CHARACTERIZATION AND PROPERTIES OF NATURAL RUBBER/STYRENE BUTADIENE RUBBER/RECYCLED ACRYLONITRILE BUTADIENE RUBBER (NR/SBR/rNBR) BLENDS

by

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LIST OF ABBREVIATIONS AND SYMBOLS

µm	micrometer
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflection
CB	Carbon Black
cm	centimeter
CRM	Crumb Rubber Materials
CV	Conventional Vulcanization
E_B	Elongation at Break
ENR	Epoxidized Natural Rubber
EV	Efficient Vulcanization
FTIR	Fourier Transform Infrared
GRG	General Rubber Goods
GTR	Ground Tire Rubber / Ground Tyre Rubber
IRG	Industrial Rubber Goods
ISNR	Indian Standard Natural Rubber
Kg/m3	relative density
M_{100}	Modulus at 100% Elongation
MA	Maleic Anhydride
M_H	Maximum Torque
M_L	Minimum Torque
mm	millimeter
MPa	Megapascal
MRB	Malaysian Rubber Board

MREPC	Malaysian Rubber Export Promotion Council
NBRv	Virgin Acrylonitrile Butadiene Rubber
nm	nanometer
NR	Natural Rubber
phr	part per hundred rubber
PP-g-MA	Polypropylene-grafted-Maleic Anhydride
PRI	Plastic Retention Index
Qm	total swollen weight
R&D	Research & Development
R-EPDM	Recycled Ethylene Propylene Diene Monomer
RHC	Rubber Hydrocarbon
RHP / RH	Rice Husk Powder / Rice Husk
rNBR	Recycled Acrylonitrile Butadiene Rubber
RSS	Ribbed Smoke Sheet
SBR-r	Recycled Styrene Butadiene Rubber
SEM	Scanning Electron Microscope
Semi-EV	Semi Efficient Vulcanization
SIR	Standard Indonesian Rubber
SMR CV	Standard Malaysian Rubber Constant Viscosity
SMR GP	Standard Malaysian Rubber General Purpose
SMR L	Standard Malaysian Rubber Light Color
SMR	Standard Malaysian Rubber
SR	Synthetic Rubber
St	Styrene
STR	Standard Thailand Rubber

t_2	Scorch Time
t_{90}	Cure Time
TARRC	Tun Abdul Razak Research Center
TCR	Trelleborg Cold Reclaiming
TPV	Thermoplastic Vulcanizate
TSR	Technical Specified Rubber
USA	United States of America
Vr	volume fraction of the swollen rubber
Vs	molar volume of the solvent

LIST OF NOMENCLATURES

ACN	Acrylonitrile group
BR	Polybutadiene Rubber
$CaCO_3$	Calcium Carbonate
CR	Chloroprene Rubber
DTDM	4,4'-dithibismorpholine
EPDM	Ethylene Propylene Diene Monomer
EVA	Ethylene Vinyl Acetate
IR	Polyisoprene Rubber
NBR	Acrylonitrile Butadiene Rubber
PP	Polypropylene
PS	Polystyrene
SBR	Styrene Butadiene Rubber
TMTD	tetramethylthiuram disulphide
TMTPA	trimethylolpropane triacrylate
TOR	Trans-Polyoctylene Rubber

Pencirian dan Sifat-Sifat Adunan Getah Asli/ Getah Stirena Butadiena/Getah Nitril Butadiena Kitar Semula (NR/SBR/rNBR)

ABSTRAK

Penggunaan getah kitar semula dalam adunan-adunan getah telah menjadi kaedah paling mudah dan kos yang efektif dalam mengitar semula produk getah terbuang. Peningkatan permintaan terhadap sarung tangan lateks nitril dan penggunaan yang tinggi dalam pasaran kini telah menyebabkan banyaknya sarung tangan nitril terpakai dan terbuang dihasilkan setiap hari. Oleh itu, sisa sarung tangan nitril, terutamanya yang cacat dan buangan daripada proses-proses pengeluaran, telah digunakan semula untuk membangunkan adunan getah pertigaan baru daripada getah asli/getah stirena butadiena/getah akrilonitril butadiena kitar semula (NR/SBR/rNBR). Pertamanya, adunan-adunan NR/SBR/rNBR disediakan pada nisbah adunan berbeza, iaitu 50/50/00, 50/40/10, 50/30/20, 50/20/30, 50/10/40, 50/00/50, 40/50/10, 30/50/20, 20/50/30, 10/50/40 dan 00/50/50 (bsg/bsg/bsg) menggunakan penggiling bergulung dua pada suhu bilik, dan ciri-ciri dan sifat-sifat adunan-adunan tersebut dikaji dan dibandingkan. Peringkat seterusnya dalam kajian ini bertujuan utama untuk memperbaiki sifat-sifat regangan dan fizikal adunan dengan menyiasat kesan saiz butiran getah akrilonitril butadiena kitar semula (rNBR) yang berbeza, penyerasian dengan getah asli terepoksida (ENR 50) sebagai ejen penyerasi dan penggabungan jenis pengisi-pengisi yang berbeza terhadap adunan-adunan. Adalah penting untuk diambil perhatian tentang kehadiran pemecut tidak bertindak balas dalam rNBR, dikesan melalui analisis FTIR. Secara umumnya, peningkatan kandungan rNBR di dalam adunan (dan pengurangan salah satu juzuk getah dara), sifat-sifat regangan dan fizikal adunan NR/SBR/rNBR merosot. Walaubagaimanapun, kekuatan regangan tertinggi diperoleh daripada nisbah adunan optimum iaitu 50/30/20. Hal ini dipastikan dengan kajian SEM yang menunjukkan interaksi lemah antara rNBR dan getah dara, apabila kandungan rNBR meningkat. Kesan saiz butiran rNBR berbeza dikaji, menggunakan nisbah adunan optimum 50/30/20. Butiran rNBR terkecil S3 (1.5-800 µm) dalam adunan NR/SBR/rNBR menunjukkan sifat regangan paling rendah dibandingkan butiran rNBR lebih besar S2 (1.0-2.5 mm) dan S1 (10-15 cm). Walaubagaimanapun, adunan NR/SBR/rNBR(S3) mempamerkan masa skorj (t_2) dan masa pematangan (t_{90}) paling cepat, berbanding adunan-adunan NR/SBR/rNBR(S2) dan NR/SBR/rNBR(S1). Penambahan ENR 50, sehingga 10 bsg, memberi kesan kurang ketara pada sifat-sifat regangan dan fizikal adunan-adunan pertigaan NR/SBR/rNBR. Penambahan kandungan ENR 50 di dalam adunan telah meningkatkan kekuatan regangan secara tidak ketara, dengan penambahan lanjutan kandungan ejen penyerasi, melebihi 10 bsg, dijangka memberi penambahbaikan terhadap kekuatan regangan. Ini disokong dengan sifat-sifat fizikal dan analisis morfologi adunan-adunan tersebut. Kesan butiran-butiran rNBR di dalam adunan dihadkan dalam kehadiran ENR 50. Walaubagaimanapun, kebolehprosesan adunan menjadi lebih mudah dengan penambahan ENR 50. Akhir sekali, pengisi-pengisi seperti hitam karbon (CB), kalsium karbonat ($CaCO_3$) dan sekam padi (RH) diisikan ke dalam adunan-adunan, dibezakan kandungan dari 5 hingga 50 bsg. Penambahan pengisi, sehingga 50 bsg, meningkatkan kekerasan adunan. Pada bebanan pengisi yang sama, adunan NR/SBR/rNBR terisi CB menunjukkan kekuatan tensil dan kekerasan paling tinggi, berbanding adunan terisi $CaCO_3$ dan RH, membuktikan kesan penguatan CB berbanding pengisi lain, terutama pada bebanan lebih tinggi. Tork minimum (M_L) dan tork maksimum (M_H) adunan

NR/SBR/rNBR terisi meningkat dengan peningkatan bebanan pengisi dan meningkatkan kelikatan adunan. Peningkatan paling ketara dalam ketumpatan sambung silang adunan NR/SBR/rNBR terisi CB, berbanding $CaCO_3$ dan RH, membuktikan interaksi pengisi-pengisi dan pengisi-matrik yang lebih baik dipamerkan oleh pengisi penguat itu. Kajian ini mendedahkan bahawa adunan NR/SBR/rNBR boleh menjadi alternatif yang baik dan versatil untuk aplikasi luar, kerana mempunyai kekuatan regangan dan sifat fizikal yang baik, sesuai untuk memenuhi keperluan aplikasi.

Characterization and Properties of Natural Rubber/Styrene Butadiene Rubber/Recycled Acrylonitrile Butadiene Rubber (NR/SBR/rNBR) Blends

ABSTRACT

Utilization of recycled rubber in rubber blends preparation has provided the simplest and most cost-effective method in recycling discarded rubber products. The increasing demand for nitrile latex glove and it high consumption in current market resulted in abundance of used and waste nitrile gloves generated daily. Hence, discarded nitrile gloves, particularly the defects and rejects from the production processes, were utilized to develop new ternary rubber blends of natural rubber/styrene butadiene rubber/recycled acrylonitrile butadiene rubber (NR/SBR/rNBR). Firstly, NR/SBR/rNBR blends were prepared at different blend ratio of 50/50/00, 50/40/10, 50/30/20, 50/20/30, 50/10/40, 50/00/50, 40/50/10, 30/50/20, 20/50/30, 10/50/40, 00/50/50 (phr/phr/phr) by using two-roll mills at room temperature, and the characteristics and properties of the blends were investigated and compared. The next stages of the study are mainly aim to improve the tensile and physical properties of the blends by investigating the effect of different recycled acrylonitrile butadiene rubber (rNBR) particle sizes, compatibilization with epoxidized natural rubber (ENR 50) as compatibilizer and incorporation of different type of fillers on the blends. It is important to note the presence of unreacted accelerator in rNBR, detected from FTIR analysis. Generally, as the increasing rNBR loading in the blends (and the decreasing one of the virgin rubber constituent), the tensile and physical properties of NR/SBR/rNBR blends deteriorated. However, the highest tensile strength obtained by the optimum blend ratio of 50/30/20. This result was confirmed by the SEM study that show poor interaction between rNBR and virgin rubbers as the rNBR loading increased. The effect of different rNBR particle sizes was investigated, by using the optimum blend ratio of 50/30/20. The smallest rNBR particles S3 (1.5-800 µm) in NR/SBR/rNBR blends shows the lowest tensile properties compared larger rNBR particles S2 (1.0-2.5 mm) and S1 (10-15 cm). However, NR/SBR/rNBR(S3) blends exhibited shortest scorch time (t_2) and cure time (t_{90}) compared to NR/SBR/rNBR(S2) and (S1) blends. The addition of ENR 50, up to 10 phr, had insignificant effects on the tensile and physical properties of NR/SBR/rNBR ternary blends. The increasing ENR 50 content in the blends had insignificantly increased the tensile strength, with further addition of the compatibilizer, exceeding 10 phr, is expected to further improve the tensile strength. This is supported by the physical properties and morphology analysis of the blends. The effects of rNBR particles in the blend had restricted in the presence of ENR 50. However, the processability of the blends become easier with the addition of ENR 50. Lastly, fillers like carbon black (CB), calcium carbonate ($CaCO_3$) and rice husk (RH) was incorporated into the blends, varies from 5 to 50 phr. The addition of fillers, up to 50 phr, increased the hardness of the blends. At the same filler loading, CB-filled NR/SBR/rNBR blends exhibited highest tensile strength and hardness compared to $CaCO_3$-filled and RH-filled blends, proving its reinforcing effect compared to other fillers, especially at higher filler loading. Minimum torque (M_L) and maximum torque (M_H) of filled NR/SBR/rNBR blends increased with increasing filler loading and increased the viscosity of the blends. The most significant increase in crosslink density of CB-filled NR/SBR/rNBR blends, compared to $CaCO_3$ and RH, proved the better filler-filler and filler matrix interaction possesed by the reinforcing filler. The present work reveals that NR/SBR/rNBR blends

could be a good and versatile alternative for outdoor applications, due to its good tensile and physical properties, suitable to meet the demands of the applications.

CHAPTER 1

INTRODUCTION

1.1 Recycling Scenario in Malaysia

Solid waste generation and management has become major social and environmental issues in many developing countries in Asia, including Malaysia. Rapid economic growth, urbanization and changing trend of waste generation in these countries highlights the importance of an efficient solid waste management in order to overcome the mounting problem on landfills and solid waste disposal centers (Budhiarta, Siwar & Basri, 2012; Marshall & Farahbakhsh, 2013; Rockson, Kemausuor, Seassey & Yanful, 2013; Terazano et al., 2005). Poor waste management can cause health and environmental problems, thus intensive research and development has been extensively carried out in order to implement the cost effective and compatible solution for good solid waste management (Henry, Yongsheng & Jun, 2006; Nemerow, Agardy, Sullivan & Salvato; 2009; Othman, Noor, Abba, Yusuf & Hassan, 2013; Wilson, 2007).

Recycling is defined as a process of separating and converting waste into usable products that benefits people, which includes the effort of recovering and reusing waste from various sources (de Oliveira Simonetto & Borenstein, 2007). Recycling is purposely practiced to conserve energy and to reduce the burden of waste materials on the environment, as it helps lower greenhouse gas emissions, reduce water and air pollutions as well as environmental and economic costs, reduce health risks, save natural resources and save space in the landfills (Bolaane, 2006; Kinnaman, 2006; Martin, Williams & Clark; 2006; van den Bergh; 2008).

The recycling practices have been done for so many years; even before the term had existed and the importance and benefits of recycling has been publicly stressed in last few decades (Palliser, 2011). People in yesteryears had reused materials and refashioned them into new needed items, which is considered as simple recycling. Since then, the recycling practices has vastly developed, specifically on the class of materials that can be recycled and new technologies on recycling had been introduced.

Malaysian government has recognized the importance of solid waste recovery, especially from the industrial sites, which allows the industries to reduce manufacturing costs, increase efficiency of resources utilization, promotes environmental friendly product design and reduce negative impacts on environment and human health, thus provides alternative resources and reduces dependency on natural resource such as petroleum for plastics (Mohamed, 2009; Dewulf & van Langenhove, 2005; Pongracz & Pohjola, 2004). For all the benefits and advantages of it, the recovery and recycling of industrial solid waste, like the scrap iron, steel, aluminium, carton boxes, paper, glass, plastics and rubber, has become an important support industry for developing and industrial countries like Malaysia and seen to be the best alternative for managing the solid waste in factories and plants (Mohamed, 2009). Industrial waste recovery has been identified as an emerging economic activity and has become an important support industry for the past decade to ensure the sustainability of the manufacturing industries. Polymeric materials, such as plastics and elastomers, has been one of the most generated solid wastes in Malaysia, from both municipal and industrial sites, and this fact highlighted the need for these materials to be recycled extensively.

1.1.1 Polymer Recycling

Polymer recycling can be classified into two; industrial scrap recycling and post-consumer recycling. The former has been long practiced by many groups, primarily involves recovering and reusing polymer wastes that resulting from manufacturing operations, which is a simpler than the post-consumer recycling. Industrial scrap recycling is motivated by economics, which collectors collected a particular type of polymer wastes in a central location before recycling process take place (Stein, 1992). However, post-consumer recycling is a much complicated and difficult process, due to the problem in sorting out the various type of consumed polymer products into a specific type of polymer after consumption (Stein, 1992). This problem could lead to deterioration in the properties of polymer product for the next life cycle. Separation of plastics before recycling is not impossible to be implemented, but the first step to achieve it is by educating the local community about the importance of recycling and how it can be effectively done.

Polymer recycling and recovery also can be differentiated by terminology used to describe it. Primary recycling can be describe as mechanical reprocessing of polymer waste into a product with equivalent properties, or also called as close-loop recycling. This is the most practical when the polymer constituent can be effectively separated from contamination and can be stabilized against degradation during reprocessing. Secondary recycling is much similar to the primary recycling, only for deterioration in