethane coating reinforced by ZnO nanoparticles were prepared by solution blending. Mechanical properties of the prepared films were measured by using the universal testing machine. It was found that Young's modulus and tensile strength of polyurethane films were improved by addition of ZnO nanoparticles. An optimal ZnO content was 2.0 wt%. Compared with pure polyurethane films, ultraviolet light fastness and the climate resistance of the ZnO doped polyurethane films were also improved. The abrasion resistance was tested by using a pencil-abrasion-resistance tester, showed that the abrasion resistance of 2.0 wt% ZnO nanoparticle filled polyurethane coating was improved. The antibacterial experiment showed that the ZnO nanoparticles doped with polyurethane films exhibited excellent antibacterial activity, especially for *Escherichia coli* or *E.coli.* From IR spectra analysis the absorbance of the isocyanate before and after milling and after evaporation demonstrated that the isocyanate content hardly decreased. So NCO–OH reaction would not affect on the property of the prepared PU coatings.

Chapter 3

Experimental Details

3.1 Chemicals

1. Natural rubber (NR) – Rib smoke sheet (RSS-3) SL Rubber (2000) Co., LTD.
2. Precipitated silica Tokusil®255, Tokuyama Siam.Co., LTD.
3. Sulfur (commercial grade), Charoenkit Chemical. Co., LTD.,Thailand.
4. Stearic acid (commercial grade), Chemmin Co., LTD.,Thailand.
5. Zinc-Oxide (ZnO), Nano Material Technology Co., LTD.
6. Nano Zinc-Oxide (nano-ZnO), Nano Material Technology Co., LTD.
7. Coated nano-ZnO with Silane (KBM 403 and KBE 603),
   Nano Material Technology Co., LTD.
8. Naphthanic oil (Merck KGaA, 64271 Damstadt, Germany)
9. Polyethylene glycol (PEG), Exxon Co., LTD.,Thailand.
10. Antioxidant (Santo grade, 6PPD), Charoenkit chemical Co., LTD.,Thailand.
11. Mercaptobenzothiazole disulfide (MBTS), Charoenkit Chemical. Co., LTD.,Thailand.
12. Tetra methyl thiuram disulfide (TMTD), Charoenkit Chemical. Co., LTD.,Thailand.

3.2 Apparatus

1. Two-roll mill (Lab Tech Engineering Co., LTD)
2. Compression molding machine (Lab Tech Engineering Co., LTD)
3. Mold 6x6 inch with 2 millimeter thickness
4. Curelastomer® (Moving Die Rheometer; MDR), (Monsanto Co., LTD)
5. Mooney viscometer (Model C-R6A), (Shimadzu Corporation, Japan)
6. Universal tester model 4301 (Intro Enterprises Co., LTD)
7. Durometer hardness tester shore A (Societa per azioni Milano, Italia)
8. QUV accelerated weathering testers (Zwick Co., LTD)
9. Dynamic mechanical thermal analyzer (DMTA), (Rheometric scientific Inc.)

3.3 Procedures

3.3.1 Preparation of Rubber Compounding and Vulcanization

3.3.1.1 Rubber Compounding Preparation

- Chemicals were prepared according to the formula shown in Table 3.1 Total weight of the rubber used was 400 grams.

Table 3.1 Recipe of rubber vulcanization [4]

Chemicals	Formula (phr)
Natural rubber (NR)	100
Antioxidants (6 PPD)	1
Precipitated silica	30
Lubricant-Naphthanic oil	5
Activator-Stearic acid	2
Poly ethylene glycol (PEG 400)	0.5
Activator - ZnO, nano-ZnO, Coated nano-ZnO with silane KBE 603 and KBM 403	1, 2 , 3 , 4, 5
Accelerator-MBTS	1
Accelerator-TMTD	0.5
Sulfur (S)	2

- Natural rubber was masticated sheet in the two-roll mill by cut and fold using blade for compounding rubber.

- Repeat cut and fold for 3-5 minutes.

- Add all chemicals except vulcanizing agent (sulfur) and accelerators (MBTS and TMTD).

- Repeat cut and fold for 5 minutes resulting in good mixing and dispersion of those chemicals.

- Take out the rubber compound sheet with thickness of 3-5 millimeter.

3.3.1.2 Measurement of Viscosity by using Mooney Viscometer

- Cut the rubber compound sheet into 2 pieces of square shape with 2x2 inch for 8 specimens.

- Place a square of sample on either side of the rotor.

- During measurement, the sample is allowed to preheat for 1 minute at 100°C.

- Then the torque is recovered after the time period.

- The reading obtained is recovered as ML1+4 (100°C).

Where M is Mooney viscosity number

L is large rotor

1 is the time in minutes for preheated time

4 is the time in minutes after starting the motor at which the reading is taken

100°C is the temperature of the test.

3.3.1.3 Rubber Vulcanization

- Place the rubber compound sheet in two-roll mill again and add vulcanizing agent (sulfur) and accelerator (MBTS and TMTD).

- Repeat cut and fold for 5 minutes. The resulting in good mixing of chemicals, take the rubber compound sheet off.

3.3.1.4 Measurement of Cure Curve by using Cure Meter (MDR)

- Cut the rubber compound sheet into one piece of square shape with 2x2 inch.
- Place a square shape of sample on either side of the rotor of roterless cure meter.
- The sample is heated at 150°C.
- The lower die is oscillated and the torque transducer on the upper die senses the force being transmitted through the rubber.

3.3.1.5 Compression of Samples by using Compression Molding Machine

- Cut the remained rubber compound sheet into square shape with 6x6 inch.
- Place into the mold.
- Compress the sample at 150°C.
- Time used in compression molding machine is 1.2 times of cure time ($t_{c(90)}$).

3.3.1.6 Cut the Sample by using Cutting Specimen Machine

- Cut the sample used dumbbell mold by using cutting machine.
- Cut the sample 8 pieces per formula.

3.3.1.7 Measure Width and Thickness

- Measure width by using vernier.
- Measure thickness by using micrometer.
- Measure 3 points per specimens.
- Calculate the average values.

3.3.2 Mechanical Properties Testing

3.3.2.1 Tensile Testing by using Universal Testing Machine

- The value for each sample was taken as the median value of five specimens.
- The specimen were tested in tension mode by using universal tester (ASTM D412 (Load cell 5 kN, test speed 500 mm/min))
- The test specimens for each composition were tested and tensile strength, % elongation at break (%EB) and rubber modulus (M100) were determined.

3.3.2.2 Measurement of Hardness by using Durometer Shore A (ASTM D2240)

- The remain specimens were finally tested hardness by using Durometer Shore A (ASTM D2240).
- Measure 10 points per formula.
- Calculate the average values.

3.3.3 Aging Properties Testing

3.3.3.1 QUV Testing by using QUV Accelerated Weathering Tester

- The standard sample holders can hold one sample 3 x 12 inches (75 x 300 mm) or two samples 3 x 6 inches (75 x 150 mm).
- Determine the condition of testing. To a cycle of exposure to intense ultraviolet radiation for 4 hours followed by moisture exposure by condensation for 4 hours. Various cycles are defined depending upon the intended end use application.
- Test for 2 weeks by taking the 8 samples (i.e., 4 samples for conventional ZnO and another 4 samples for nano-ZnO) out from the tester every week.

- The specimens were tested for tensile strength and hardness by using Universal Testing Machine and Durometer Shore A (ASTM D2240) respectively.

3.3.3.2 Glass Transition Temperature by using Dynamic Mechanical Thermal Analysis (DMTA)

- Test specimens are typically 56 x 13 x 3 mm, cut from the center section of an ASTM Type I tensile bar, or an ISO multipurpose test specimen.

- The test specimen is clamped between the movable and stationary fixtures, and then enclosed in the thermal chamber. Frequency, amplitude, and a temperature range appropriate for the material are input. The Analyzer applies torsional oscillation to the test sample while slowly moving through the specified temperature range at the conditions as follows:

- Frame Size: Large 34 mm
- Center Clamp: Large 12 mm
- Thickness: 0.762 mm (of each sample)
- Length: 6.35 mm (of each sample)
- Displacement: 0.5 – 1.3 mm
- Force constant: 1,700 ± g
- Spring constant: 2,600 ± 20% microns/kg (or 2,340 – 2,850)
- Shaft mass: 60 ± 20%
- Frequency at 0.01 rad/sec
- Temperature at 26 ^{0}C $\geq$ (temp. at room)
- Initial Temperature at 30.0 ^{0}C
- Final Temperature at -100.0 ^{0}C
- Ramp Rate 3.0 ^{0}C/min by Dynamic Temperature Ramp Test

3.4 Experimental Flow Chart

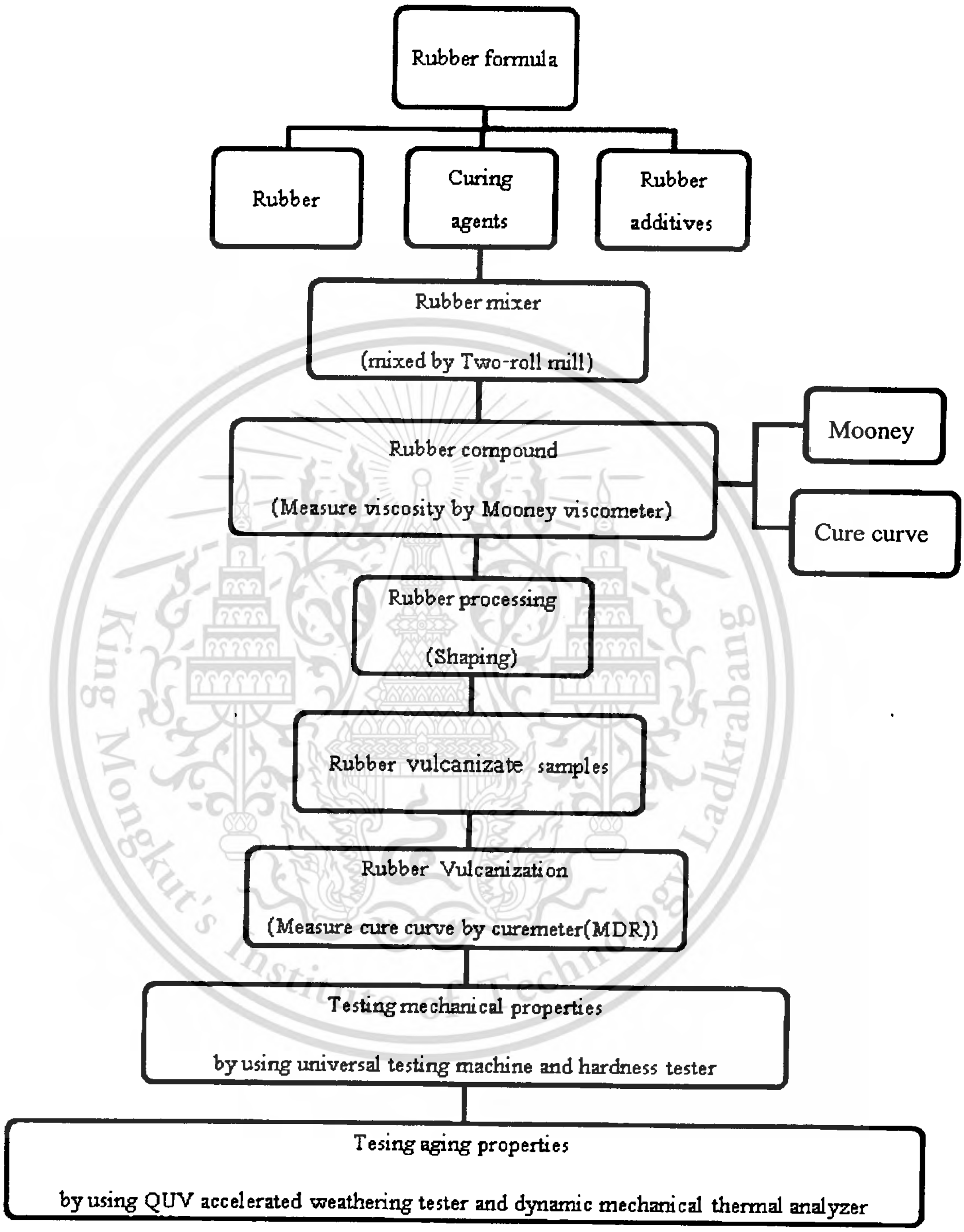


Figure 3.1 Schematic diagram of the experimental procedures

Chapter 4

Results and Discussion

In this research work, application of nano-ZnO as a rubber additive was explored using NR as a model rubber. Comparative study between conventional ZnO and nano-ZnO was carried out. Effects of silane coating on nano-ZnO were also investigated. Standard rubber formulas were compounded by using a two – roll mill and shaped into samples by using compression molding technique. Then, several properties of the rubber samples were characterized including cure characteristics (i.e., scorch time (t_{s2}), cure time (t_{c90}), CRI, and M_{HF}) and mechanical properties (i.e., tensile strength, % elongation at break, rubber modulus (M100)). In this work, some factors affecting rubber properties were studied, such as, ZnO loading (1-5 phr), effects of silane coating (KBE 603 and KBM 403), etc.

4.1 Effects of ZnO on Cure characteristics

The effects of ZnO loading on cure characteristics of the NR vulcanizates are shown in Table 4.1. With increasing ZnO loading, the rubber vulcanizates were decreased in cure time ($t_{c(90)}$) and scorch time(t_{s2}). In curing mechanism by using sulfur/accelerator/activator, ZnO reacts with stearic acid to get zinc stearate (a form of soluble Zn^{2+} ions in rubber) that acts as an activator to help breaking sulfur-accelerator bonds (as shown in Figure 2.14). However, if the ZnO loading is too much, cure characteristic can be delayed since ZnO might be agglomerated and insoluble in rubber. The smaller the particle, the higher surface area.

Table 4.1 Cure characteristic of different ZnO filled NR vulcanizates

Types / Number (phr)	**Scorch time** (t_{s2}) (s)	**Cure time** ($t_{c(90)}$) (s)	**CRI**	**MHF** (kgf.cm)
1 phr				
ZnO (conventional)	270.0	403.2	0.8	320.0
Nano-ZnO (uncoated)	252.0	489.6	0.4	440.0
Coated nano-ZnO with Silane KBE 603 (Amino group)	187.2	360.0	0.6	400.0
Coated nano-ZnO with Silane KBM 403 (Epoxy group)	324.0	432.0	0.9	260.0
2 phr				
ZnO (conventional)	273.6	489.6	0.5	420.0
Nano-ZnO (uncoated)	396.0	608.4	0.5	400.0
Coated nano-ZnO with Silane KBE 603 (Amino group)	252.0	396.0	0.7	476.0
Coated nano-ZnO with Silane KBM 403 (Epoxy group)	396.0	576.0	0.6	360.0
3 phr				
ZnO (conventional)	324.0	550.9	0.4	380.0
Nano-ZnO (uncoated)	403.2	644.4	0.4	460.0
Coated nano-ZnO with Silane KBE 603 (Amino group)	280.8	432.0	0.7	400.0
Coated nano-ZnO with Silane KBM 403 (Epoxy group)	504.0	752.4	0.4	390.0
4 phr				
ZnO (conventional)	331.2	576.0	0.4	370.0
Nano-ZnO (uncoated)	432.0	676.8	0.4	420.0
Coated nano-ZnO with Silane KBE 603 (Amino group)	273.6	504.0	0.4	440.0
Coated nano-ZnO with Silane KBM 403 (Epoxy group)	540.0	781.2	0.4	400.0
5 phr				
ZnO (conventional)	396.0	616.3	0.5	380.0
Nano-ZnO (uncoated)	468.0	698.4	0.4	420.0
Coated nano-ZnO with Silane KBE 603 (Amino group)	252.0	446.4	0.5	460.0
Coated nano-ZnO with Silane KBM 403 (Epoxy group)	612.0	860.4	0.4	420.0

Figures 4.1-4.3 show cure characteristics of different ZnO loadings (1-5 phr). It was found that scorch time (t_{s2}) and cure time ($t_{c(90)}$) were increased. Normally when ZnO is added in rubber, it decreased cure characteristic due to ZnO reacted with stearic acid to get zinc stearate that help to breaking sulfur-accelerator bonds and more efficiency to soluble in rubber. But in this work, some ZnO particles might form agglomerates and insoluble in rubber causing cure characteristic to delay.

Cure characteristics compared between conventional ZnO and nano-ZnO were shown in Figures 4.1-4.3. The particle size of nano-ZnO is smaller than those of conventional ZnO. The influence of the size affects to efficiency of reaction of ZnO with stearic acid because the smaller particle size has high surface area. So nano-ZnO should have more efficient to react with stearic acid to get more zinc stearate that is better act as the activator to soluble in rubber than conventional ZnO. Therefore, the cure characteristic of nano-ZnO is normally lower than the cure characteristic of conventional ZnO. In contrast, in this work the cure characteristic of nano-ZnO was higher than the cure characteristic of conventional ZnO. This might attribute to poor dispersion of nano-ZnO because it has small particle sizes and high surface areas that can agglomerate easily. As a result, nano-ZnO might not be insoluble in rubber affecting an increase in cure characteristic. Therefore, more efficiency of nano-ZnO shall depend on mixing and high shear force to get good distribution and dispersion.

Figures 4.1 and 4.2 show the nano-ZnO coated with silane expects that reduce polarity of nano-ZnO and good dispersion in rubber. However, the result was unexpected. This might be explained as follows:

1. In the process of nano-ZnO synthesis, some acids might be by products that can retard crosslinking. It has been known that acid can interfere accelerator, yielding delay in cure characteristics.
2. Nano-ZnO coated with silane KBM 403 that has epoxy groups as functional groups might hold or react with the crosslinking agents and retard the reaction.

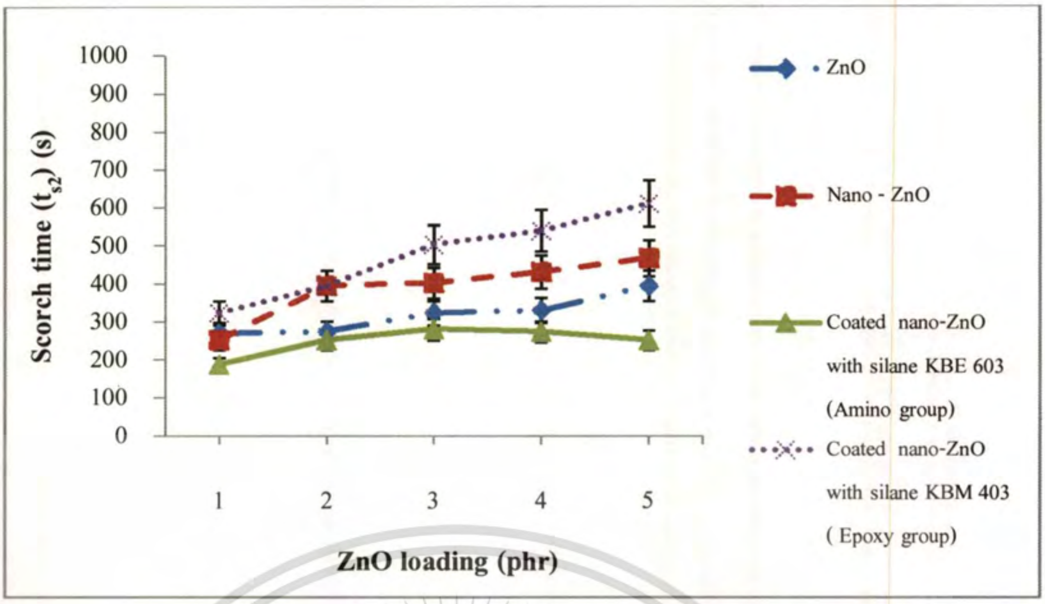


Figure 4.1 Scorch time (t_{s2}) (s) of different ZnO loadings filled NR vulcanizates

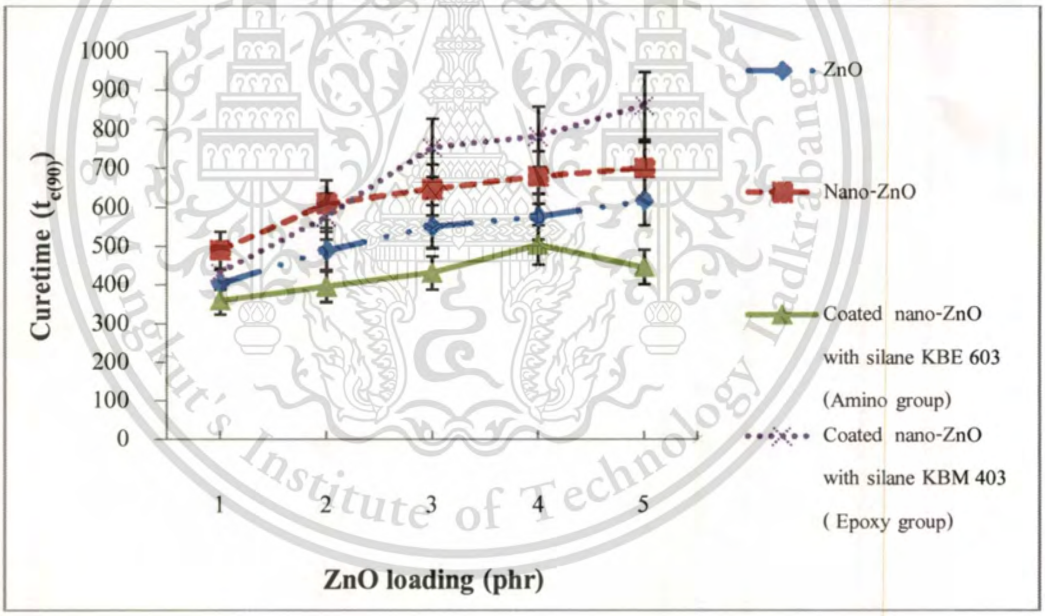


Figure 4.2 Cure time ($t_{c(90)}$) (s) of different ZnO loadings filled NR vulcanizates

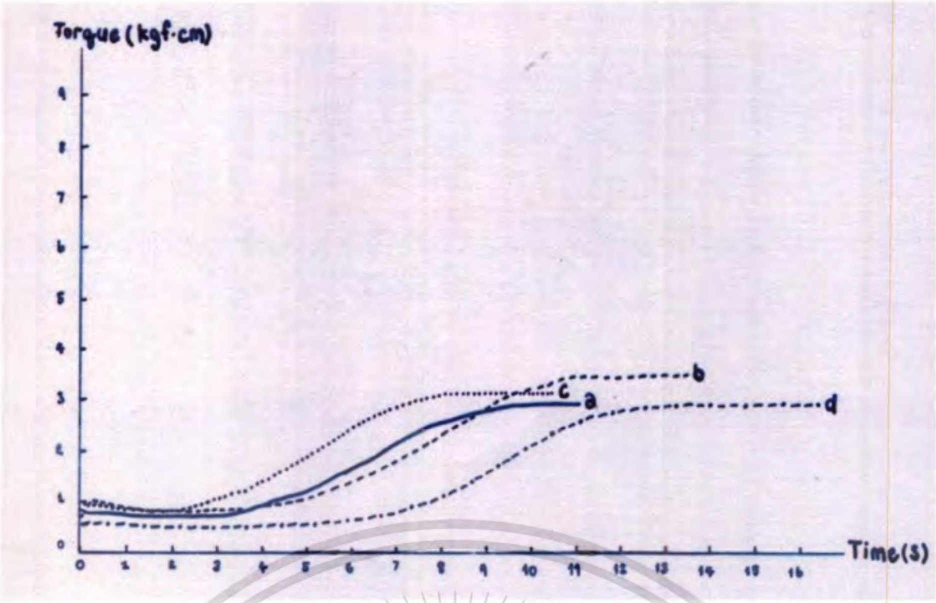


Figure 4.3 Rheographs of different ZnO filled NR vulcanizates. (a) conventional ZnO, (b) nano-ZnO, (c) nano-ZnO coated with silane KBE 603 and (d) nano-ZnO coated with silane KBM 403 at 3 phr ZnO loading.

4.2 Effects of ZnO on mechanical properties

4.2.1 Effects of ZnO loading

The effects of ZnO loading on the mechanical properties were illustrated in Figures 4.4-4.7. With increasing ZnO loading, the values of tensile strength and elongation at break were quite similar. These are because the particles of ZnO react with stearic acid resulting in zinc stearate as an activator to help breaking sulfur-accelerator bonds. On the other hand, when the ZnO loading was excess over an optimum volume, the tensile strength and elongation at break were decreased. The voids or defects in rubber vulcanizates resulting in particles of ZnO agglomeration was lower mechanical properties.

Rubber modulus of rubber vulcanizated is presented in Figure 4.6. It can be seen that rubber modulus of rubber vulcanized was increased with increasing ZnO loading. This may be due to the increase in ZnO loading causing replacement of rubber with ZnO solid particles. Therefore, the rubber lost elasticity and become stiffen.

Figure 4.7 shows the hardness of rubbers with various of ZnO loadings. When ZnO loading was increased, the hardness values are increased slightly. This can be explained by the same reasons as the increase of modulus.

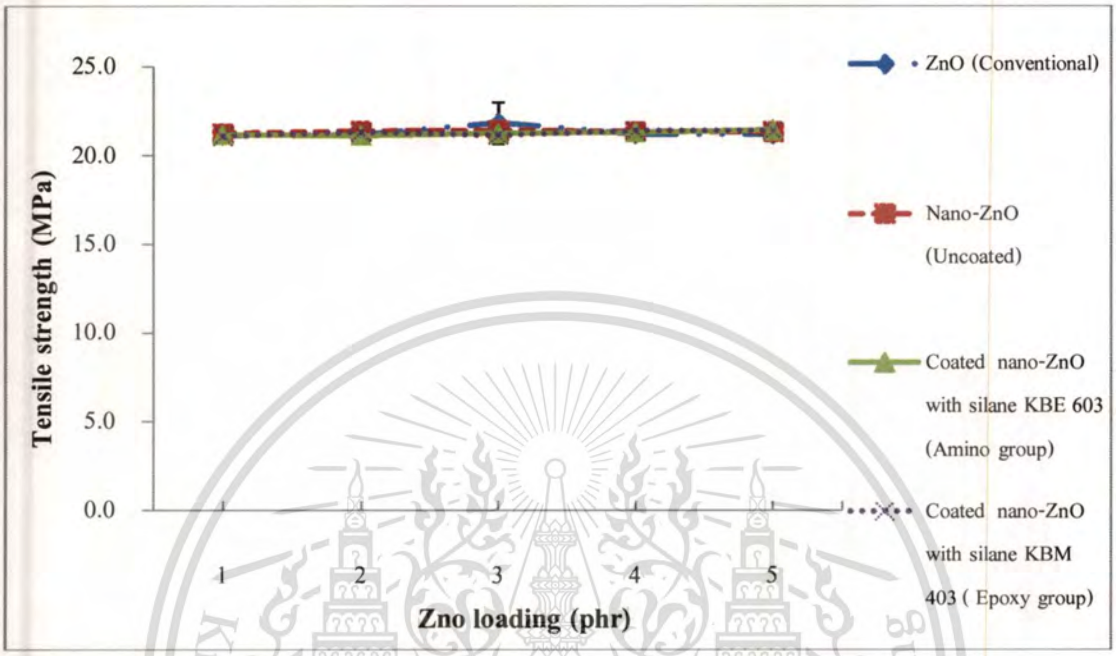


Figure 4.4 Tensile strength of different ZnO loadings filled NR vulcanizates

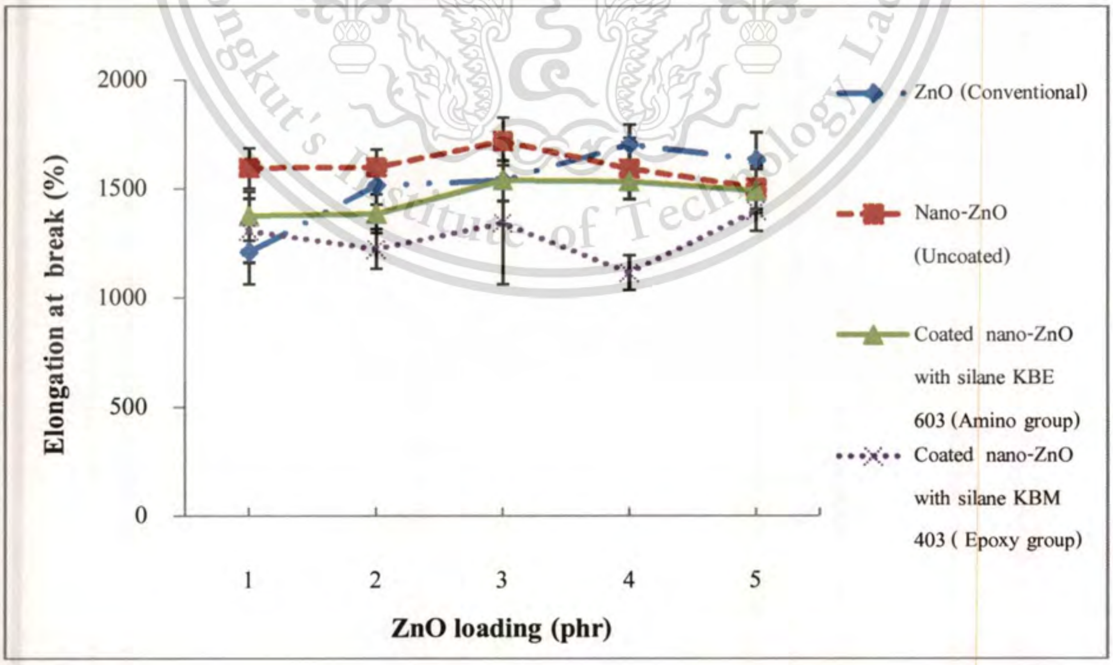


Figure 4.5 Elongation @ break of different ZnO loadings filled NR vulcanizates

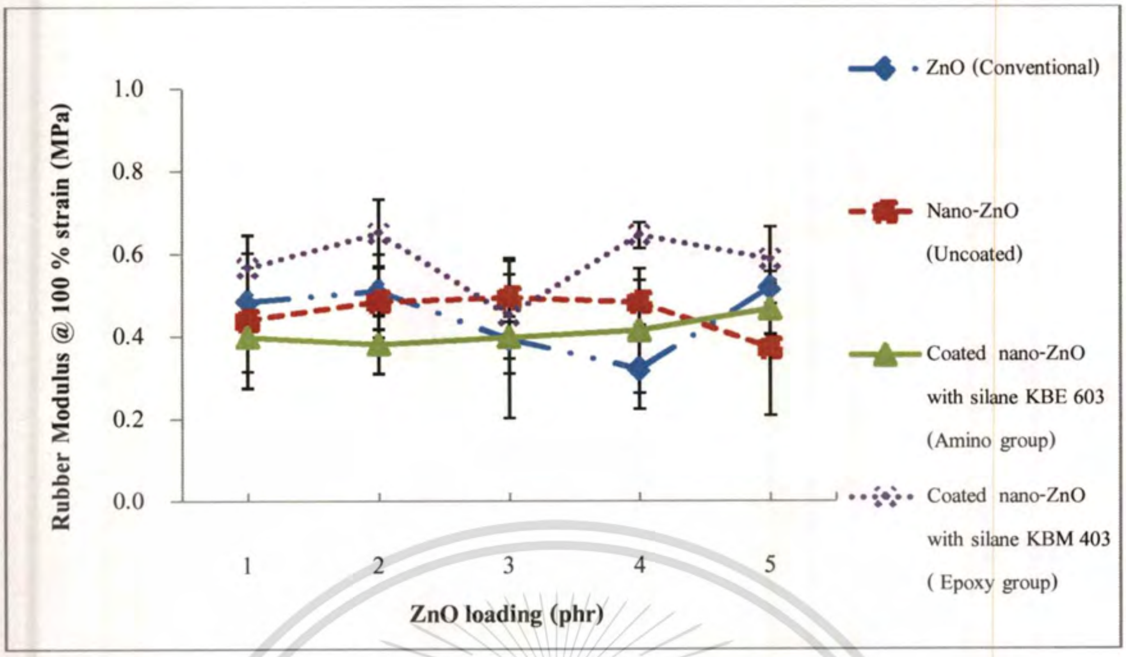


Figure 4.6 Rubber modulus @ 100 % strain of different ZnO loadings filled NR vulcanizates

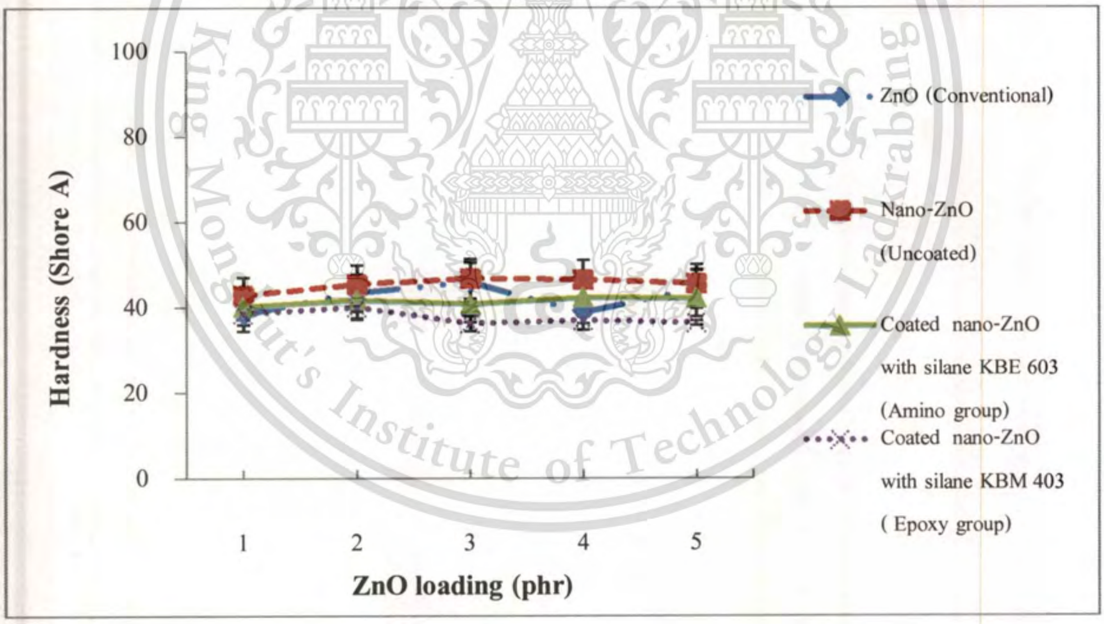


Figure 4.7 Hardness of different ZnO loadings filled NR vulcanizates

4.2.2 Effects of types of ZnO and nano-ZnO coating

In this part, the effects of types of ZnO were studied. The ZnO loading was fixed at 3 phr. It was observed that the small particle size of ZnO had effects on solubility of ZnO in rubber because it has high surface area and good distribution that is resulted in tensile strength and elongation at break. This might be explained as follows:

1. Nano-ZnO had higher tensile strength and elongation at break than conventional ZnO because nano-ZnO has smaller particles size and higher surface area.
2. By comparison between coated nano-ZnO with silane KBE603 (amino groups) and coated nano-ZnO with silane KBM403 (epoxy groups) the rubber vulcanizates of both ZnO showed similar mechanical properties. The epoxy groups coated nano-ZnO and amino groups coated nano-ZnO were similar in tensile strength and elongation at break. As seen from cure characteristics of both coated nano-ZnO, it was found that the amino silane coated nano-ZnO had better curing efficiency than the epoxy silane coated nano-ZnO. This might cause better mechanical properties of the rubber.

Figure 4.11 shows the rubber modulus of rubbers using different types of ZnO. It can be seen that rubber modulus of nano-ZnO was higher than conventional ZnO. Both of coated nano-ZnO also yielded similar rubber modulus. The hardness of rubbers using different types of ZnO was shown in Figure 4.12. It was found that nano-ZnO had higher hardness values. The results were in good agreement with the rubber modulus results.

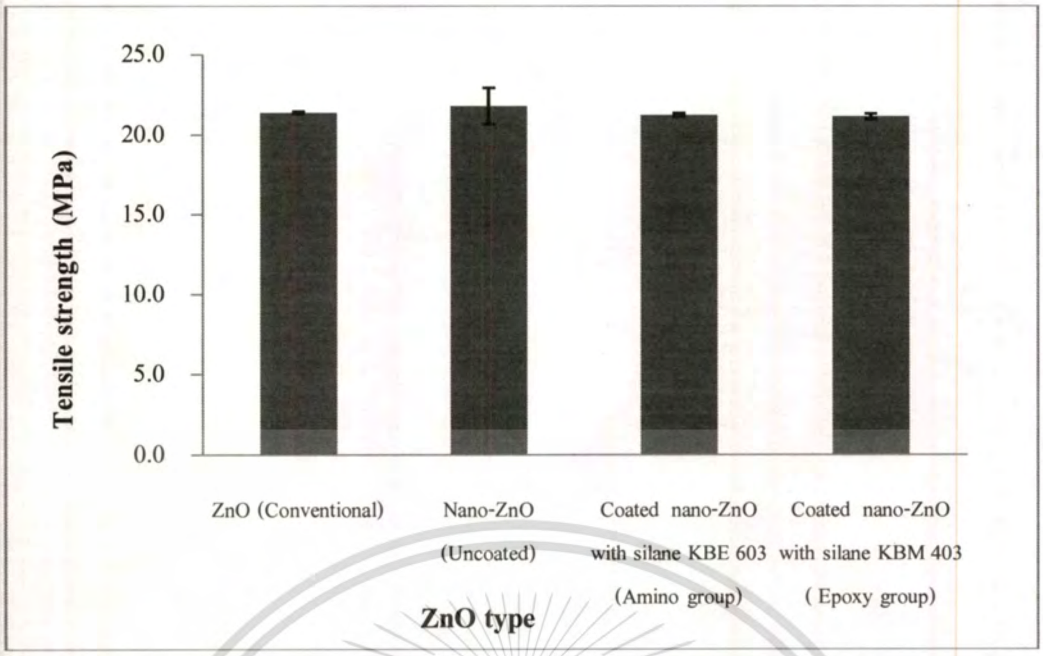


Figure 4.8 Tensile strength of different types of ZnO filled NR vulcanizates (3 phr loading)

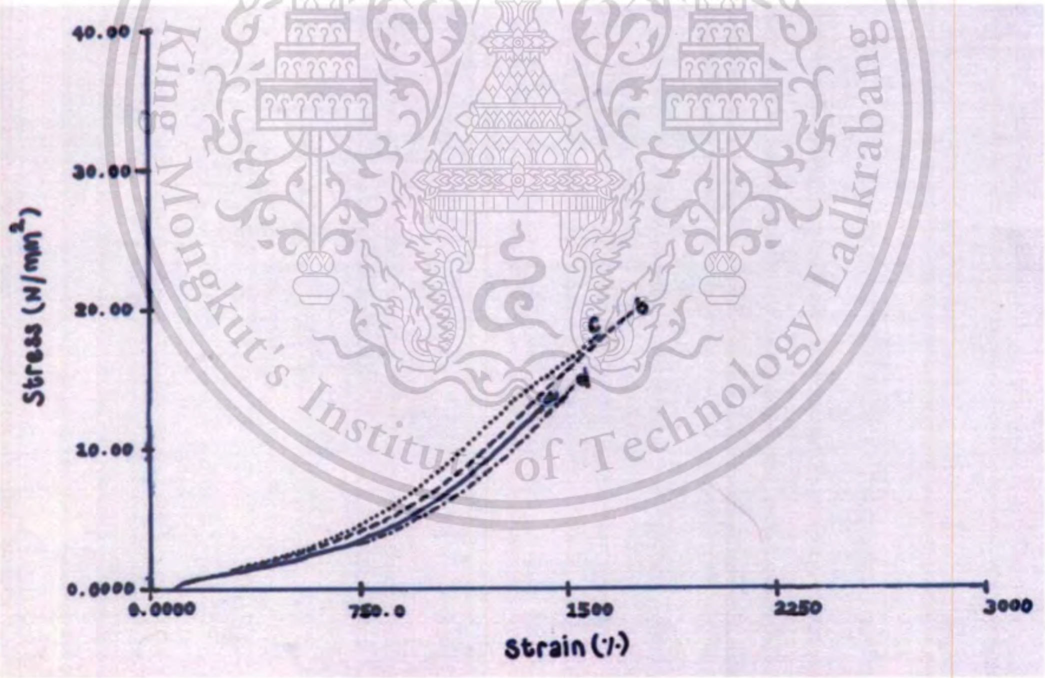


Figure 4.9 Stress-strain curves of different ZnO filled NR vulcanizates. (a) conventional ZnO, (b) nano-ZnO, (c) nano-ZnO coated with silane KBE 603, (d) nano-ZnO coated with silane KBM 403 at 3 phr ZnO loading.

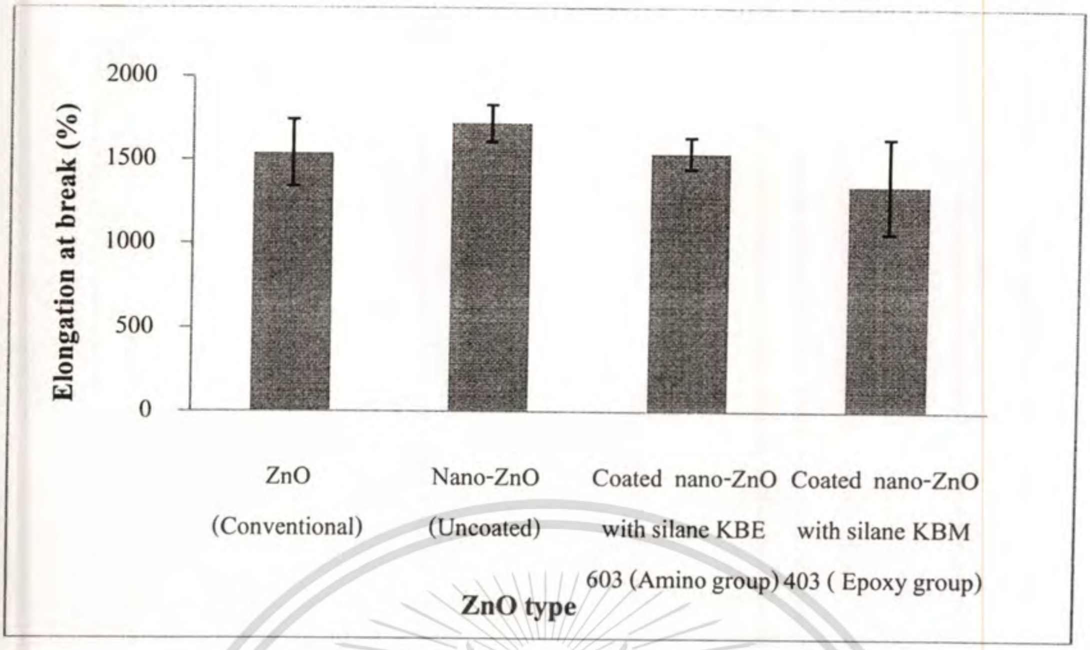


Figure 4.10 Elongation @ break of different types of ZnO filled NR vulcanizates (3 phr loading)

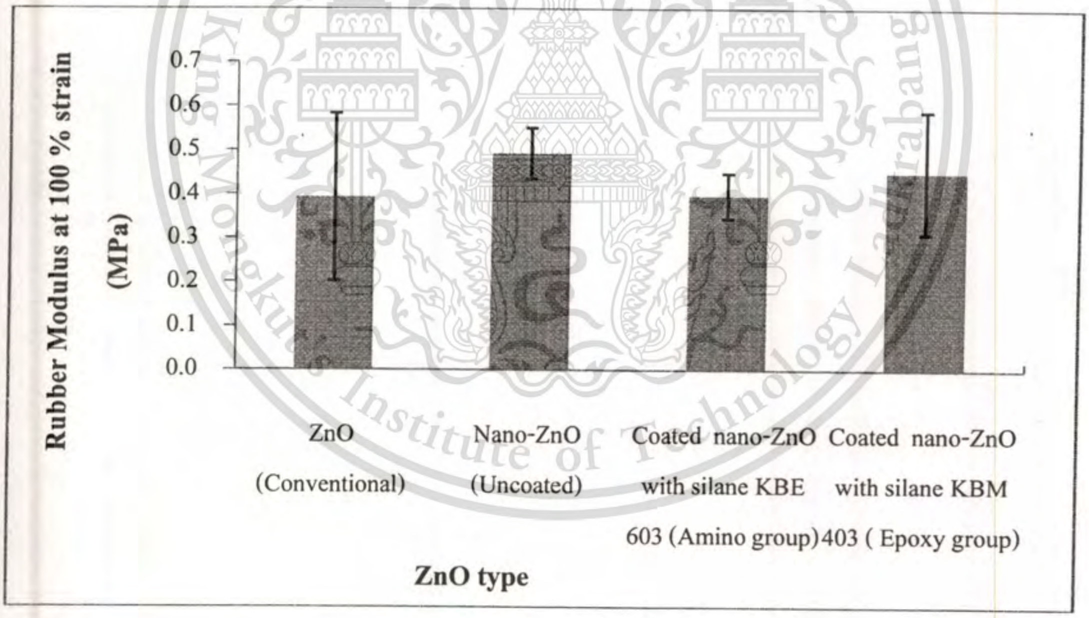


Figure 4.11 Rubber modulus at 100 % strain of different types of ZnO filled NR vulcanizates (3 phr loading)

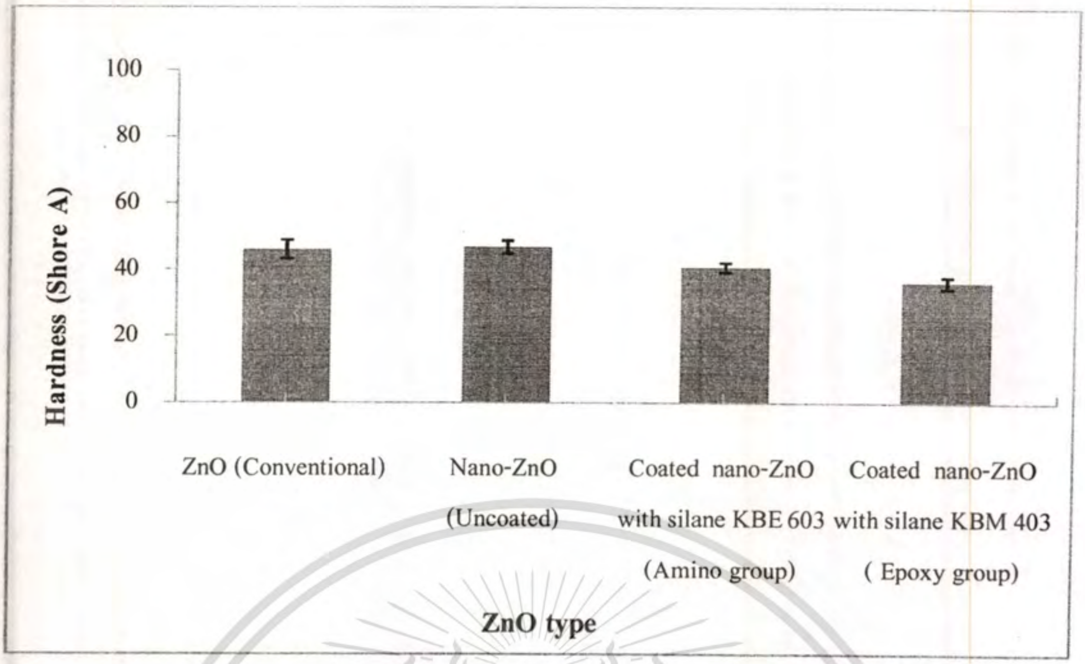


Figure 4.12 Hardness of different types of ZnO filled NR vulcanizate (3 phr loading)

4.3 Effects of ZnO on Aging Properties

4.3.1 UV resistance

The result of UV resistance property is shown in Figures 4.13-4.15 which compared between conventional ZnO and nano-ZnO at 3 phr by using QUV tester. It can be seen that nano-ZnO had better UV resistance than conventional ZnO because the particle sizes of nano-ZnO is smaller than wavelength of UV. The UV wavelengths cover a range from approximately 400 to 800 nm that is bigger than the particle of nano-ZnO; thus the UV wavelength cannot pass through the particles of nano-ZnO. As a result, nano-ZnO had better UV resistance than the conventional ZnO.

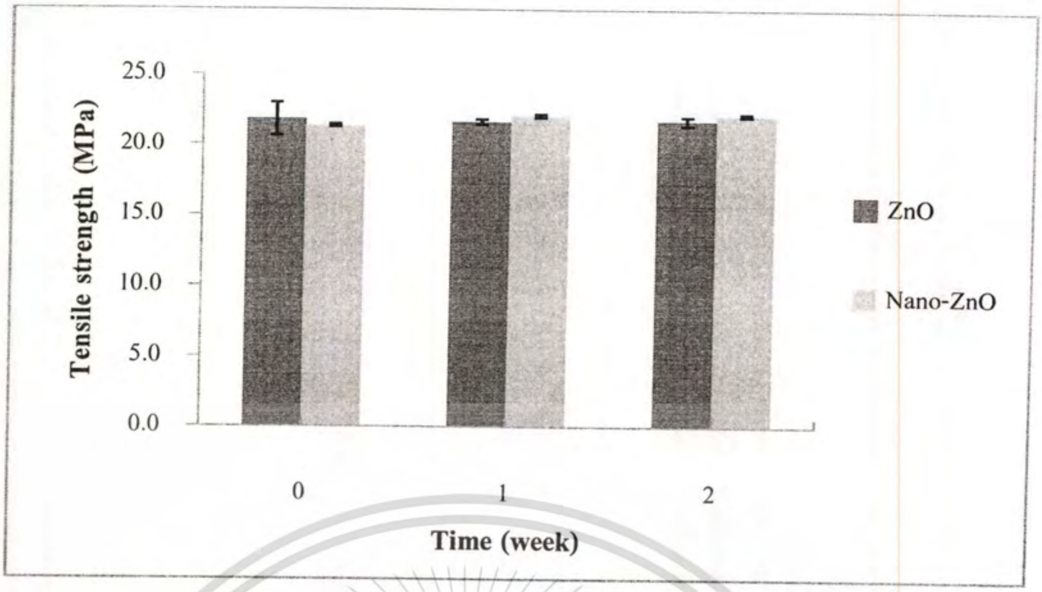


Figure 4.13 Tensile strength of NR vulcanizates filled with various times (3 phr loading)

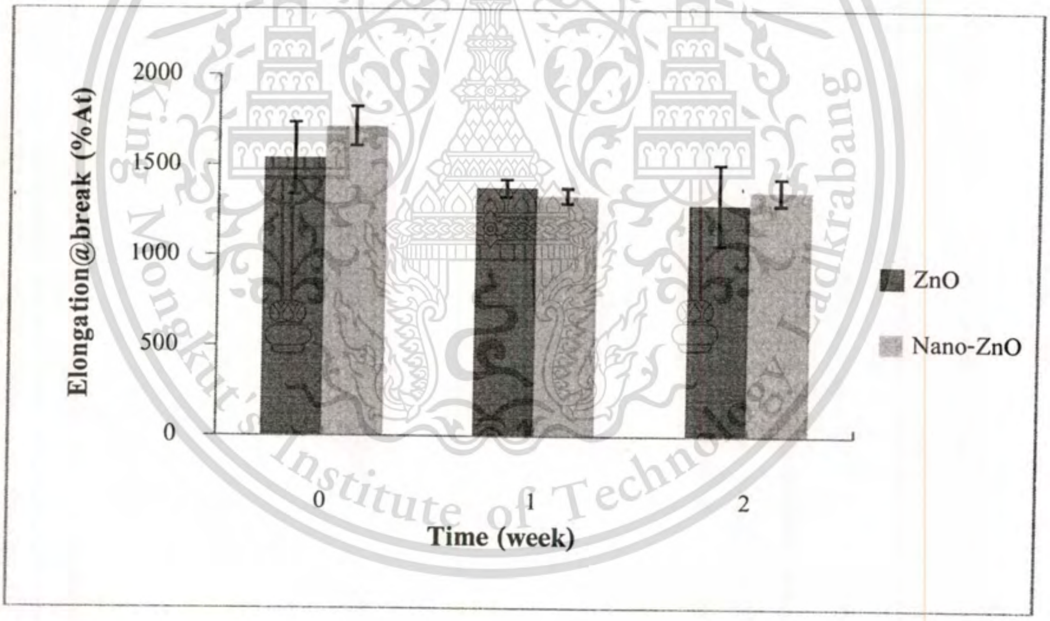


Figure 4.14 Elongation @ break of NR vulcanizates filled with various times (3 phr loading)

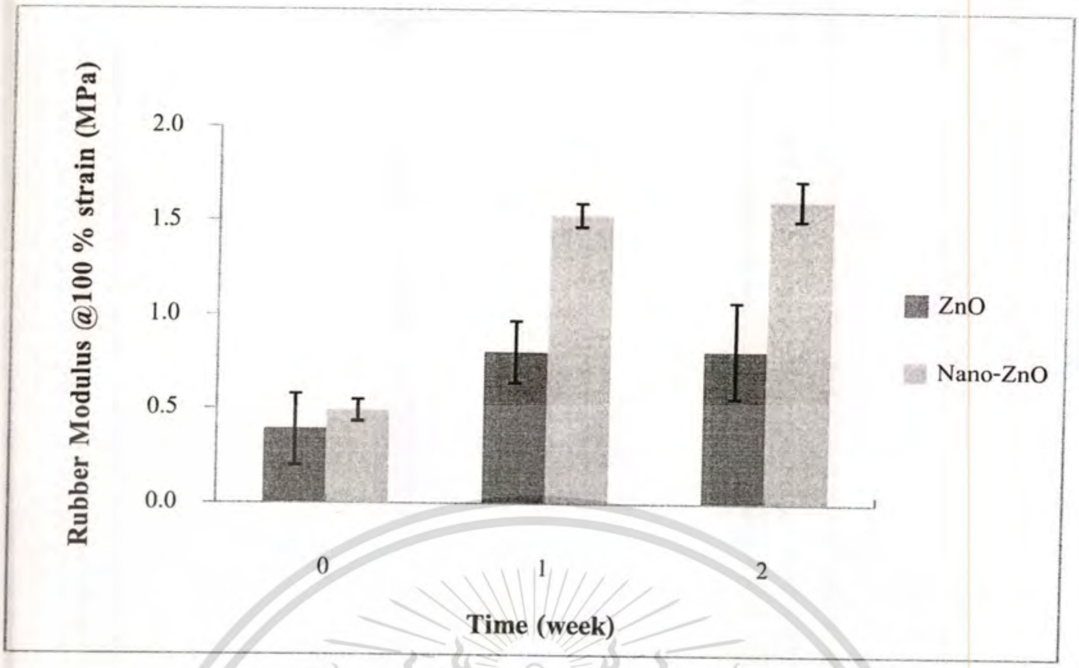


Figure 4.15 Rubber modulus @ 100 of NR vulcanizates filled with various times (3 phr loading)

4.4 Effects of ZnO on Thermal Properties

4.4.1 Glass Transition Temperature

The effects of types of ZnO on glass transition temperature (Tg) of rubber vulcanizates are shown in Table 4.2. The glass transition temperature of uncured natural rubber is -73°C which is usually below the glass transition temperature of rubber vulcanizates. From the experiment, the glass transition temperature of rubber vulcanizates using conventional ZnO was -86.7°C and glass transition temperature of rubber vulcanizates using nano-ZnO was -86.6°C. Glass transition temperatures of both conventional ZnO and nano-ZnO were similar. This can be explained by the same reason as the effects of nano-ZnO on cure characteristics and mechanical properties. Due to the very small particle sizes and high surface areas of the nano-ZnO, good dispersion and good distribution of the nano-ZnO in rubbers cannot be achieved. Therefore, the nano-ZnO agglomerates would behave and perform as the activator similar to the conventional ZnO.

Table 4.2 Glass transition temperature of different types ZnO filled NR vulcanizates

Types of ZnO	**Tan _ delta** (tanθ)	**Tg (°C)**
ZnO @ 3 phr	1.406	- 86.7
Nano-ZnO @ 3phr	1.123	- 86.6

Chapter 5

Conclusion

5.1 Conclusion

The aim of this research work was focused on comparative study between conventional ZnO and nano-ZnO in order to use ZnO as an additive in rubber industries. The results showed the effects of compounding ingredients, i.e., ZnO loading and types, cure characteristics on mechanical properties, aging properties and thermal properties, were investigated. The results can be summarized as follows:

- With increasing ZnO loading, the rubber vulcanizates were decreased in cure time ($t_{c(90)}$) and scorch time (t_{s2}). However when the ZnO loading was increased, cure characteristics of some types of ZnO (such as nano-ZnO) were delayed. This might be attributed to ZnO agglomerates. The cure characteristic of coated nano-ZnO was differed than the cure characteristics of conventional ZnO, i.e., nano-ZnO coated with silane KBM 403 retarded cure characteristics.

- With increasing ZnO loading, the values of tensile strength and elongation at break were increased slightly. On the other hand, if the ZnO loading was excess over an optimum volume, the tensile strength and elongation at break were decreased due to ZnO agglomeration. Rubber modulus of rubber vulcanized was increased with increasing ZnO loading. Nano-ZnO had higher tensile strength and elongation at break than conventional ZnO.

- Coated nano-ZnO with silane KBM 403 which has epoxy groups as the functional groups had poor tensile strength and elongation at break than coated nano-ZnO with silane KBE 603 which has amino groups as the functional groups. Rubber modulus of nano-ZnO was highest than conventional ZnO.

- Nano-ZnO had better UV resistance than conventional ZnO and glass transition temperatures of both conventional ZnO and nano-ZnO were quite similar.

5.2 Suggestion for Future Works

From this work, the following recommendations for the future studies can be proposed as follows:

1. To improve nano-ZnO dispersion in rubbers, other pre - dispersed methods might be used, such as, nano - ZnO materbatch.

2. The nano-ZnO should be applied to use in industry but better dispersion method should be carried out.

3. The suitable functional groups and methods of applying the coupling agent should be studied.

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APPENDICES

Appendix A: Influence of compounding parameter filled various ZnO loadings

Table A1 Mechanical properties of vulcanizates filled with various ZnO loadings

ZnO Loading (phr)	M 100 (MPa)	M 300 (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Hardness (Shore A)
1	0.5 ± 0.04	1.1 ± 0.04	21.1 ± 0.03	1,212 ± 66	38 ± 0.7
2	0.5 ± 0.04	1.1 ± 0.10	21.1 ± 0.08	1,515 ± 39	44 ± 0.6
3	0.4 ± 0.08	1.3 ± 0.07	21.4 ±0.04	1,539 ± 90	46 ± 0.9
4	0.3 ± 0.04	1.2 ± 0.02	21.2 ± 0.04	1,705 ± 40	39 ± 0.9
5	0.5 ± 0.02	1.2 ± 0.02	21.2 ± 0.04	1,635 ± 55	44 ± 0.6

Table A2 Mechanical properties of vulcanizates filled with various nano-ZnO loadings

ZnO Loading (phr)	M 100 (MPa)	M 300 (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Hardness (Shore A)
1	0.4 ± 0.07	1.3 ± 0.05	21.2 ± 0.05	1,594 ± 41	43 ± 0.7
2	0.5 ± 0.04	1.3± 0.04	21.4 ± 0.11	1,598 ± 37	45 ± 0.8
3	0.5 ± 0.03	1.4 ± 0.03	21.8 ± 0.52	1,118 ± 49	47 ± 0.6
4	0.5 ± 0.02	1.3 ± 0.02	21.3 ± 0.04	1,593 ± 62	46 ± 0.7
5	0.4 ± 0.07	1.3 ± 0.03	21.3 ± 0.05	1,506 ± 44	46 ± 0.4

Table A3 Mechanical properties of vulcanizates filled with various coated nano-ZnO with silane KBE 603 loadings

ZnO Loading (phr)	**M 100 (MPa)**	**M 300 (MPa)**	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Hardness (Shore A)**
1	0.4 ± 0.04	1.1 ± 0.04	21.1 ± 0.04	1,376 ± 50	40 ± 0.5
2	0.4 ± 0.03	1.1 ± 0.07	21.1 ± 0.08	1,387 ± 39	42 ± 0.9
3	0.4 ± 0.02	1.2 ± 0.03	21.2 ± 0.04	1,538 ± 42	41 ± 0.5
4	0.4 ± 0.07	1.3 ± 0.06	21.3 ± 0.07	1,532 ± 36	42 ± 0.6
5	0.5 ± 0.03	1.4 ± 0.02	21.4 ± 0.01	1,491 ± 45	42 ± 0.4

Table A4 Mechanical properties of vulcanizates filled with various coated nano-ZnO with silane KBM 403 loadings

ZnO loading (phr)	**M 100 (MPa)**	**M 300 (MPa)**	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Hardness (Shore A)**
1	0.6 ± 0.04	1.1 ± 0.04	21.1 ± 0.04	1,310 ± 66	39 ± 0.4
2	0.6 ± 0.04	1.3 ± 0.03	21.3 ± 0.04	1,226 ± 41	40 ± 0.9
3	0.5 ± 0.06	1.1± 0.06	21.1 ± 0.08	1,346 ± 126	36 ± 0.6
4	0.6 ± 0.01	1.3 ± 0.01	21.4 ± 0.04	1,117 ± 35	37 ± 0.2
5	0.6 ± 0.04	1.4 ± 0.03	21.4 ± 0.04	1,403 ± 43	37 ± 0.2

Appendix B: Influence on Mooney characteristics of different types of ZnO

Table B1 Mooney Viscosity (ML1+4 100°C)

Types / Number (phr)	**Mooney Viscosity**
1 phr	
ZnO (conventional)	40.6
Nano-ZnO (uncoated)	70.6
Nano-ZnO coated with Silane KBE 603 (Amino group)	89.0
Nano-ZnO coated with Silane KBM 403 (Epoxy group)	40.6
2 phr	
ZnO (conventional)	42.7
Nano-ZnO (uncoated)	76.6
Nano-ZnO coated with Silane KBE 603 (Amino group)	84.1
Nano-ZnO coated with Silane KBM 403 (Epoxy group)	42.0
3 phr	
ZnO (conventional)	64.7
Nano-ZnO (uncoated)	81.3
Nano-ZnO coated with Silane KBE 603 (Amino group)	80.3
Nano-ZnO coated with Silane KBM 403 (Epoxy group)	42.9
4 phr	
ZnO (conventional)	41.4
Nano-ZnO (uncoated)	88.0
Nano-ZnO coated with Silane KBE 603 (Amino group)	81.5
Nano-ZnO coated with Silane KBM 403 (Epoxy group)	54.0
5 phr	
ZnO (Conventional)	56.5
Nano-ZnO (uncoated)	91.3
Nano-ZnO coated with Silane KBE 603 (Amino group)	79.7
Nano-ZnO coated with Silane KBM 403 (Epoxy group)	56.6

Appendix C: Influence on Aging Properties (QUV testing) of different types of ZnO

Comparison between ZnO (conventional) and nano-ZnO (uncoated) at 3 phr

Table C1 Mechanical properties of ZnO in UV testing

Properties	Before UV Testing	After UV Testing	
	0 week	1 week	2 weeks
M 100 (MPa)	0.4 ± 0.11	0.8 ± 0.08	0.8 ± 0.13
M 300 (MPa)	1.3 ± 0.09	1.7 ± 0.09	1.8 ± 0.20
Tensile strength (MPa)	21.8 ± 0.15	21.7 ± 0.16	21.8 ± 0.16
Elongation @ break (%)	1,539 ± 89	1,376 ± 24	1,286 ± 111
Hardness (Shore A)	46 ± 0.9	48 ± 0.3	48 ± 0.7

Table C2 Mechanical properties of nano-ZnO in UV testing

Properties	Before UV Testing	After UV Testing	
	0 week	1 week	2 weeks
M 100 (MPa)	0.5 ± 0.04	1.0 ± 0.04	1.0 ± 0.05
M 300 (MPa)	1.4 ± 0.04	2.1 ± 0.13	2.2 ± 0.13
Tensile strength (MPa)	21.4 ± 0.05	22.1 ± 0.06	22.2 ± 0.05
Elongation @ break (%)	1,718 ± 49	1,334 ± 21	1,357 ± 37
Hardness (Shore A)	47 ± 0.6	50 ± 0.8	50 ± 1.0

Table C3 Hardness (Shore A) at 3 phr

Hardness (Shore A)	Before UV Testing	After UV Testing	
	0 week	1 week	2 weeks
ZnO (conventional)	46 ± 0.9	48 ± 0.3	48 ± 0.7
Nano-ZnO (uncoated)	47 ± 0.6	50 ± 0.8	50 ± 1.0

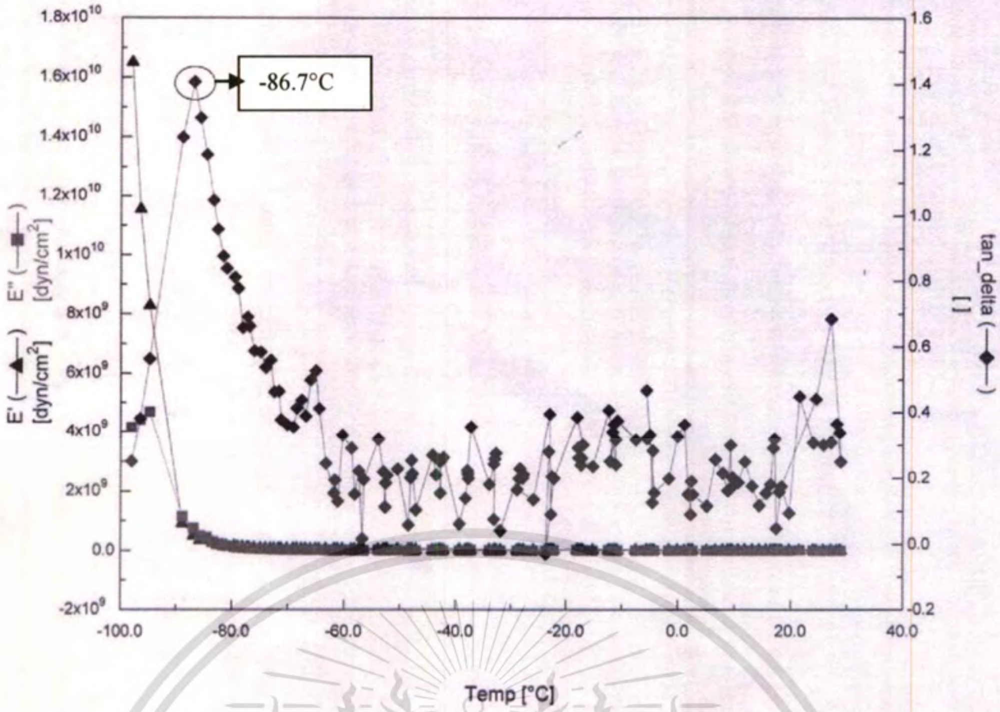

Figure C1 DMTA curve of conventional ZnO filled NR vulcanizates

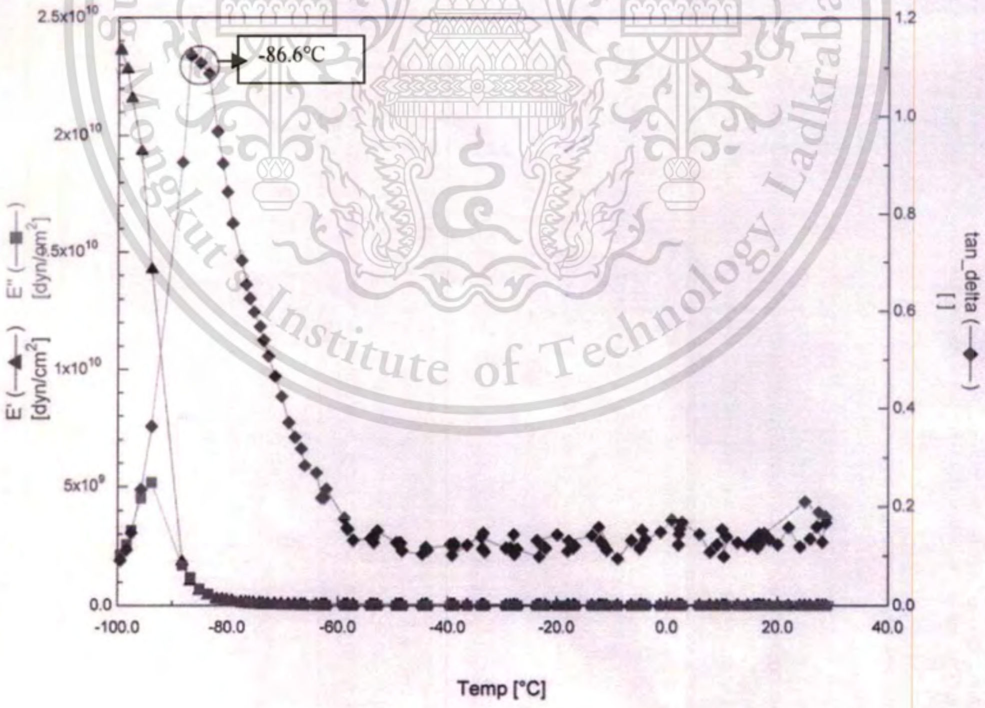

Figure C2 DMTA curve of nano-ZnO filled NR vulcanizates