

CHARACTERIZATION AND PROPERTIES OF STYRENE
BUTADIENE RUBBER/RECYCLED ACRYLONITRILE-
BUTADIENE RUBBER (SBR/NBR_r) BLENDS

By

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Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

February 2011

DEDICATION

Mami, Papa, Niza and family

ACKNOWLEDGEMENTS

Bismillaahirrahmaanirrahiim,

A special acknowledgement to Universiti Malaysia Perlis and Ministry of Higher Education (MOHE) for the scholarship to undertake this study.

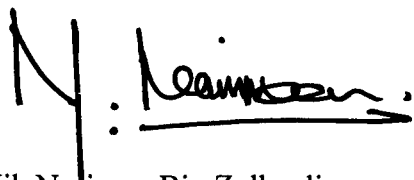
First of all, I am heartily thankful to my supervisor, Professor Dr Hanafi Bin Ismail, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the study. Compassionately that he was always there to listen, patiently, giving advice and showed me different ways to approach a research problem and the need to be persistent to accomplish any goal. In addition, the remembrance as a first champion in P/Grad Super Series on your trophy will be remaining in my days. I also wish to express my appreciation to my second supervisor, Dr Azura Abd Rashid, who made many valuable suggestions and gave constructive advice to improve the quality of this thesis.

Special gratitude are due to Professor Dr Ahmad Fauzi Bin Mohd Noor, Dean and all the technical staff in School of Materials and Mineral Resources Engineering for taking intense academic interest in this study as well as providing valuable suggestions. My utmost appreciation goes to Mr Segar, Mr Rokman, Mr Che Mat Hassan, Mr Rashid, Mr Azam, Mr Faizal, Mr Shahril, Mr Khairi, Mr Halim and Mr Mokhtar for their valuable assistance in the field. Without their help, the research would not have been accomplished in time. I would also like to show my appreciation to Universiti Sains Malaysia for awarding me the short term grant (USM-RU-PGRS) which has supported me during my three years of research.

I am indebted to my many student colleagues especially Sung Ting, Yamuna, Razif, Basri, Ragu, Kahar, Hamid, Faizal, Firdaus Lendu, Zunaida, Jai, Firdaus, Nik Akmal, Zharif and Mat Shah for providing a stimulating and fun environment in which to learn and grow. I would like to express special thanks to Niza for her motivation, encouragement and assistance during completion of this thesis.

Most importantly, my special appreciation goes to my parents, Zulkepli bin Hj Abd Hamid and Nik Khairani Binti Mohamad. This is the best honour to show my gratitude thus I dedicate this thesis for them. Above all, I wish to thank my entire family for their patient, encouragement and understanding along my study.

Lastly, it is a pleasure to thank those who made this thesis possible. I offer my regards and blessings to all of those who supported me in any respect during the completion of the thesis.

A handwritten signature in black ink, appearing to read 'N. Noriman', with a long horizontal flourish extending to the right.

Nik Noriman Bin Zulkepli

February 2011

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LIST OF SYMBOLS

t_2	Scorch time
t_{90}	Cure time
M_L	Minimum torque
M_H	Maximum torque
E_b	Elongation at break
M_{100}	Stress at 100% elongation
kGy	Kilogray
MeV	Megaelectron volt
phr	Part per hundred of rubber
T_m	Melting temperature
T_c	Crystallization temperature
T_g	Glass transition temperature
ML_{1+4}	Mooney viscosity
V_s	Molar volume of the solvent
V_r	Volume fraction of the swollen rubber
Q_m	Total weight swelling
θ_1	The initial angle (450)
θ_2	The maximum rebound angle
kg/m^3	Relative density
ΔT	Heat build-up
kJ/mol	Kilojoule per mol
m^2/g	Unit for BET surface area

LIST OF ABBREVIATIONS

HAF	High abrasion furnace
phr	Part per hundred rubber
NR	Natural rubber
NBR	Acrylonitrile butadiene rubber
NBRv	Virgin acrylonitrile butadiene rubber
NBRr	Recycled acrylonitrile butadiene rubber
SBR	Styrene butadiene rubber
W-EPDM	Waste ethylene propylene diene monomer
TPEs	Thermoplastic elastomers
TPVs	Thermoplastic vulcanizates
GRT	Ground rubber tire
CB/Sil	Carbon black/Silica
ASTM	American society for testing and materials
OAN	Oil absorption number
COAN	Oil absorption number compressed
CBS	N-cyclohexyl-2- benzothiazyl sulfenamide
ENR-50	Epoxidized natural rubber (50 mol%)
TOR	Trans Polyoctylene Rubber
MDR	Monsanto moving die rheometer
IRHD	International Rubber Hardness Degree
JIS	Japanese Industrial Standard
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared
ATR	Attenuated total reflection
ISO	International organization for standardization
Si69	Silane coupling agent

**PENCIRIAN DAN SIFAT-SIFAT ADUNAN GETAH STIRENA
BUTADIENA/GETAH KITAR SEMULA AKRILONITRIL-
BUTADIENA (SBR/NBRr)**

ABSTRAK

Pengitaran atau penggunaan semula sarung tangan getah kitar semula akrilonitril-butadiena (NBRr) dengan pencampuran getah sintetik stirena butadiena (SBR) boleh mewujudkan suatu peluang terhadap alternatif produk baru. Keputusan untuk siri pertama mendapati bahawa adunan getah SBR/NBRr memiliki sifat-sifat penambahbaikan pada kekuatan tensil, pemanjangan takat putus (E_b) and juga kelesuan (fatig) terutama mengandungi NBRr tidak melebihi 15 phr berbanding dengan adunan getah SBR/NBRv. Pada siri kedua pula, didapati adunan getah SBR/NBRr yang mempunyai saiz NBRr yang paling halus (S1; 117-334 μm) menunjukkan interaksi antara-muka yang baik di antara NBRr dan matrik SBR dan ini ditunjukkan dengan penambahbaikan pada keseluruhan sifat-sifat pematangan dan mekanikal berbanding dengan adunan SBR/NBRr yang memiliki saiz NBRr yang lebih besar [0.85-15.0 mm (S2) dan bentuk helaian terus (S3)]. Dengan pengurangan saiz, pemprosesan akan bertambah efisien (minimum tork rendah, M_L) dan luas permukaan sentuhan akan meningkat di mana akan menyebabkan ikatan pelekatan-dalaman yang efisien, seterusnya menyumbangkan kepada penambahbaikan sifat-sifat tertentu. Dalam siri ketiga, penambahan 5 phr getah *trans-polyoctylene* (TOR) sebagai agen pembantu pemprosesan telah menambahbaik pelekatan antara-muka NBRr dengan matrik SBR, seterusnya meningkatkan keserasian adunan getah SBR/NBRr. Sifat-sifat pematangan seperti masa pematangan, t_{90} dan masa skorj, t_2 yang pendek serta pemprosesan yang efisien dan juga sifat-sifat mekanikal/fizikal seperti kekuatan tensil, modulus tensil (M_{100}),

kekerasan, kelesuan dan ketumpatan penyambungsilangan adunan getah SBR/NBRr yang telah dicampurgaul dengan TOR didapati meningkat berbanding adunan getah SBR/NBRr yang tidak dimasukkan TOR. Sementara itu pada siri keempat, penambahan 10 phr getah asli terepoksida (ENR-50) juga telah menambahbaik keserasian adunan getah SBR/NBRr. Secara keseluruhan sifat-sifat pematangan dan mekanikal adunan getah SBR/NBRr dengan kehadiran ENR-50 memiliki t_{90} dan t_2 yang pendek, pemprosesan yang lebih efisien dan juga peningkatan dalam kekuatan tensil, kekerasan serta termal yang baik. Pada siri kelima, didapati penggabungan Si69 dalam adunan getah SBR/NBRr telah menambahbaik sifat-sifat pematangan seperti masa t_{90} yang pendek serta pemprosesan yang efisien. Manakala penambahbaikan bagi sifat-sifat mekanikal seperti kekuatan tensil, kelesuan dan kekerasan pada adunan getah SBR/NBRr dengan CB/Sil/Si69 telah dipengaruhi oleh darjah ketumpatan sambung-silang. Pada siri keenam, kesan adunan getah SBR/NBRr terhadap pendedahan kepada pencuacaan semulajadi telah menunjukkan kemerosotan sifat-sifat terutamanya selepas 6 bulan. Walubagaimanapun, kebanyakan modifikasi terhadap adunan getah SBR/NBRr telah menunjukkan variasi penambahbaikan pada pengekal sifat-sifat tensil.

CHARACTERIZATION AND PROPERTIES OF STYRENE BUTADIENE RUBBER/RECYCLED ACRYLONITRILE-BUTADIENE RUBBER (SBR/NBR_r) BLENDS

ABSTRACT

The recycling or reuse of waste rubber from recycled acrylonitrile-butadiene rubber glove (recycled NBR glove) by means of blending together with synthetic rubber styrene butadiene rubber (SBR) can give an opportunity as an alternative product. Results in first series indicated that SBR/NBR_r blends particularly having NBR_r content up to 15 phr, exhibited improvement in tensile strength, elongation at break, E_b and fatigue value compared with SBR/NBR_v blends. Meanwhile, in second series SBR/NBR_r blends with the smallest size of NBR_r particles (S1, 124-334 μm) showed an improved overall cure characteristics and mechanical properties compared with all other blend ratios contains of bigger sizes of NBR_r particles [0.85 – 15.0 mm (S2) and direct sheeted form (S3)]. At third series, addition of 5 phr of trans-polyoctylene rubber (TOR) as compatibilizer improved the adhesion between NBR_r and the SBR matrix, thus improving the compatibility of SBR/NBR_r blends. Most of cure characteristics and mechanical properties of compatibilised SBR/NBR_r blends were improved compared with uncompatibilised SBR/NBR_r blends. Meanwhile in fourth series, the addition of 10 phr of epoxidized natural rubber (ENR-50) also enhanced the compatibility of the SBR/NBR_r blends. Overall cure characteristics and mechanical properties showed that SBR/NBR_r blends with the presence of ENR-50 have lower t_{90} , t_2 and M_L and improved the tensile strength, hardness and thermal properties. At fifth series, the incorporation of Si69 has improved the cure characteristics such as lower t_{90} and M_L . Overall improvement on mechanical properties such as tensile properties, fatigue and hardness of the blends

with Si69 were influenced by the degree of crosslinked density as the silica content is increased. On sixth series the investigation on natural weathering test of all series of SBR/NBRr blends showed weakening in overall properties particularly after 6 months exposure. However, most of the SBR/NBRr blends with modification showed better tensile properties with variations of tensile retention.

CHAPTER 1: INTRODUCTION

1.1 Recycling of waste rubber

1.1.1 An outlook and trend

The waste disposal in the world is a big concern and changing to be ever increasingly serious with the industry development and the population growth. Over the last few decades, intensive research and development efforts have been directed towards finding cost effective and compatible solutions for waste minimization and utilization (Guo et al., 2010). Recycling of waste rubber has become an important global issue which can solve three major problems; wasting of valuable rubber, health and environment pollution (Wu and Zhou, 2009). The environment concern and waste management created by waste rubber and discarded tyres have become serious in recent years. The global annual production level has reached to about 21.50 million tonnes in 2006 (Rubber Industry Report, 2007). Production costs of polymeric materials obtained from the waste are frequently higher than those of similar materials made of original polymers. Thus, one has to try to lower the costs of the material recycling by, e.g., elimination or, at least, reduction of the scale of the costly process of waste sorting. Rubbers have many applications, ranging from footwear to automobile tyres, because of their unique mechanical properties such as good elastic behaviours even at large deformation, and good energy absorbing capacity. Therefore, improvement of the mechanical properties of the materials produced from the blends of rubber waste may be accomplished by the application of suitable compatibilizers, crosslinking additives, and/or electron radiation, which leads to an increase in the interfacial adhesion of macromolecules of the polymers forming a given blend. In this way, for example, impact strength of such materials

can be enhanced (Czvikovszky, 2003 and Z'enkiewicz and Dzwonkowski, 2007). The materials obtained from recycling processes should be utilised, if possible, in areas in which any inferior mechanical properties would play an insignificant role. Consequently, the mechanical properties of these materials should be thoroughly examined, but such investigations should be performed with great care because any deviation from standards and rules relating to both the making of measurements and the interpretation of results might cause serious errors (Z'enkiewicz and Kurcok, 2008).

1.1.2 Malaysia as rubber manufacturer

The Malaysian rubber-based industry has performed well in the last two decades. Malaysia is currently the world's ninth largest consumer of all rubber, following China, USA, Japan, India, Germany, France, South Korea and Russia and the fifth largest consumer of natural rubber behind China, the USA, Japan and India (<http://www.mrepc.com/industry/>). Malaysia is renowned worldwide for its high quality, competitively priced rubber products. Malaysian rubber products manufacturers comprise multinationals from various countries including the USA, Europe and Japan, as well as locally-owned medium and small sized enterprises. Table 1.1 and 1.2 illustrates the statistical summary of world synthetic rubber and prices situation from International Rubber Study Group (Rubber Statistical Bulletin, January-March 2010 edition, International Rubber Study Group). These companies are able to supply a whole range of rubber products such as medical gloves, automotive components, beltings and hoses. In other view, Malaysia also is the leading supplier of examination and surgical gloves, satisfying 45% of the world's demand. Examination gloves are mainly used in the medical and health care

facilities. Furthermore, Malaysia is known as the world's leading supplier of foley catheters and latex thread (vulcanized rubber thread and cord). Latex thread is mainly used in the apparel industry as elastic bands and supports. Other important latex products include condoms, balloons, finger stalls, teats and soothers. Malaysia has produces a wide range of rubber products (Table 1.3) such as hoses, beltings, seals, wires and cables for the world market.

Table 1.1 Statistical summary of world synthetic rubber (Rubber Statistical Bulletin, January-March 2010 edition, International Rubber Study Group)

Synthetic Rubber Production ('000 tonnes)	2007	2008				2009			
	Year	Q1	Q2	Q3	Q4	Year	Q1	Q2	Q3
North America	2790	675	655	595	485	2410	410	507	579
Latin America	684	183	174	155	128	639	114	175	162
European Union	2684	701	686	613	549	2550	474	519	559
Other Europe	1285	356	331	289	207	1182	224	240	281
Africa	71	21	22	19	14	75	14	15	15
Asia/Oceania	5916	1454	1577	1493	1404	5927	1453	1575	1631
TOTAL	13430	3390	3444	3162	2788	12784	2689	3030	3227

Table 1.2 Synthetic rubber price (Rubber Statistical Bulletin, January-March 2010 edition, International Rubber Study Group)

Synthetic Rubber Prices	2007	2008				2009			
	Year	Q1	Q2	Q3	Q4	Year	Q1	Q2	Q3
USA Export Values US Dollar \$/tonne	2012	2018	2374	2879	2774	2511	2168	1598	1838
Japan SBR Export Value '000Yen/tonne	222	231	243	287	278	260	199	170	180
France, SBR Export Value £/tonne	1483	1493	1566	1798	1951	1702	1628	1441	1522

Table 1.3 Malaysia's Export of Selected Rubber Products, 2005 – 2008
(Source: Department of Statistics, Malaysia)

Rubber Products	2005 Value (RM Million)	2006 Value (RM Million)	2007 Value (RM Million)	2008 Value (RM Million)
Gloves, other than surgical gloves	3,793.23	4,624.52	5,095.24	5,991.92
Surgical gloves	706.87	758.39	780.41	916.34
Catheters	647.71	469.92	670.02	285.22
Vulcanized rubber thread and cord	574.20	745.66	720.86	615.48
Wire, cable and other electrical conductors	60.96	86.74	103.04	22.84
Piping and tubing	216.72	223.08	307.60	338.31
Sheath contraceptives	115.78	143.75	151.71	212.50
Belting	55.22	57.92	62.15	59.31
Precured tread of non-cellular rubber	33.69	33.51	38.89	10.88
Cellular rubber lined with textile fabric on one side	24.94	17.23	13.40	6.56
Finger stalls	9.51	9.85	8.67	4.46
Teats & soothers	9.30	12.32	17.36	14.14
Pipe seal rings of unhardened vulcanized rubber	3.43	2.38	1.53	0.50

1.1.3 Utilization

Recycling rubber waste contributes to a cleaner environment by using indestructible rubber discards as well as lowering production costs as reclaimed rubber is cheaper than virgin or natural rubber. Example, Rubplast was set up in 1988 as a joint venture between Malaysian Rubber Development Corporation (Mardec) and Bombay-based India Coffee and Tea Distribution Company, in response to the problem of rubber waste (<http://www.rubplastmalaysia.net/>). The company processes 500 tonnes of rubber waste each month, turning them into reclaimed rubber that is mostly exported to rubber product manufacturers abroad. At the Rubplast factory, rubber glove waste, both rejects from manufacturers as well as soiled ones from factories, form 35% of the waste that is recycled (Fig 1.1). Others

are scraps from rubber product manufacturers, rubber treads, rubber fleshing (scraps from tyre manufacturers), nylon-belted tyres, tubes and rubber foam (from cushions and mattress in Singapore, recyclers are paid S\$200 (RM460) for every tonne of rubber waste recycled because of their effort in minimising waste.



Figure 1.1 Rubber gloves are processed into reclaimed rubber at the Rubplast factory(<http://thestar.com.my/news/story.asp?file=/2006/6/13/lifefocus/14433323&sec=lifefocus>, Tuesday, June 2006)

In recent years, the practice of recycling has been encouraged and promoted by increasing awareness in environmental matters and the subsequent desire to save resources. Together with the relatively high cost of polymers and sometimes high levels of scrap material generated during manufacture, recycling becomes a viable and attractive option (Perez et al., 2010). Even the revelation regarding re-utilization of rubber products in many circumstances, few people still do not realize the significant of bringing back those waste and become value added materials or products. In fact, rubber recovery can be a difficult process, however the important

of reclaiming or recycling the rubber could be explained as recovered rubber can cost half that of natural or synthetic rubber; recovered rubber has some properties that are better than those of virgin rubber; producing rubber from reclaim requires less energy in the total production process than does virgin material; it is an excellent way to dispose of unwanted rubber products, which is often difficult; it conserves non-renewable petroleum products, which are used to produce synthetic rubbers; recycling activities can generate work in developing countries and many useful products are derived from reused tyres and other rubber products, if tyres are incinerated to reclaim embodied energy then they can yield substantial quantities of useful power. For example, in Australia, some cement factories use waste tyres as a fuel source. (<http://www.practicalaction.org>. Practical Action, The Schumacher Centre for Technology & Development).

1.2 Research background

The utilization of waste rubber powder in polymer matrices provides an attractive strategy for polymer waste disposal. Addition of scrap or recycled rubber in the form of either ground waste vulcanizates or reclaim in rubber compounds gives economic as well as processing advantages. In attempt to lowering the cost of rubber compounds, the use of cross-linked rubber particles has beneficial effects such as faster extrusion rate, reduced die swell and better molding characteristics (Srivanasan et al., 2008).

While most Malaysian glove manufacturers are racing to expand production and stay ahead in this competitive industry, one concern is that not enough attention is being given to environmental issues. According to world report from The EDGE, Malaysian gloves have been used as a global standard benchmark. The conventional

glove market, which is dominated by Malaysian manufacturers, global consumption is about 140 billion pieces of gloves annually and able to produce three billion pieces a year or even more within three years. One of the major factors that influence recyclable of rubber gloves is the cost of rubber gloves is still very low. However, they can be used up to seven times after reconditioning (<http://www.ecoglove.com>).

Recycled latex has become a focus of attention compared to reclaimed rubber due to the lightly cross-linked and high quality nature of rubber hydrocarbon (George and Rani, 1996, Anandhan et al., 2003). The use of acrylonitrile- butadiene rubber (NBR) latex in glove production has increased all over the world due to its excellent resistance to puncture and tears as well as the non-existence of leachable allergenic proteins, unlike natural rubber latex. Nitrile is an alternative to NR latex. Nitrile is a synthetic material, and as such, does not have protein. Therefore nitrile gloves are not likely to cause allergies in people. It interacts to the heat of the wearer's hand in order to create a snug fit. This is ideal for increased sensitivity. Nitrile rubber gloves are also soft and resist chemicals much like NR latex. However, its ability to resist liquids is not as documented as latex is. Nitrile is appropriate for the auto and industrial fields. It is also used in dental and pharmaceutical fields (<http://www.wisegeek.com/what-are-the-different-types-of-rubber-gloves.htm>). Like vinyl, they are less elastic than natural rubber latex (NRL) but are significantly more durable (Micheal, 2001, Welker and McDowell, 1999). They feature good physical properties and provide the wearer with good dexterity. Nitrile gloves are resistant to many chemicals but like other glove types are sensitive to alcohol degradation. They have been found to be sensitive to ozone degradation and the elastomers can be somewhat brittle, possessing a higher modulus and greater

stiffness than NRL (Graves and Twomey, 2002). While they are abrasion and puncture-resistant, once breached, they tear easily resulting in breaks where their varied colours help to identify glove pieces that may end up in food (<http://www.foodsafetymagazine.com/article.asp?id=1358&sub=sub1>). Unlike other latex gloves, nitrile gloves have low resistance to friction and are very easy to slide on. There are a few other reasons that nitrile gloves are more popular than other latex or vinyl gloves, including a higher degree of flexibility and superior solvent resistance (<http://www.wisageek.com/what-are-nitrile-gloves.htm>).

Nitrile gloves are currently used in many areas such as the medical field and, to a greater extent, the food industry, automotive industry, etc. As a result, significant quantities of discarded gloves are generated worldwide daily. In Malaysia, the output of nitrile rubber gloves was found abundant. Most of this material originates from medical, industrial as well as research activities. As a fact, nitrile rubber is widely use due to great oil resistance, heat and plasticizer and low gas permeability, high shear strength for structural applications and also its resilience makes NBR the perfect material for disposable used in lab, cleaning, and examination gloves (<http://www.gloves.com.my/files/Building%20Blocks%20of%20Nitrile%20Gloves.pdf>). However, after a certain period of time these polymeric materials are not use and mostly discarded.

In recent year considerable emphasis has been given to utilize either plastics or rubber waste (such as tyres) in an environment-friendly manner. Through the rubber recycling technology (the blending of polymer, especially elastomers together with recycled waste) can meet the performance and processing requirements to manufacture a wide range of rubber based products such as road and

playground surfaces, recycled rubber flooring, adhesive glues, sporting mats, floats, marine and automotive parts, and so much more. Many elastomers that have dissimilar chemical structure are blended to improve processability, performance, durability, physical properties, and to achieve an economic advantage. Elastomers with similar polarities and solubility characteristics can be easily combined to produce a miscible polyblend. In applications where excellent solvent resistance is not crucial, it is often desirable to replace acrylonitrile-butadiene rubber (NBR) with emulsion styrene-butadiene rubber (E-SBR) in order to reduce raw material costs. Unfortunately, NBR has limited compatibility with non-polar polymers such as SBR, polybutadiene (BR) and natural rubber (NR). However, the low acrylonitrile NBR grades can be blended with SBR over the full range of concentrations, without significant deterioration of mechanical vulcanizate properties. In fact, a number of these blends are used in several critical applications such as NBR/SBR blends are used to compensate the volume decrease in oil seal applications (Shield et al., 2001). Therefore, regarding to the present output of nitrile glove, perhaps the utilization of nitrile waste (glove) will be a great deal of interest in the rubber industry about the development of cost effective techniques to convert waste and used rubber into a processable form in future.

1.3 Problem statements

It is well known that direct material recycling and reshaping is difficult because of the irreversible three-dimensional crosslinking of rubber. It means that they cannot be re-melted or dissolved in organic solvents. The three dimensional network of sulfur-cured elastomers has the following types of chemical bonds with their bond dissociation energies (Table 1.4). Many attempts have been made to reuse

waste rubbers by reclamation (Benazzouk et al., 2006; Chou et al., 2007), devulcanization (Jana and Das, 2005; Debapriya et al., 2006; Zhang et al., 2007b), high pressure and high temperature sintering (Mui et al., 2004), fuel recovery (Jasmin et al., 2007) and other (Bredberg et al., 2002). Most processes are based on mechanical shear, heat, and energy input together with a combination of chemicals such as oils, accelerators, amines, or disulfides to reduce the concentration of sulfur crosslinks in the vulcanized rubber (Myhre and MacKillop, 2002).

Accordingly, scrap rubber is generally incinerated or discarded in landfills. These methods cannot be the final solution because they have caused many problems, such as soil and air pollution. Since most rubber products are sulfur vulcanized and protected with antidegradants, they produce sulfur and nitrogen oxides on combustion. These gases are not acceptable in the environment; therefore the burning of scrap rubber may not be an acceptable solution in the long term (Myhre and MacKillop, 2002).

Table 1.4 Bond strength of different bonds in rubber network (Rajan et al., 2007)

Type of bond	Bond dissociation energy (kJ/mol)
C-C, carbon-carbon bonds	349
C-S-C, sulphur-carbon bonds	302
C-S-S-C, sulphur-sulphur bonds	273
C-S _x -C (x ≥ 3), sulphur-sulphur bonds	256

Grinding is the basic step for recycling scrap rubber, and ground rubber (GR) has been used as the raw material not only for the production of reclaimed rubber but also for various applications, such as fillers for rubber, fillers for thermoplastic compounds, and modifiers for asphalt concrete. From economic and environmental

points of view, the use of GR as a filler for rubber compounds has more merit than other methods because it does not need additional processing, reactions, or treatments, and the chemical nature of the various ingredients in GR can be maintained (Kim et al., 2007). Meanwhile, the rubber waste is ground to powder and then devulcanised with the aid of oils and chemicals (a reversal of the process which hardens rubber latex with the addition of sulphur) to become soft reclaimed rubber, normally done under high heat in a chamber. However, most of these processes were either conducted at high temperature, which lead to a higher degradation of the rubber backbones, or used chemicals as devocalizing agents, which lead to a higher cost and environmental pollution. Every year large numbers of papers are published on the recycling of vulcanized rubber products where the rubber powder is used as filler or blended with virgin rubber or the modified rubber powder is incorporated in different composite materials (Siddique and Naik, 2004 and Benazzouk et al., 2007).

The most important recycling process currently is to utilize waste rubber as a very finely ground powder, produced either by ambient temperature mechanical grinding or by cryogenic shattering. In general, the powder rubber is combined with virgin elastomer compounds to reduce the costs with the additional advantage of an improvement of the processing behaviours. However, some loss in physical properties and performance is observed (Rajan et al., 2007). This factor has motivated the search for cost effective in situ regeneration or devulcanization of the scrap rubber to provide recycled material with superior properties.

1.4 Research objectives

The aims of these studies were to define the prospective of recycled NBR glove (NBRr) as a part in styrene butadiene rubber-based blends (SBR/NBRr blends). Therefore it can be outline as follows;

- i) To determine the characteristics and properties of styrene butadiene rubber/virgin acrylonitrile-butadiene rubber (SBR/NBRv) blends with styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.
- ii) To determine the effects of different size of recycled acrylonitrile-butadiene rubber and its blend ratio on properties of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.
- iii) To examine the effects of trans-polyoctylene rubber (TOR) and epoxidized natural rubber (ENR-50) as a compatibilizer on properties of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.
- iii) To determine the effects of carbon black/silica (CB/Sil) hybrid filler in the presence of silane coupling agents (Si69) on properties of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.
- vi) To study the effects of natural weathering test on tensile properties and morphology of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.

CHAPTER 2: LITERATURE REVIEW

2.1 Recycled rubber waste: An approach and utilization

In recent years, the practice of recycling has been encouraged and promoted by increasing awareness in environmental matters and the subsequent desire to save resources. Together with the relatively high cost of polymers and sometimes high levels of scrap material generated during manufacture, recycling becomes a viable and attractive option. The recycling of scrap material, and mixing with virgin material, is the most common solution (Pérez et al., 2010). The development of suitable technology in waste rubber recycling is an important issue faced by the rubber industry. Lee et al., (2009) studied the effect of physical treatments of waste rubber powder on the mechanical properties of the revulcanizate. An efficient grinding machine was designed, used in the powdering of waste rubber tire with ozone/ultrasonic devulcanization which applied onto the surface of waste tire powder. As a results, the ozone/ultrasonic treatment was found to be the most effective treatment to improve the mechanical properties of waste rubber powder revulcanizate. In almost all commercial applications, the reclaimed rubber is used in a blend with virgin rubber. Incorporation and dispersion of reclaim rubber into the virgin rubber plays important roles in product quality and production economy. Rajan et al. (2006a), observed that reclamation of natural rubber latex based rubber using 2,20-dibenzamidodiphenyldisulphide as reclaiming agent is an optional methodology for recycling of waste latex rubber (WLR). Kumar et al. (2007) revealed a possible techniques that can examine both recycled rubber-virgin rubber properties; either increasing the effective surface area by reducing the granulate size or by surface modification of granulates so that it can improve the adhesion between

the matrix and granulates. Dierkes et al. (2007) studied the influence of different amounts of reclaim on the properties of a virgin compound in terms of mechanical and dynamic viscoelastic properties, crosslink density and distribution and sulfur distribution between the matrix and the reclaim. They summarized that the mechanical and viscoelastic properties are affected by the following factors; a) presence of gel in the reclaim; b) adhesion of the reclaim to the matrix; c) particle size of the reclaim; d) sulfur distribution between the matrix and reclaim; e) crosslink density and distribution. The decrease in tensile strength with increasing concentrations of reclaim with respect to the decrease in the molecular weight of the sol fraction in the reclaim and the presence of the crosslinked gel. The reclaim particle acts as an obstacle for stress transmission within a continuous matrix resulting in an initiation of failure expressed by lower tensile strength. The stress accumulates on the interface between the reclaimed particle and the matrix and fracture starts from this point. With increasing concentrations of reclaim, the concentration of weak spots increases and the tensile strength of the system decreases. Rajeev and De (2004), has come out with a review on the utilization of waste rubber and waste plastics for the preparation of thermoplastic elastomers (TPEs). TPEs based on ground rubber tire (GRT), waste ethylene propylene diene monomer (W-EPDM) rubber, waste nitrile rubber, recycled rubber, latex waste, and waste plastics are described with respect to composition and physical properties. It was found that part of the rubber phase or plastics phase or both in the rubber-plastics blend can be replaced with corresponding waste polymer for the preparation of thermoplastic elastomers. In many cases, the materials prepared from waste polymers show properties comparable to those prepared from fresh polymers. However, in some cases, the materials prepared from waste rubber or waste plastics

cannot be classified as TPEs, as the blend compositions show very low elongation at break. Modification of the waste polymer or the use of compatibilizers results in stronger composites. Yun and Isayev (2003) studied about the superior mechanical properties of ultrasonically recycled EPDM rubber. They found that the tensile strength of revulcanized EPDM is much higher than that of the original vulcanizates with elongation at break being practically intact. The investigation on utilization of powdered EPDM scrap in EPDM compound by Jacob et al. (2003a), revealed that processability studies of the compounds show that in the range of selected shear rates, addition of waste W-EPDM particles improves the extrusion characteristics like-reduced die swell, better surface smoothness and lesser distortion.

2.1.1 A terminology used for recycling

Recycling can be known as the processes where the reject or scrap rubber is converted into a reusable material to make new products. Meanwhile, reclaiming is processes that break down vulcanized rubber by heat in the presence of chemicals or high-pressure steam. The break down of reject or scrap rubber can be accomplished by devulcanization (breaking sulfur-sulfur bonds) or by depolymerisation (breaking polymer chains). The reclaiming procedure consists of two technologies which the reject or scrap rubber is first chopped into pieces and ground into fine particles known as crumb. In the second technology, the crumb is subjected to heat in the presence of chemicals and then followed by intensive friction milling such as cryogenic. All reclaiming processes require the input of energy. Figure 2.1 show the summary of reclaiming of rubbers by physical and chemical processes. The two processes that were most often used were the heater process and the pan process. The major process at the present time is to utilize the scrap rubber as a very finely

ground crumb. In general, the crumb rubber is combined with virgin elastomer compounds to reduce cost. However, there is some loss in physical properties and performance. This factor has motivated the search for cost effective in-situ regeneration or devulcanization of the scrap rubber to provide superior properties. Reversion is a term used in rubber industry to describe decreases in the mechanical properties (namely modulus and strength) at the end of the curing period or during service.

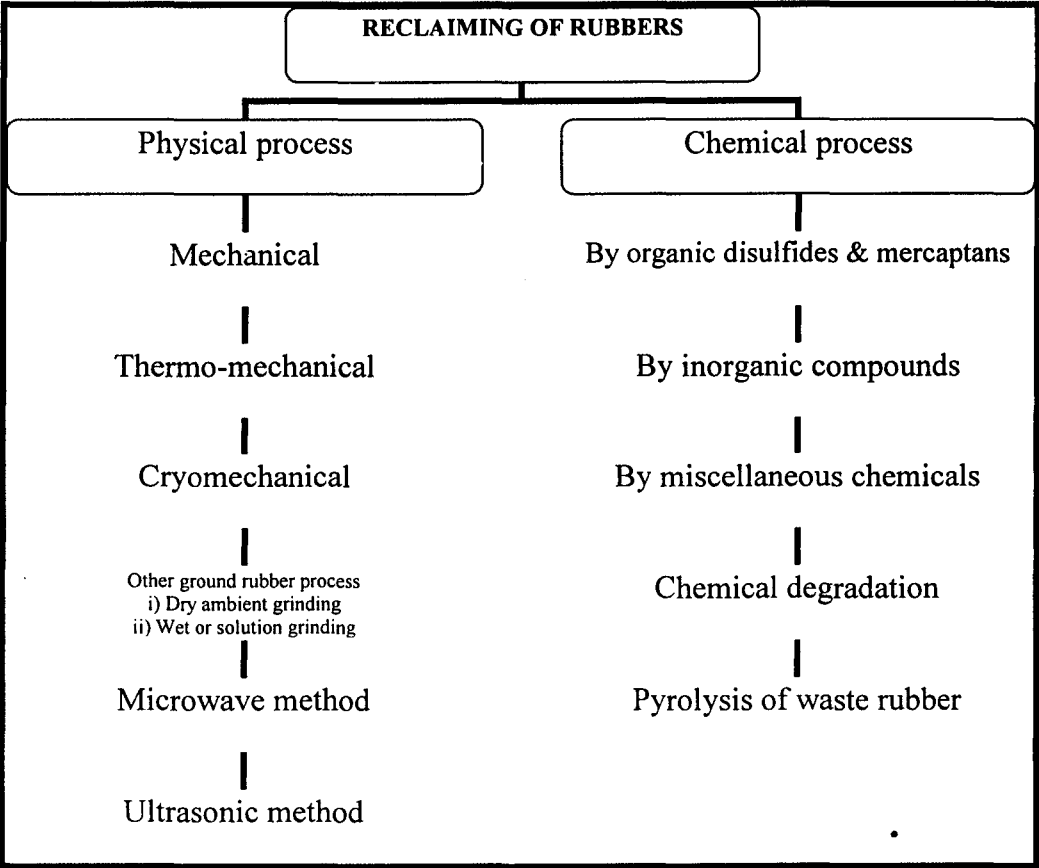


Figure 2.1 The summary of reclaiming of rubbers by physical and chemical processes (Adikari et al., 2000)

2.1.2 Grindings and powdered recycled rubber

The simplest approach of rubber recycling is the grinding of vulcanizates and utilization of the powdered rubber. Powdered rubber is unique as filler because of its larger size (in the range of microns) and lower modulus, when compared to other commercial fillers used in the rubber industry. Like other fillers, the polarity (either the surface functional groups or the polar nature of the polymer) and the structure (either spongy, chain-like aggregates or free-flowing powder) of ground vulcanizates affect the physicochemical properties of ground rubber-filled vulcanizates. When added to the same base compound (that is, when the composition of the powdered rubber and the matrix are the same), powdered rubber can act as an extender to the rubber matrix, with a minimum change in compound properties. When the compositions of the powdered rubber and the matrix are different, the factors controlling the loading level for maximum performance include the compatibility of: elastomeric systems, curing systems, hardness difference, and tensile strength requirements. The technique of preparation of powdered rubber greatly influences the particle size and surface topography, which in turn affects the mechanical properties of the powder-filled compositions. The common methods of powdering the rubber vulcanizate such as i) ambient grinding (Adhikari et al., 2000), ii) cryogenic grinding (Liang and Hao, 2000) iii) wet grinding (Klingensmith and Baranwal, 1998), iv) extrusion (Khait and Torkelson, 1999) and v) abrasion (Jacob et al., 2000).

Even the production cost which depends upon liquid nitrogen consumption, cryogenic grinding is more economical than ambient grinding (for production of finer mesh size powders) due to; i) since cryogenically frozen rubber pulverizes more easily than rubber at ambient temperatures, there is less wear and tear of the

machinery, and maintenance costs are significantly reduced and ii) degradation of the rubber, due to the heat buildup during shearing, is negligible in the cryogenic grinding method, in contrast to the ambient method.

Besides the composition of the powdered rubber, the other parameters affecting the performance properties are the particle size and its distribution, shape, surface topography, and the surface functionalities (that is, the presence of polar groups on the particle surface). Figure 2.2 illustrates (a) the ultra-fine powdered rubber ($< 10 \mu\text{m}$) exists as aggregates which break down under shear (b) a typical abraded particle separated out by the ultrasonic dispersion technique.

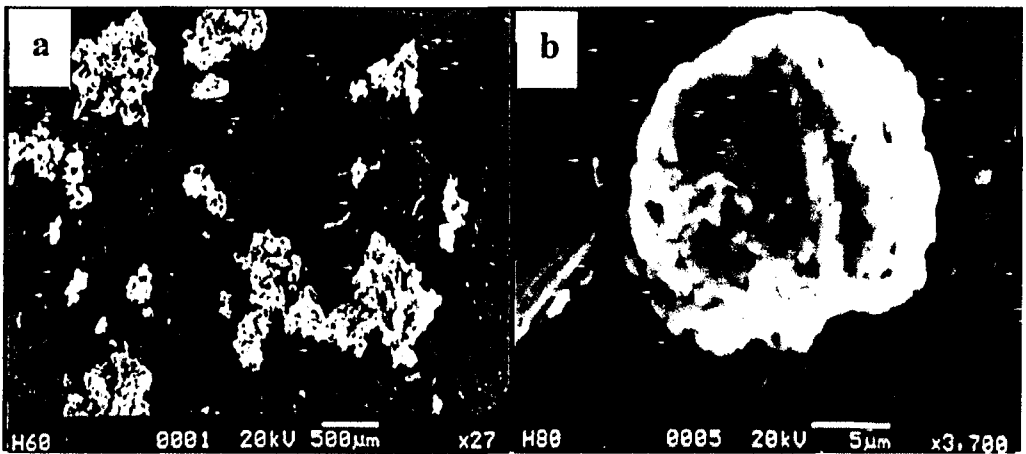


Figure 2.2 illustrates (a) the ultra-fine powdered rubber ($< 10 \mu\text{m}$) exists as aggregates which break down under shear (b) a typical abraded particle separated out by the ultrasonic dispersion technique (Jacob et al., 2003a)

2.1.3 Properties of recycled rubber blends based on study case

2.1.3.1 The influence on rheology

In two series of study involving waste from EPDM, Jacob et al., (2000 and 2003a) highlight that with the addition of EPDM-abraded powder (highly filled and oil extended) into a gum EPDM rubber compound results in increased Mooney viscosity but lower high shear viscosity. The drop in viscosity at higher shear rates

for the EPDM compound containing EPDM powder with high amount of oil and carbon black may be due to the wall slippage facilitated by the plasticizer migration. It is also found that the viscosity increases (at all shear rates) with the increasing amount of filler present in the powdered rubber. Gibala et al. (1996) studied the cure and mechanical behaviour of rubber compounds containing ground vulcanizates. They found that the increase in Mooney viscosity by the addition of ambient ground powder is more than that by the addition of the same amount of cryoground rubber, which can be ascribed to the better interaction between the convoluted and rough surface of the spongy, ambient ground rubber and the matrix.

2.1.3.2 The influence on curing characteristics

Addition of ground rubber affects the scorch time, optimum cure time, rate of cure, and state of cure of the rubber compound, depending upon the nature of the polymer in the matrix and the characteristics of the rubber powder (Gibala et al., 1996). Ishiaku et al. (2000) studied the effect of convoluted rubber vulcanizate powder, obtained from the sanding process of polishing rubber balls, on the properties of NR compound. It was observed that scorch time and cure time decrease and the tendency toward reversion increases with increasing powder concentration. The effect of cryoground rubber on properties of NR has been studied by Phadke et al. (1986). It has also been found that the maximum torque (M_H) and the Δ torque decrease with the addition of ground rubber. The reasons suggested for the decreased M_H value are the plasticizer (acetone extractables) migration from the ground rubber to the matrix rubber and migration of free sulfur from the matrix rubber to the cross-linked particles (ground rubber) because there exists a concentration gradient between the cross-linked and matrix rubber phases.

2.1.3.3 The influence on mechanical properties

There are several reports on mechanical properties of ground rubber-filled rubber vulcanizates. The factors affecting the performance of a vulcanizate containing powdered rubber are the particle size, hardness, and aging condition of the precursor rubber article; filler content in the particle; and the particle-matrix rubber interaction. Ismail et al. (2002a) investigated the comparison properties of recycle rubber powder (RRP), carbon black and calcium carbonate filled natural rubber compounds. They found that the tensile strength, tensile modulus, and hardness increase with increase in CB loading, whereas elongation at break, resilience, and swelling properties show opposite trend. For RRP and calcium carbonate filled natural rubber compounds, the tensile strength increases up to 10 phr and starts to deteriorate at higher filler loading. The other properties such as tensile modulus, hardness, elongation at break, resilience, and swelling percentage show a small change (increase or decrease) with increase in RRP and calcium carbonate loading in natural rubber compounds. In other study, the effect of recycled rubber powder (RRP) on cure characteristics, tensile properties and swelling behaviour of natural rubber (NR) compounds was investigated in the concentration range of 0 to 50 phr (Ismail et al., 2002b). Results indicate that the with increasing RRP loading also gives natural rubber compounds better resistance towards swelling and reduces the elongation at break but the tensile stress, M100 (stress at 100% elongation) and M300 (stress at 300% elongation), increases slightly. However, the tensile strength increases up to 10 phr of RRP and then decreases.

Burford and Pittolo (1984) studied the effect of hardness of the rubber powder (ambient-ground, using shear mill equipped with 1-mm size screen) on the failure properties of unfilled and carbon black-filled butadiene rubber compounds.

Hardness of the powdered rubber has been varied by varying the filler content or the dosage of the curing agent. It is found that increasing hardness of the rubber powder causes progressive reduction in tensile strength and elongation at break, but increase in modulus. Jacob et al. (2003a), studied on utilization of powdered EPDM scrap in EPDM compound. It was found that the mechanical properties of the vulcanizates indicate that the optimum loading is 300 phr of recycled EPDM. Although 100 phr of powdered rubber contributes to a slight increase in modulus (at 100% elongation) of the vulcanizate, further addition up to 500 phr results in negligible changes only. At higher elongation (i.e., at 300% elongation) the modulus increases continuously, implying that the contribution of carbon black content in the particles to the modulus is evident only at higher strains. The tension set at 100% elongation for the vulcanizates is low and is independent of the powder loading (Table 2.1).

Table 2.1 Effect of powdered rubber (abraded) loading on the mechanical properties of powdered rubber-filled vulcanizates ^{a,b}, Jacob et al. (2003a)

Property	Mix Designation			
	W ₀	W ₁₀₀	W ₃₀₀	W ₅₀₀
Tensile strength, MPa	1.50 (1.26)	5.66 (5.65)	11.50 (10.33)	9.61 (11.31)
Elongation at break, %	157 (107)	411 (264)	649 (335)	544 (346)
Modulus at 100% elongation, MPa	1.17 (1.20)	1.35 (1.95)	1.31 (2.56)	1.40 (2.86)
Modulus at 300% elongation, MPa	—	3.86 (—)	4.08 (9.13)	4.59 (9.51)
Heat build-up (ΔT) at 50°C, °C	1	10	12	13
Hysteresis loss ($\times 10^{-6}$), J/m ²	0.003	0.007	0.010	0.012
Rebound resilience, %	75	70	67	64
Tension set (at 100% elongation), %	c	2	2	2
Tear strength, kN/m	8.9	18.8	27.3	26.7

^a Values in parentheses stand for the aged specimens (150°C for 72 hr).
^b Formulations contain EPDM, 100; ZnO, 5; stearic acid, 1; TMTD, 1; MBT, 0.5; and sulfur, 1.5 (in phr), in addition to the powdered EPDM rubber. The subscript in the mix designation indicates the amount of powdered rubber (in phr) present in the composition.
^c Could not be determined; the sample broke.

Naskar et al., (2000) studied the effect of GRT of different particle sizes on the properties of NR compound. It is found that smaller particles contain less amount of polymer (i.e., NR, BR, SBR) but higher amount of fillers (i.e., carbon black, silica) and metals (i.e., copper, manganese, iron). Hence, the NR compounds containing smaller GRT particles show higher physical properties, but poor aging resistance, because the metals act as prooxidants (Table 2.2).

Table 2.2 Properties of NR vulcanizates containing 30 Phr of GRT^a (Naskar et al., 2000)

Physical Properties	G ₀ ^b	G ₁ ^c	G ₂ ^d
Tensile strength, MPa	14.0 (8.8)	4.2 (2.5)	8.0 (2.5)
Elongation at break, %	1175 (770)	620 (360)	860 (400)
Tear strength, kN/m	28.2 (20.3)	18.5 (10.6)	21.1 (9.7)

^a Values in parentheses stand for the aged samples (100°C for 36 hours).
^b Compound without GRT.
^c Particle size 52–72 mesh (300–215 μm)
^d Particle size 100–150 mesh (150–100 μm)

2.1.4 Acrylonitrile butadiene rubber (NBRr) glove

Nitrile gloves are made from a synthetic polymer exhibiting rubber-like characteristics when vulcanized. The polymer is manufactured as solids and emulsion, and can be processed like natural rubber latex. Compared to natural rubber, softness, feel, modulus, solvent resistance, and tensile and tear-strengths are designed easily in nitrile production. Unlike natural rubber, which is polyisoprene, nitrile polymers consist of three monomers: acrylonitrile, butadiene, and any one of many carboxylic acids. Performance features of the finished glove are controlled

through the use of these monomers and their associated formulation ingredients, such as zinc oxide, sulfur, and process accelerators.

Due to its polar molecular structure, acrylonitrile generally provides permeation to a variety of solvents and other chemicals. Within nitrile polymers, acrylonitrile contributes resistance to hydrocarbon oils, fats, and solvents. In contrast, natural rubber has very poor resistance to these chemicals. Along with sulfur and chemical accelerators used in the vulcanization process, butadiene enhances elasticity. In the finished glove, this polymer contributes softness, flexibility, and rubber-like feel. Interacting with zinc oxide to create ionic bonds during compound formulation, carboxylic acids contribute tensile strength and abrasion- and tear resistance in the finished glove. They also enhance solvent resistance, a characteristic absent in natural rubber because it lacks any carboxyl functionality. Nitrile has production process advantages over natural rubber, too. Natural rubber is linear polymer which must be precured to strengthen it before dipping. In comparison, nitrile polymers are inherently crosslinked so that little or no precuring is necessary to enhance their strength. The degree of crosslinking is altered through process conditions and the addition of chemical chain modifiers.

Another important difference between the two materials is the fact that natural rubber contains proteins, which act as stabilizers. Proteins remain in the finished glove, and thus, cause allergic reactions in sensitive glove users. Contrast this to nitrile, which contains no proteins because it is stabilized with anionic surfactants. A valuable feature to the semiconductor industry is the ability of nitrile gloves to more effectively dissipate electrostatic charges. Plus, due to their better abrasion resistance, they slough off significantly fewer particles, which contaminate critical manufacturing environments (<http://www.techniglove.com/nitrile.html>).

2.1.5 Synthetic rubber

2.1.5.1 Styrene butadiene rubber (SBR) (Henderson, 1987, Hofmann, 1989a)

Styrene butadiene rubber (SBR) is a general purpose multitalented synthetic rubber with many trades name; GRS, Buna S, ASRC, Ameripol, Baytown, Carbomix, Copo, FR-S, Gentro, Krylene, Krymix, Krynol, Philprene, Plioflex and Synpol. SBR is much like NR in most of its properties and is the lowest-cost and highest volume elastomer available. Although the physical properties are slightly poorer than that NR, SBR is tougher and slightly resistant to heat and flex cracking and can be readily substituted for natural rubber in many applications with significant cost savings. The advantages of SBR such as excellent impact strength; very good resilience, tensile strength, abrasion resistance and flexibility at low temperatures (Long, 1985a).

Major application characteristics: good physical properties; excellent abrasion resistance; but sensitive to oil, wastewater and ozone; electrical properties good, but not outstanding. The elastomer is used widely in pneumatic tires, shoe heels and soles, gaskets and even chewing gum. It is a commodity material which competes with natural rubber. Latex (emulsion) SBR is extensively used in coated papers, being one of the most cost-effective resins to bind pigmented coatings. It is also used in building applications, as a sealing and binding agent behind renders as an alternative to PVA, but is more expensive. In the latter application, it offers better durability, reduced shrinkage and increased flexibility, as well as being resistant to emulsification in damp conditions (<http://en.wikipedia.org/wiki/Styrene-butadiene>).