THE EFFECT OF NANOSILICA FILLER ON CURING CHARACTERISTICS, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF STANDARD CAMBODIAN NATURAL RUBBER NANOCOMPOSITES

by

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LIST OF ABBREVIATIONS

APTES	(3-aminopropyl)triethoxysilane
A/S	Accelerators/Sulphur
ASTM	American Standard for Testing and Materials
CB	Carbon black
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
CNT	Carbon nanotube
CRI	Cure Rate Index
CRRI	Cambodia Rubber Research Institute (CRRI)
CV	Conventional vulcanization
DSC	Different Scanning Calorimetry
DTA	Different Thermal Analysis
DTG	Derivative Thermogravimetry
Eb	Elongation at break
EV	Efficient vulcanization
FTIR	Fourier Transform Infrared
GDR	General Department of Rubber
Ha	Hectare
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
JIS	Japan Industrial Standard
KBr	Potassium Bromide
MAFF	Ministry of Agriculture, Forestry and Fisheries
MDR	Monsanto Moving Die Rheometer
NR	Natural rubber
NS	Nanosilica

Phr	Part per hundred of rubber
Psi	Pounds per square inch
SCRL	Standard Cambodian Rubber grade L
SEM	Scanning Electron Microscopy
Semi-EV	Semi efficiency vulcanization
SMR	Standard Malaysian Rubber
SVR	Standard Vietnamese Rubber
TCPTS	3-Thiocyanatopropyl-triethoxysilane
TEM	Transmission Electron Micrographs
TGA	Thermogravimetric Analysis
TS	Tensile Strength
TSR	Technically Specified Rubber

LIST OF SYMBOLS

%	Per centage
C	Compression set
d	Thickness
F	Force
g	gram
min	minutes
nm	nanometer
M100	Tensile modulus at 100% elongation
M300	Tensile modulus at 300% elongation
M_H	Maximum torque
M_L	Minimum torque
MPa	Mega Pascal
Si-69	Bis[3-(triethoxysilyl)propyl] tetrasulfide
TESPT	Bis(triethoxysilylpropyl)tetrasulfide
t_{90}	Cure time
t_i	Final thickness of specimen
t_n	Thickness of the spacer bar
t_o	Original thickness of specimen
t_s	Thickness of the spacer bar
t_{s2}	Scorch time
[X]	Crosslink Density
V_r	Volume fraction or rubber
V_s	Molecular volume of toluene
W_A	Weight of unswollen rubber (g)

W_B	Weight of swollen rubber (g)
χ	Interaction parameter
ρ_r	Density of rubber (g/cm^3)
ρ_s	Density of toluene (g/cm^3)

KESAN PENGISI NANOSILIKA KE ATAS SIFAT-SIFAT PEMATANGAN, MEKANIKAL DAN MORPOLOGIKAL BAGI NANOKOMPOSIT PIAWAI GETAH ASLI KEMBOJA

ABSTRAK

Nanosilika (NS) dan maerogel adalah bahan mesoporous yang ringan, ketumpatan pukal yang rendah, terma konduktiviti yang rendah dan luas permukaan yang tinggi dengan rangkaian mikrostruktur yang terdiri daripada liang bersaiz nano. NS telah digunakan sebagai pengisi dalam nanokomposit piawai getah asli kemboja (PGAK). 3 bsg bahan pengisi NS telah menunjukkan CRI yang pendek dengan kekuatan tensil dan pemanjangan takat putus yang baik berbanding pengisi maerogel. Penambahan agen-agen pengganding silana Bis[3- (trietokxisilil)propil] tetrasulfida (Si69) dan (3-aminopropil)trietokxisilana (APTES) dengan 3 bsg NS telah mengurangkan kumpulan silanol semasa proses pencampuran seperti yang ditunjukkan dalam spektrum FTIR. Ianya memberikan masa pematangan yang pendek kerana kehadiran kumpulan amina di dalam APTES. Pembebanan optimum 1.5 bsg APTES dan 3 bsg NS telah dijalankan dengan sistem-sistem pematangan yang berbeza (CV dan semi-EV). Sebelum penuaan, sistem CV menunjukkan kekuatan tensil yang tinggi dengan penurunan yang signifikan ke atas kekuatan tensil selepas penuaan berbanding sistem semi-EV. Sistem semi-EV menunjukkan masa pematangan yang lebih pendek dan mempunyai kestabilan terma yang lebih baik berbanding sistem CV kerana amaun pencepat yang tinggi dengan sambung silang yang lebih stabil. Pengisi hibrid NS/mika dengan 1.5 bsg APTES telah meningkatkan sifat-sifat mekanikal komposit PGAK berbanding pengisi-pengisi hibrid NS/$CaCO_3$ dan NS/china clay disebabkan keupayaan semulajadi mika untuk meningkatkan modulus dan kekuatan tensil komposit.

THE EFFECT OF NANOSILICA FILLER ON CURING CHARACTERISTICS, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF STANDARD CAMBODIAN NATURAL RUBBER NANOCOMPOSITES

ABSTRACT

Nanosilica (NS) and maerogel, which are mesoporous light solid materials, low bulk density, low thermal conductivity, and high surface area with microstructure network consists of nano sized pore. NS was used as filler in Standard Cambodian Rubber (SCRL) nanocomposites. 3 phr of NS filler showed a shorter CRI with higher tensile strength and Elongation at break than maerogel filler. The addition of silane coupling agents; Bis[3-(triethoxysilyl)propyl] tetrasulfide (Si69) and (3-aminopropy)triethoxysilane (APTES) with 3 phr of NS reduced silanol group during mixing process as observed from FTIR spectrum. Its provided short cured time due to the presence of amine groups in APTES. The optimum loading of 1.5 phr of APTES and 3 phr of NS were carried out with different curing systems (CV and Semi-EV). Before ageing, CV system showed higher tensile strength with significant decrease in tensile strength after ageing compared to Semi-EV system. Semi-EV system exhibited shorter cured time and better thermal stability compared to CV system due to high amount of accelerator with stable crosslinking. The hybrid filler of NS/mica with 1.5 phr of APTES gave the enhancement on mechanical properties of SCRL composites than hybrid fillers of NS/$CaCO_3$ and NS/china clay due to the nature ability of mica to enhance modulus and tensile strength of SCRL composites.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Natural rubber (NR) is one of the most commercial polymers. Polymer chains in rubber are long and flexible with a coiled and kinked nature. The unique physical and chemical properties of NR are low hardness, high elasticity, high elongation at break, and swell more than double its size in organic solvents but it is impermeable to water (Thomas and Stephen, 2010). The nature of NR is sticky when it warm and brittle when it cold. These properties are limitation of many rubber products for certain applications. The discovery of vulcanization technology by Charles Goodyear and Thomas Hancock plays a significant role in rubber industries with more than 1000 of rubber products such as tires, hoses, belts, gaskets, seals, bearing, bushings, mounts and also there are applications in automotive industries, especially in the modern passenger car.

Beside the vulcanization process, fillers are the most important things to improve the properties of end used applications of rubber. Carbon Black (CB) has been used as a filler to enhance overall properties of NR behavior. Both CB and NR are organic materials which gives good interaction between filler-rubber compounds. CB is widely used in rubber industry, especially in tyre industries and seal products. However, it is limited for some specific applications due to its black color. Hence, mineral fillers such as silica, calcium carbonate ($CaCO_3$), talc, mica and so on, which

are inexpensive, natural and abundant materials are used as fillers in NR especially for light colour products (Heinrich, 2011, Dick, 2003).

Polymer/ nano-filler composites have received an intense attention and become a core focus of nanoscience and nanotechnology today (Bhattacharyya et al., 2008, Sarawade et al., 2010). The automotive manufactures are planning to build the 150,000 mile car which can be driven reliably with low maintenance for more than ten years. For realizing this vision, rubber parts manufacturers need to improve the quality of their parts with significant reduction in dimensional variation. Effective test methods are essential to achieve this goal (Dick, 2003). Development of new tyre requires high performing elastomeric materials. Hence, the choice of fillers is crucial. There are 3 main factors of a filler that determine it reinforcement abilities. They are particle size, structure and characteristics of surface (Leblanc, 2002). Usage of nanoparticles such as layered silicates, carbon nanotube and nanosilica (NS) were used to achieve products with improved properties for end use application. Compare with microfiller-reinforced rubber, nanofiller-reinforced rubber exhibits high hardness, modulus, anti-aging, gas barrier properties flammability and good rubber compatibility (Thomas and Stephen, 2010, Shanmugharaj et al., 2007).

1.2 Problem Statements

Rubber plantation in Cambodia grew significantly in vast lands from 60, 406 ha in 2005 until 213, 104 ha in 2011 and keep on growing. The Cambodia Government has estimated that the rubber trees will continue to be planted to cover 300, 000 ha of land with an average production of 290, 000 tons by 2020. However, Cambodia still has limited knowledge of natural rubber composites when most of dry

rubber product is exported to nearby countries such as China, Vietnam, Malaysia, and Singapore. Phanny (2011) has studied SCR 10 and SCR L composites with addition of 30 phr of CB filler. He compared SCR 10 and SCRL with Standard Malaysian Rubber (SMR) and Standard Vietnamese Rubber (SVR 3L). Both SCRL and SCR 10 gave better tensile, tear and tensile modulus properties of compound than SMR and SVR 3L. However, SCRL gives higher tensile strength than SCR 10. In this research, SCRL was used as a matrix to produce natural rubber (NR) nanocomposites with different types of fillers (maerogel and NS) and hybrid fillers (NS/$CaCO_3$, NS/china clay and NS/mica). This work is expected to be very useful for future rubber composite in Cambodia.

The small amount of maerogel and nanosilica (NS); 1 – 5 phr were used as fillers instead of high amount of silica due to their low thermal conductivity, high surface area, small particle size (10 – 20 nm) with more ability to reduce the heat transfer and improve mechanical properties of NR composites. Although they improve overall material performance there are still challenge in handling because nanoparticles tend to aggregate due to silanol group (Si-OH) content in maerogel and NS fillers which lead to strong filler-filler interaction (Sae-oui et al., 2004, Sae-oui et al., 2006). During processing, particle aggregation resulted in reduction of thermal and mechanical properties of nanocomposites. Silane coupling agents were extensively used to improve good filler-matrix interaction where the silanol group needs to be reduced. Two functional groups, hydrolyzable alkoxy group (-OCH_3 or –OC_2H_5) and the organo-functional group composed in silane coupling agent which react with silanol group to form siloxane linkages. They can couple with non-polar materials (natural rubber). It is known that natural rubber is organic materials and

minerals fillers are inorganic materials. Hence, incompatibility between rubber and fillers exists. However, the maximum properties of its components can only be attained through modification of fillers. Hence, interaction between hydrophobic (rubber) and hydrophilic (fillers) need to be improved in order to obtain good physical and chemical properties in NR matrix.

Sae-oui et al. (2004) have compared the different types of silane coupling agents; 3-thiocyanatopropyl triethoxy silane (Si-264) and Bis[3-triethoxysilyl)propyl] tetrasulfide (Si-69) in NR composites. The results revealed that, Si-69 performs better than Si-264 by providing rubber vulcanizates with lower heat build-up. In this study, (3-aminopropy)triethoxysilane (APTES), which composed of a silane moiety and amine group (NH_2) is used to compare with Si-69. The amine group accelerated the reaction in NR composites hence will gives shorter curing time than Si-69.

Hybrid fillers composites can improve the performance of rubber product which single fillers loadings cannot be attained with reduction in cost of the final products. Silica/CB hybrid filler with ratio of 0/50, 10/40, 20/30, 30/20, 40/10 and 50/0 were carried out by Rattanasom et al. (2007). 20 phr of silica and 30 phr of CB give better overall mechanical properties. Especially, the compound containing 20 phr of silica is more practical than the compound containing 30 phr of silica due to high amount of CB which can easily incorporated into NR than silica. Hybrid of CB/Maerogel filers with ratio of 20/0, 19/1, 18/2, 17/3, and 17/3 with 0.5phr of Si-69 filled in NR composites has been carried out by Siti Rohana (2011). The results revealed that 17/3 phr of CB/Maerogel loadings in NR composites improved the

mechanical properties, solvent transport and heat ageing properties which attributed from the partial replacement of CB by maerogel which reduced the amount of oxidation catalysts.

This work focused on NS/$CaCO_3$, NS/china clay and NS/mica hybrid fillers in SCRL composites. The presence of $CaCO_3$, china clay and mica in NR can improve the compression set and hardness which normally attributed from the large particles of fillers while retaining the good tensile strength, tear, tensile modulus and elongation at break from small NS particles (Thomas and Stephen, 2010).

1.3 Objectives of the study

The main aim of this study was to investigate the effect of nanofillers to improve overall properties of Cambodian standard natural rubber (SCRL) nanocomposites. The specific objectives of this research are as follows:

i. To determine the effect of maerogel and nanosilica fillers on properties of SCRL nanocomposites.
ii. To compare the effect of fillers modification with Si-69 and APTES coupling agents on mechanical properties of SCRL nanocomposites.
iii. To compare the effect of different curing systems (CV and Semi-EV) on the properties of Cambodian natural rubber nanocomposites.
iv. To determine the effect of hybrid fillers (NS/$CaCO_3$, NS/china clay and NS/mica) on mechanical properties of SCRL nanocomposites.

1.4 Scope of the study

This research focused on the morphology, structure, properties and application of Cambodian NR nanocomposites with unmodified and modified nanofillers. It investigated the effect of fillers/natural rubber interaction, compatibility between matrix and fillers using modified and unmodified nanofillers. Moreover, it also studied the effect of nanosilica hybrid fillers (NS/$CaCO_3$, NS/china clay and NS/mica) on properties of Cambodian NR with CV systems. Tensile, tear, hardness, compression set, SEM, FTIR and TGA were done to support this research study.

1.5 Organization thesis

This thesis is divided into five chapters which explained and discussed the entire research work in detail.

- **Chapter 1** covers the general introduction of the research background, problem statement and the objectives of study and scope of studies.
- **Chapter 2** contains the literature reviews on some fundamental concepts of rubber composites together with some review of related work reported in the literature.
- **Chapter 3** explains the material specifications, sample preparation and research methodology carried out in this study.
- **Chapter 4** focused on the results and discussion, with all the data and observations presented in graphs, tables, and figures. This is followed by a discussion of the results and data obtained from the tests conducted. All the points of discussion are according to the objectives of this study.

- **Chapter 5** includes the conclusion and summary of the entire research work and findings. This chapter also includes the proposal for the future work recommendations and improvements to be done on this project in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber

Natural Rubber found in the liquid of a tree named Hevea braziliensis. The origin of Hevea braziliensis tree is in the southern equatorial region of America, especially in the Amazon valley. It can grow up to 30 m in height with a main trunk of about 50 cm in diameter (Kothandaraman, 2008, Dick, 2001). For the past hundred years, it was planted conversely in many tropical areas around the world. In 1876, Sir Henry Wickham gathered 70,000 Hevea rubber seeds in Brazil and also rubber seeds were grown in Southeast Asia, especially in Malaysia, Sri Lanka, and Indonesia while synthetic rubber was a product of industrialized countries like the United States, Japan and Europe.

Tyre products account for approximately 60% of the synthetic rubber and 75% of natural rubber is used, and this industry employs about half a million workers worldwide (Chaiear, 2001). Since 2005, more than 14 million acres, containing more than 2 million rubber trees, have been cleared out of dense jungles and rain forests in Southeast Asia. The basic conditions for commercial growth were temperatures at 70 to 90 °F, heavy rainfall over the year, and elevations preferably not higher than a thousand feet above sea level. NR was the most resourceful for fabrication into rubber products and accounted for practically 100% of all rubber usage before World War II. Two-thirds of this total usage is for tyres. However, NR did not become an important industrial commodity until the discovery of sulfur vulcanization in 1839

and the invention of the pneumatic tyre in 1888 by John Dunlop. Table 2.1 shows properties of NR and synthetic rubber and their common use. Figures 2.1 and 2.2 show a rapid growth of world rubber production and rubber consumption. World rubber production and consumption were increased from 2000s until early 2008. However, early the last quarter of 2008, both world rubber production and consumption were heading into recession and continue to drop down dramatically in 2009 due to economic crisis (MacGregor, 2005, Board, 2012).

Table 2.1 Some important Natural rubber and synthetic rubber, its properties and common uses (Chaiear, 2001).

Type of rubber/elastomer	Properties	Common uses
Natural rubber	General purpose; not oil resistant, swollen by solvents; deteriorates when exposed to oxygen, ozone, and UV light	Tyres, shock mounts, seals, couplings, bridge and building bearing, footwear, hoses, conveyor belts, moulded products, linings, rolls, gloves, condoms, medical devices, adhesives, carpet backing, thread, foam
Polyisoprene (IR)	General purpose; synthetic natural rubber, similar properties	Same as natural rubber above
Styrene-butadiene	General purpose: Second World War natural rubber substitute; poor oil/solvent resistance	Tyres (75%), conveyor belts, sponges, moulded goods, footwear, hoses, roll coverings, adhesives, waterproofing, latex carpet backing, foam products
Polybutadiene (BR)	Poor oil/solvent resistance; subject to weathering; high resilience, abrasion resistance and low temperature flexibility	Tyres, shoes, conveyor belts, transmission belts, toy super balls

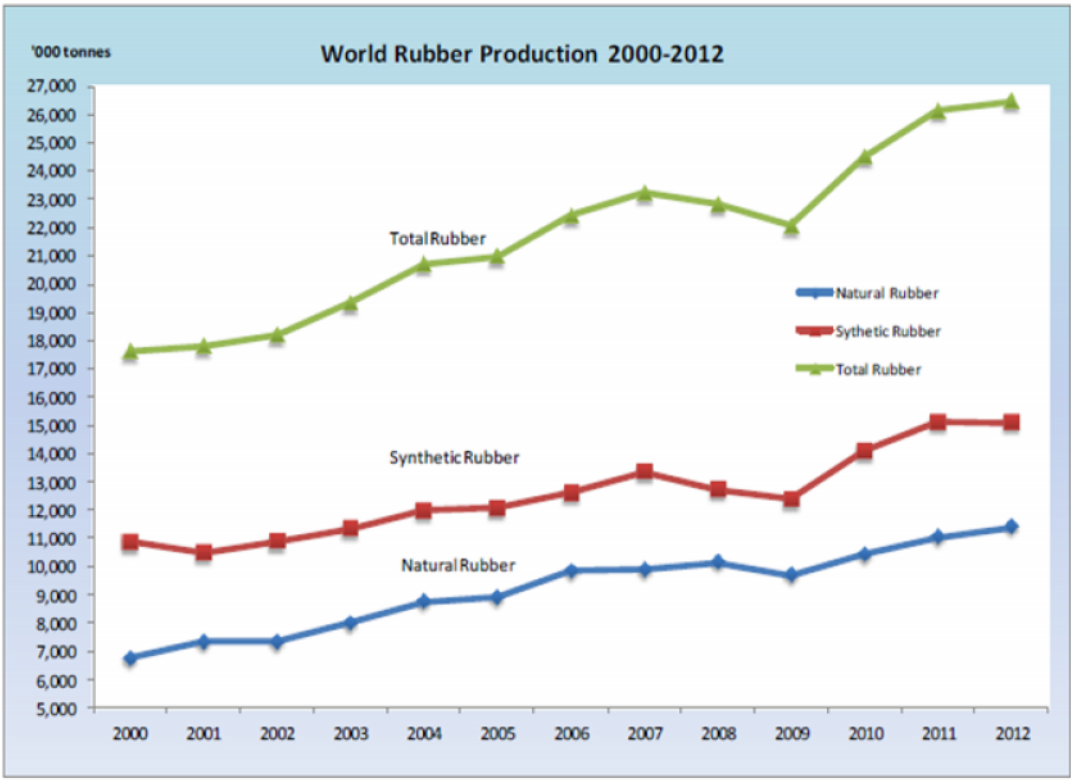

Figure 2.1 World Rubber production (Board, 2012)

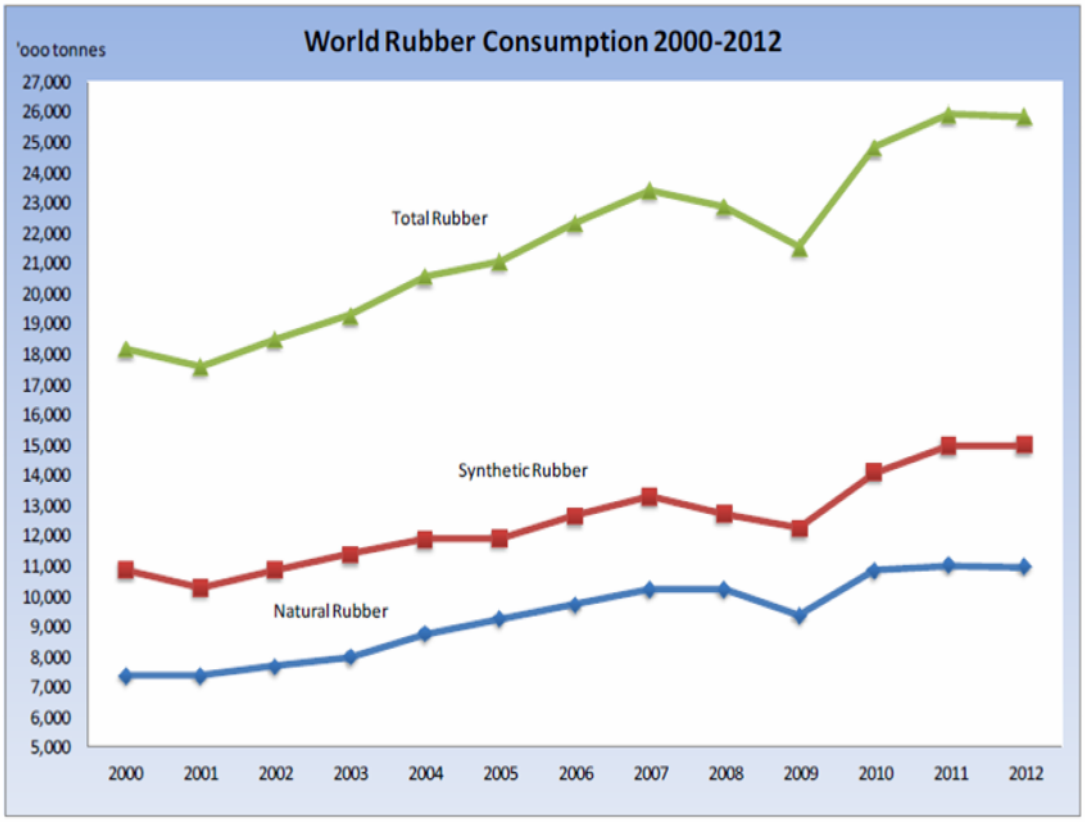

Figure 2.2 World Rubber comsumption 2000-2012 (Board, 2012)

2.1.1 Properties of Natural Rubber

NR is a high-molecular-weight polymer of isoprene with chemical structure is *cis*-1,4-polyisoprene (Figure 2.3). Two carbon atoms are joined together by a double bond and locked in a rigid structure. Due to the presence of an asymmetric carbon atom, *cis* (two similar groups attached to each carbon in the same sides) and *trans* (two similar groups attached to each carbon in the opposite sides) formation are possible (Simpson, 2002). There are at least 200 different species of plants such as goldenrod and dandelion (Table 2.2). Molecular chain of NR is basically composed of hydrogen and carbon which molecular weight is 200, 000 – 500, 000 $g.mol^{-1}$, wallace plasticity (P_o=0.30 min), density(ρ_r=0.9055 g/cm^3). It is known that, the unique physical and chemical properties of NR are low hardness, elongation at break, and swell more than double its size in organic solvents. The resistance to heat, oxygen and ozone is poor because of highly carbon-carbon double bonds content in its chemical structure. However NR has extremely high resilience, high tensile strength, good tear resistance and high fatigue to failure in cured state (MacGregor, 2005, Thomas and Stephen, 2010).

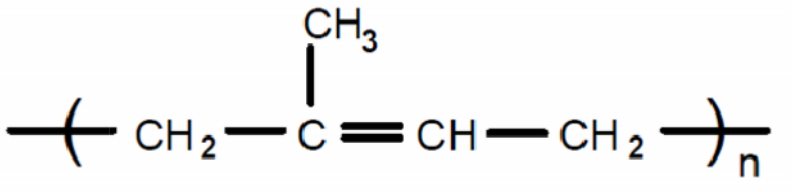

Figure 2.3 Repeat unit for NR (polyisoprene) (Simpson, 2002)

Table 2.2 Some Common Rubber-Bearing Plant Species (MacGregor, 2005)

Name	Countries
Funtumia elastica	Africa
Landolphia	Africa
Castilloa elastic	Mexico
Manihot glaziovii(ceara)	South America
Ficus elastic	India, Burma
Taraxacum koksagys	Russia
Parthenium argentatum(Guayule)	Mexico, United States (California)
Cryptostegia grandiflora	United States (Florida)

2.2 Cambodian Rubber

2.2.1 History of Cambodian rubber plantation

In early 1910s, rubber plantations had been cultivated in Veal Rinh district (Shihanouk Province) in Cambodia by Mr. Bouillard. By 1914, rubber plantation was established over an area of 150 ha. It was apparently increased during the early 1920s on the vast scale in Chup and Chamcar Loeu plateau to European plantations following the granting of concession. Even though overproduction of rubber all over the world impaired the international rubber price during the early 1930s, concerted efforts and agreements among producers managed to stabilize prices. Approximately 20 per cent of the total rubber plantations in Indochina come from Cambodia's rubber plantation in 1937s. After the independence from French in 1953, there were around 30,000 ha of rubber plantation, which had emerged extensively in basaltic red

plateau region in Kampong Cham and Kratie Provinces by private estate plantations. At the end of the 1960s, the area cultivated with rubber reached 62,000 ha, where 48,000 ha belonged to private companies and the rest was belonged to village plantations. Total production was about 52,000 tons of rubber. Figure 2.4 shows the brief history of NR production in Cambodia, 1921 – 2011 (Jecelyne Delarue and Noel, 2008).

Unfortunately, Cambodia's rubber production was declined as a result of declaring a conflict between North Viet Nam and United States –backed Government of South Viet Nam along the Cambodian-Vietnamese border adjacent to the rubber growing areas between 1970 and 1979 and was take overed by Khmer rouge (1975-1979) subsequently. The production had plummeted to fewer than 10,000 tons. Following the Socialist regime, rubber plantations revived through village plantations to the Provinces and their productions had been risen to 43,000 tons. By 1991, the Cambodia Rubber Research Institute (CRRI) was established with the objective to upgrade the rubber yields and production (Jecelyne Delarue and Noel, 2008, Hang, 2009, Raya et al., 2012).

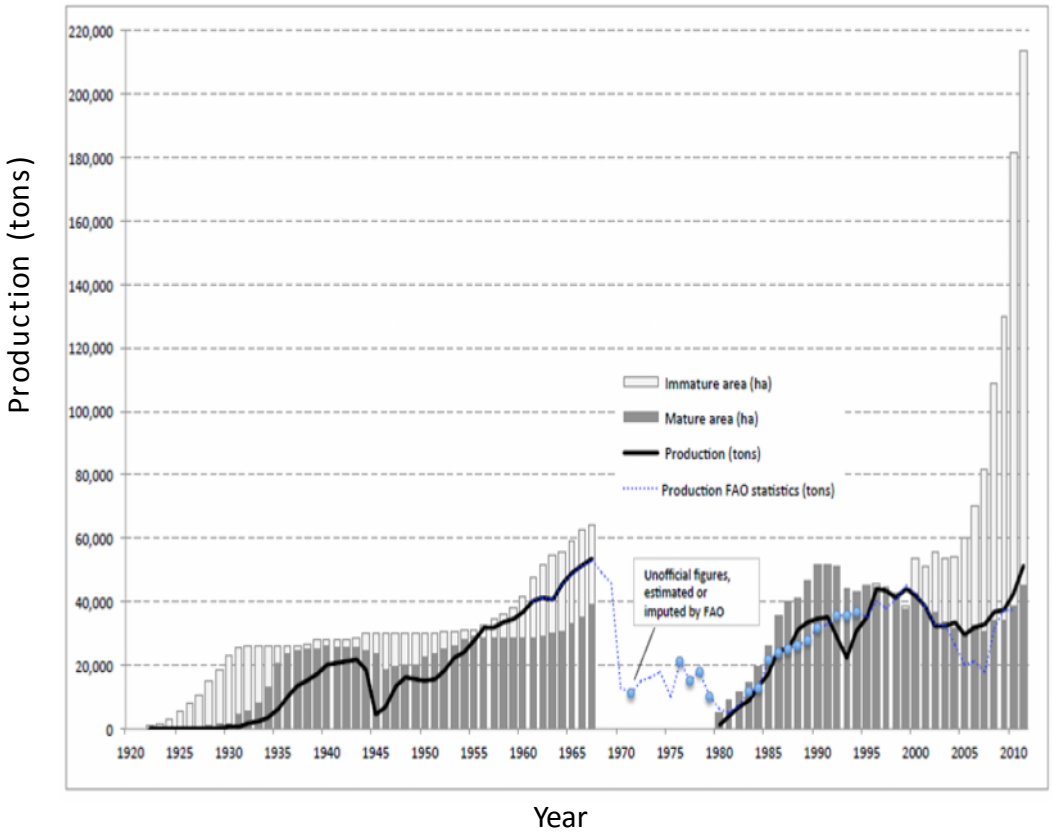

Figure 2.4 Natural rubber production in Cambodia 1921-2011 (MAFF, 2011)

2.2.2 Current development of the Cambodian rubber

In the past two years, the development of the Cambodian rubber sector has been significantly noticeable with the rise in prices of both natural and synthetic rubber, which accelerated smallholders, private companies, and state-run estates to expand their harvested areas. By 2007, total rubber plantations area was 82, 059 ha, in which 48% was dominated by state-owned plantations, 44% followed by smallholders, 6% came from private companies. The expansion of rubber plantations in 2008 rose nonstop approximately 30% from 2007, which had six state-run plantations as illustrated in Table 2.3. Moreover, beside traditional areas located in Kampong Cham, Kraie and Mondul Kiri, new areas emerged in Siem Reap, Preah

Vihear, Kampong Thom, Ratanakiri and potential areas located in Battambang, Pailin and Pursat as shown in Figure 2.5 (Gergely, 2007).

Table 2.3 Natural rubber plantation situaion, 2007-2008 (Hang, 2009)

	2007			2008		
	Mature	Immature	Total	Mature	Immature	Total
Rubber estates	16,740	22,731	39,471	16,378	22,073	38,451
Chup	5,722	8,625	14,347	5,884	5,814	11,698
Peam Cheang	2,064	1,400	3,464	2,000	2,030	4,030
Krek	2,639	1,764	4,403	2,290	2,140	4,430
Memot	1,778	2,755	4,533	1,900	3,000	4,900
Snuol	1,082	1,782	2,864	1,000	1,870	2,870
Chamcar Andong	1,810	3,396	5,206	1,720	4,200	5,920
Boeung Ket	1,310	2,560	3,870	1,300	2,500	3,800
CRRI	335	449	784	284	519	803
Private	3,353	2,883	6,236	5,036	12,126	17,162
Tapao	1,053	1,053	2,106	1,050	1,253	2,303
Labansiek	2,300	90	2,390	3,500	90	3,590
New investment		1,740	1,740	486	10,783	11,269
Smallholders	10,398	25,953	36,351	12,900	40,144	53,044
Total	30,491	51,567	82,058	34,314	74,343	108,657

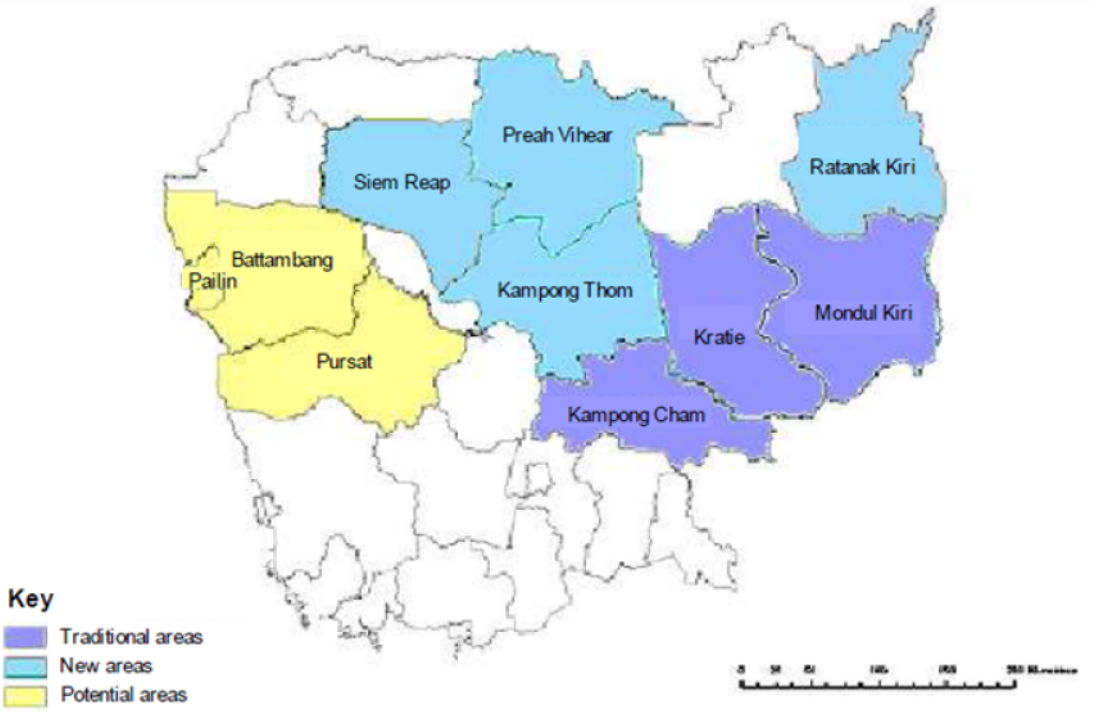

Figure 2.5 Rubber production areas (Gergely, 2007)

According to General Department of Rubber (GDR) in Ministry of Agriculture, Forestry and Fisheries (MAFF, 2011), total cultivation in Cambodia in 2011 was more than 200,000 ha, which about 45,000 ha can be tapped to producing more than 51,000 tons of NR. About 168,000 ha were used for maintenance either for replanting rubber trees on existing orchards, or for planting new trees. The estimation of Cambodian rubber production next few years will be greatly higher than today because of the strong current re-planting. Therefore, the government targets a total rubber planted area of 300,000 ha, of which 235,000 ha for harvesting, yielding and also target an average production of 290,000 tons by 2020 as shown in Table 2.4.

The main processed products are SCR L and SCR 5. However, SCR 10 and SCR 20 are produced for world demand especially for tyre industry where high grade rubber is not required. Both SCRL and SCR 5 are similar to the SMR, which accordance with technically specified rubber (TSR) as shown in Table 2.5 (Fulton and Thorpe, 1996).

Table 2.4 Cambodia's cultivation, production and exports of natural rubber (MAFF, 2011).

Year	Total planted (ha)	Immature area (ha)	Mature area (ha)	Production (tons)	Yield (kg/ha)	Exports (tons)
1922	1,224	1,224	0	0	0	…
1930	22,959	21,159	1,800	482	268	…
1940	27,977	1,970	26,007	19,988	768	…
1950	30,386	8,207	22,179	15,295	690	…
1960	41,644	13,220	28,424	37,109	1,306	40,466
1967	64,054	24,907	39,147	53,716	1,372	47,655
1980	5,000	0	5,000	1,300	260	1,454
1990	51,160	38	51,122	34,700	680	25,563
2000	53,722	11,024	42,698	42,007	980	40,066
(…)	-	-	-	-	-	-
2005	60,406	30,004	30,402	29,464	960	28,950
2006	69,994	37,604	32,390	32,077	990	31,184
2007	82,059	51,568	30,491	32,975	1,080	33,121
2008	108,510	74,197	34,313	37,050	1,080	36,000
2009	129,920	95,785	34,135	37,380	1,095	36,500
2010	181,433	143,027	38,406	42,466	1,100	45,000
2011	213,104	167,942	45,162	51,339	1,137	44,969
2020 (estimate)	300,000	65,000	235,000	290,000	1,235	-

Table 2.5 Grades classification of SMR L and SMR 10 (Fulton and Thorpe, 1996).

Parameters	SMR L	SMR 10
Dirt content (max, % wt)	0.02	0.08
Ash content (max, % wt)	0.50	0.75
Volatile matter content (max, % wt)	0.80	0.80
Nitrogen content (max, % wt)	0.60	0.60
Po (min)	35.0	30.0
PRI (min, %)	60.0	50.0
Color Lovibond scale (max)	6.00	-----

2.3 Fillers

A filler broadly can be defined as finely divided particles that are frequently used to enhance the performance and various attractive properties of the host matrix, depending on a specific application. Many researchers have contributed to the development and the use of different fillers with dimensions of nanometer level. Especially in rubber technology, the term nanoscale is not unfamiliar to a rubber specialist. Since the beginning of the twentieth century, carbon black (CB) and silica with primary particle sizes of these fillers remained in the nanometer range have been used as effective reinforcing agents in various rubber formulations for a variety of applications. Nevertheless, with these conventional fillers, the dispersion towards individual primary particles was extensively difficult to realize (Heinrich, 2011). Normally, fillers such as CB , precipitated silica, nanosilica, maerogel, silicates, calcium silicate, clays, magnesium silicate (talc), calcium carbonate, calcium sulphate and so on (Simpson, 2002, Daniel et al., 2003) were used to improve properties of NR such as mechanical properties, thermal stability, curing

characteristics and to reduce the cost of final product (Chen et al., 2009, Lazzara and Milioto, 2010, Zhu et al., 2008). The amount of reinforcement fillers upon filling in NR depends on their particle sizes, shape, and structure.

The advantages of nanofillers are not only to reinforce the rubber matrix but also to impart a number of other properties such as barrier properties, flammability resistance, electrical/electronic and membrane properties and polymer blend compatibility. During the last two decades, tremendous research work had been done on the field of polymer nanocomposites at stage of infancy as far as their application was concerned. The major challenge in this regard is to replace carbon black and silica, which are mostly used in bulk amounts in rubber compositions, by small amount of nanofillers (Heinrich, 2011, Bhattacharyya et al., 2008).

However, the non-reinforcing white fillers such as talc, calcium carbonate, frequently used as extenders to reduce the cost of the final compound, do not greatly increase the levels of measured adhesion; these are generally inert materials where they reduce the elongation and produce an increase in the compound modulus. They do not reinforce the compound and do not significantly increase the tear strength (Wootton, 2001).

2.3.1 Type of particulate fillers

There are three core groups of fillers included reinforcing fillers, semi-reinforcing fillers, and non-reinforcing fillers. CB and precipitated silica are the most significant commercial reinforcing fillers when high strength is needed. CB plays an important role on improving mechanical and electrical properties in rubber materials

(Herman. F, 2005). It mainly attributes to two effects: (i) the formation of a physically bonded flexible filler network and (ii) strong polymer filler couplings which depend on a high surface activity and specific surface of the filler particles (James, 2007). The use of precipitated silica is slightly reduced M_H, M_L due to high viscosity and slow cure rate but it has ability to attribute of tear, heat resistance and linkage to fabrics and metal in NR compounds; especially for reduction of tyre rolling resistance (Hewitt, 2007).

On the other hand, for some applications where high mechanical properties is not an important role, semi or non-reinforcing fillers such as clay, calcium carbonate, talc, and calcium silicate which improved stiffness and adhesion of vulcanizates are used strongly. However, non-reinforcing fillers are used to increase hardness and tensile strength and also they are used to decrease resilience, resistance to abrasion and tear properties; especially to reduce the cost of final product of NR composites (Sae-oui et al., 2009, Poompradub et al., 2008).

2.3.1 (a) Nanosilica

The technology of nanostructural materials is developing at an astonishing speed and is being applied extensively into many materials (Choolaei et al., 2012). Polymer/ nano-fillers composites have received intense attention hence they have become a core focus of nanoscience and nanotechnology. In this study, NS used as a filler in natural rubber to reinforce its mechanical properties and morphological behaviors. NS is produced in industrial scale to support a growing number of commercial products. It is a high porous material and has a large surface area with microstructural network (Sarawade et al., 2010, Zhu et al., 2008, Pal et al., 2010).

Figure 2.6 shows SEM image of silica nanoparticles and Figures 2.7 (a) and (b) show TEM image of silica nanoparticles without and with surface treatment. The large surface area and size of silica particle have played a key role in enhancement of the mechanical properties due to embedded silica in the polymer matrix (Rahim et al., 2011, Lazzara and Milioto, 2010, Tang and Wang, 2005).

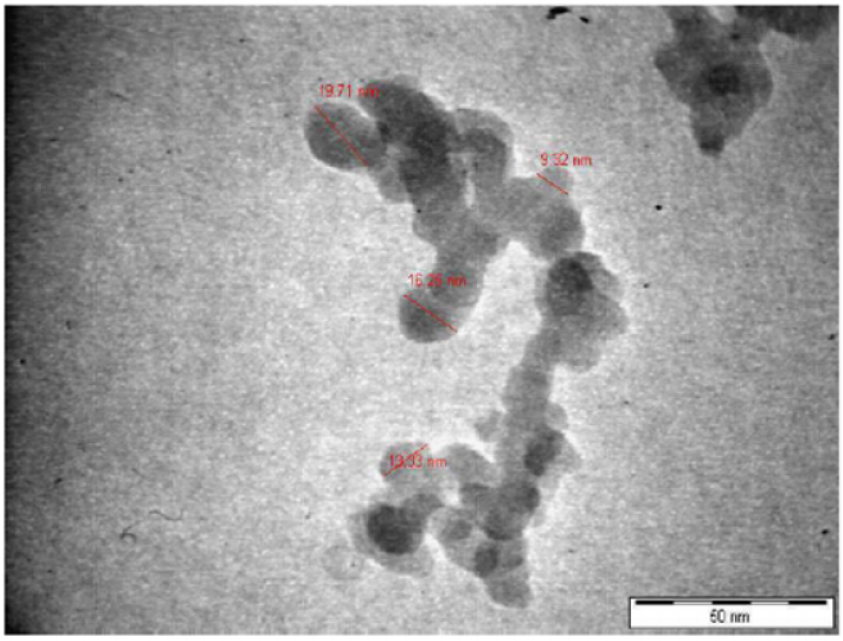

Figure 2.6 SEM image of silica nanoparticles measurements (Rahim et al., 2011)

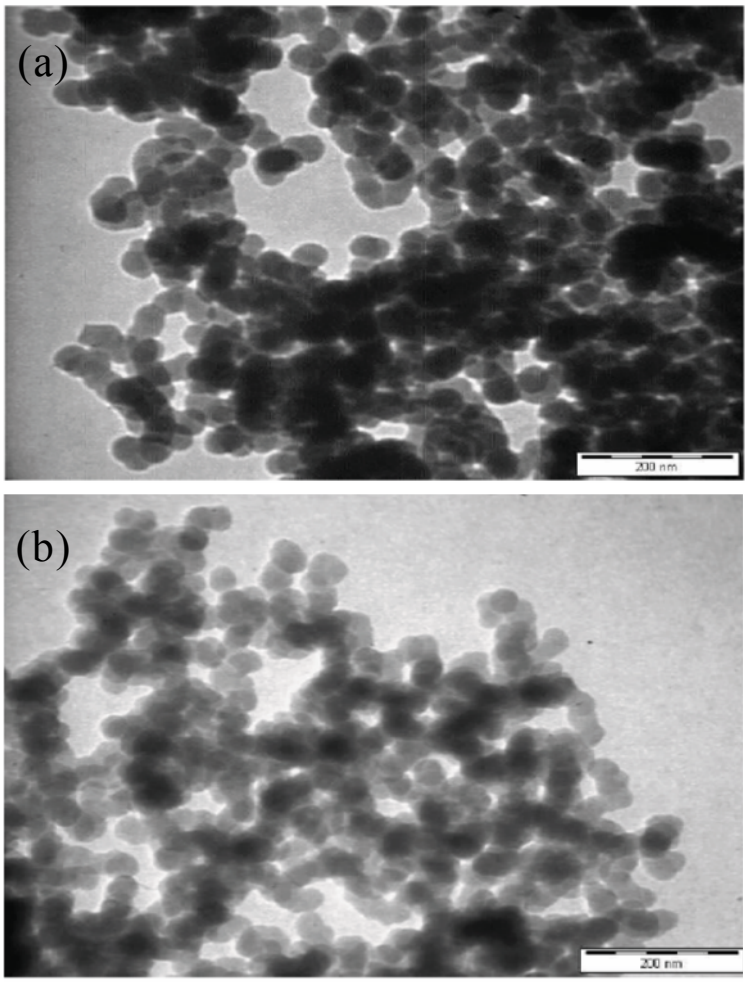

Figure 2.7 TEM image of silica nanoparticles (a): without surface treatment with high agglomeration and (b): with surface treatment with reduced agglomeration where the nanosilica particles are relatively in nanodispersed (Rahim et al., 2011)

2.3.1 (b) Maerogel

Aerogel was invented in 1932 by Kistler, an American scientist. He designated gels in which the liquid was replaced with a gas without collapsing the gel solid network. Wet gels were previously dried by evaporation and new supercritical drying technique was applied after gels being transformed to a supercritical fluid. In practice, supercritical drying includes heating a gel in an autoclave until the pressure and temperature exceed the critical temperature T_c and

pressure P_c of the liquid entraps in the gel pores to prevent the formation of liquid-vapor. Aerogel designated dry gels with a very high relative or specific pore volume depend on the nature of the solid (Michel et., 2011). The most frequently studied silica aerogels with 90 % of pore volume significantly lower in other types of aerogels. Figure 2.8 illustrates TEM micropgraphs of this aerogel and of a SiO_2 aerogel. In Figure 2.8 A, aerogel dried by the CO_2 supercritical method while Figure 2.8 B shows TEM micrograph of the aerogel in Figure 2.8 A. C. TEM micrograph of a SiO_2 aerogel made from 80% TMOS and 40% methyltrimethoxylsilane, dried by CO_2 supercritic method. Figure 2.8 D shows technical modeling of a local domain in an oxide aerogel, inspired from local zones in the TEM micrographs in Figures 2.8 B and C.

Silica aerogel is a mesoporous light solid material (Hrubesh, 1998, Schmidt and Schwertfeger, 1998), lightest and low bulk density (Obrey et al., 2011), low thermal conductivity, and high surface area with microstructure network consists of nano sized pore, superior insulating capabilities, particle with nanoscale size averaging (20 – 50 nm) (Tang and Wang, 2005, Parmenter and Milstein, 1998, Li and Wang, 2008, Soleimani Dorcheh and Abbasi, 2008, Sarawade et al., 2010). Maerogel, stand for Malaysian aerogel discovered by Malaysian researcher, Prof. Dr Halimaton Hamdan. It is a silica aerogel produced from rice husk ash which is an agricultural waste content 90 to 97% of Silicone dioxide (SiO_2) with trace amounts of CaO, MgO, K_2O, and Na_2O. Maerogel is the most suitable material to replace the conventional materials for silica aerogel production due to its high surface area, more superiority and low cost (80%) compared to current commercial aerogel. It is also non-toxic and an environmentally amorphous material which has simpler preparation

technique (Figure 2.9) and it possesses established physic-chemical properties which can be modified for specific applications (Halimation, 2009). Based on its properties (Table 2.6), maerogel can improve the mechanical properties of natural rubber composites (Tang and Wang, 2005).

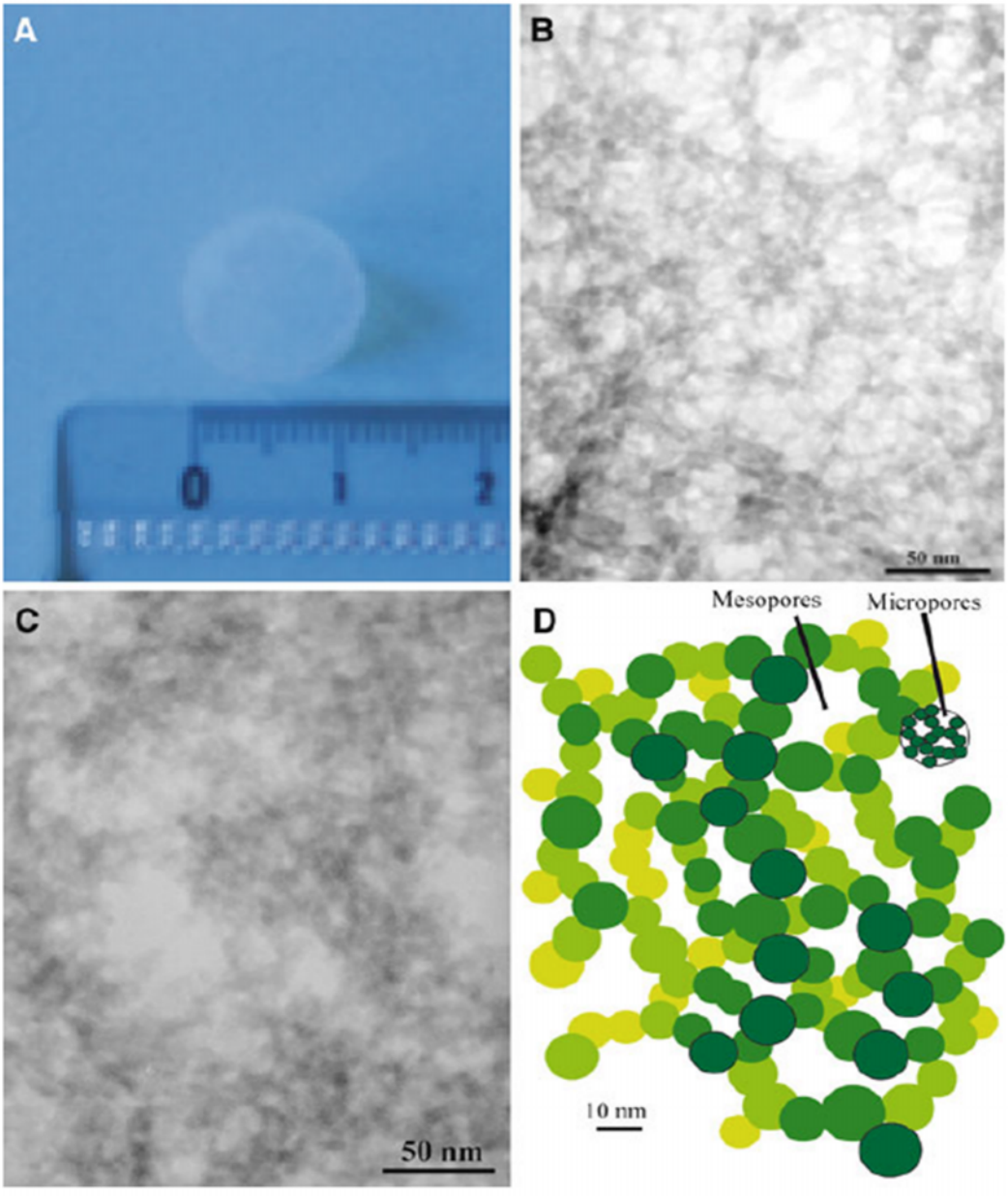

Figure 2.8 Micropgraphs of this aerogel and of a SiO_2 aerogel; (Michel et al., 2011)