UNIVERSITI TEKNIKAL MALAYSIA MELAKA

TENSILE BEHAVIOR UNDER THERMAL DEGRADATION OF THERMOPLASTIC ELASTOMER PP/ENR FILLED RECLAIMED RUBBER

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials)(Hons.)

by

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DECLARATION

I hereby, declared this report entitled "Tensile behaviour under thermal degradation of thermoplastic elastomer PP/ENR filled reclaimed rubber" is the results of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material). The member of the supervisory is as follow:

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ABSTRAK

Termoplastik elastomer semakin mendapat perhatian kerana ciri-cirinya yang menyerupai getah tervulkan dan mudah difabikat seperti termoplastik. Kajian ini memberi tumpuan kepada penghasilan bahan elastomer termoplastik baru dengan bahan daripada campuran polipropilena (PP), getah asli terepoksida (ENR) dan getah tebusguna (RR) . Kajian ini juga memberi tumpuan kepada kesan suhu dan masa pendedahan kepada sifat-sifat tegangan PP/ENR/RR campuran. Kesan suhu yang akan ditetapkan pada sampel akan dinilai sifat-sifat tegangan PP/ENR/RR campuran. Zink oksida dan asid stearik akan digunakan sebagai pengaktif, dan sulfur bertindak sebagai ejen pengawetan. Proses penyebatian lebur ini melibatkan pencampuran bahan-bahan dalam bentuk palet di dalam pencampur dalaman untuk menghasilkan bahan-bahan sebatian pada suhu operasi $180^{o}C$, kelajuan rotor ialah 60 rpm. Beberapa ujian dan analisis termasuk ujian ketumpatan, ujian tegangan, ujian kekerasan, kemikroskopan elektron imbasan (SEM) dan pemeteran kalori pengimbasan kebezaan (DSC) dijalankan untuk mencirikan sifat-sifat PP/ENR/RR. Dalam kajian ini, ianya menunjukkan bahawa peningkatan suhu dan masa pendedahan akan meningkatkan tahap kemusnahan yang dialami oleh campuran PP/ENR/RR disebabkan oleh kesan haba yang mengubah struktur dalam campuran dan seterusnya mengubah kekuatan bagi campuran tersebut.Kajian itu juga menunjukkan bahawa peningkatan tempoh dengan suhu yang tinggi telah menyebabkan sifat-sifat mekanik campuran dan tingkah laku tegangan menjadi semakin miskin. Kesan suhu ke atas sampel telah dinilai sifat-sifat tegangan campuran PP/ENR/RR.

ABSTRACT

Thermoplastic elastomer gaining attention because of its features are similar to vulcanised rubber and easy to fabricate such as thermoplastic. This study focuses on to produce the new thermoplastic elastomer material with material from the blend of polypropylene (PP), epoxidised natural rubber (ENR) and reclaimed rubber (RR). The study also focuses on the effect of of temperature and exposure time to the tensile properties of PP/ENR/RR blend. The effect of temperature that will be set on sample will be evaluated the tensile properties of PP/ENR/RR blend. Zinc oxide and stearic acid will be used as an activator, and then sulphur acts as a curing agent. The melts compounding process involve the mixing of materials in pallet form in an internal mixer to produce compound materials at operating temperature of $180^{o}C$ and rotor speed of 60 rpm. Several tests and analysis including density testing , tensile test , hardness test , scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) will be conducted to characterize the properties of PP / ENR / RR blend. In this research, it is shows that increases temperature and exposure time increase the degradation level experienced by the PP/ENR/RR blend due to the thermal effect which alters the structure of the blends and also change the strength. The research also shows that the increasing of period with high temperature had caused the mechanical properties of blend and the tensile behaviour is become poorer. The effect of temperature on sample was evaluated the tensile properties of PP/ENR/RR blend.

DEDICATION

This report is dedicated to my parents (En Araf Yahya and Puan Rohayah Ismail) and my siblings (Norfitri Afzan, Nur Hassana, Mohd Rasydan and Mohd Hazim).

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

ASTM - American Standard Test Method

BMC - Bulk Molding Compound

CBS - Cyclohexyl Benzo Thiazyl Sulphonamide

CDNS - Carbonized Dika Nutshell

C_p - Heat Capacity

CV - Conventional Vulcanisation

DCP - Dicumyl Peroxide

DCBS - Dicyclohexyl Benzo Thiazyl Sulphonamide

DOE - Design of Experimental

DPG - Diphenyl Guanidine

DSC - Differential Scanning Calorimetry

ENR - Epoxidised Natural Rubber

EPDM - Ethylene Propylene Diene Monomer

EV - Efficient Vulcanisation

FTIR - Fourier Transform Infrared

HDPE - High-Density Polyethylene

LLDPE - Linear Low-DensityPolyethylene

MBT - Mcrcaptobenzothiazole

MF - Melamine Formaldehyde

MFI - Melt Flow Index

NBR - Nitrile Butadiene Rubber

NR - Natural Rubber

PP - Polypropylene

PVC - Polyvinyl chloride

rpm	-	Rotation per Minute
RR	-	Reclaimed Rubber
RSM	-	Response Surface Methodology
SBR	-	Styrene Butadiene Rubber
SEM	-	Scanning Electron Microscopy
SEV	-	Semi-Efficient Vulcanisation
SMC	-	Sheet Molding Compound
Tg	-	Glass Transition Temperature
TGA	-	Thermogravimetric Analysis
TMTD	-	Tetramethythiuram Disulphide
TPE	-	Thermoplastic Elastomer
TPNR	-	Thermoplastic Natural Rubber
TPO	-	Thermoplastic Polyolefin
TPU	-	Thermoplastic Polyurethane
TPV	-	Thermoplastic Vulcanizate
TSE	-	Thermoset Elastomer
UF	-	Urea Formaldehyde
ZnO	-	Zinc Oxide
^{o}C	-	Celsius
M/S	-	Meter per Second
%	-	Percentage
kW	-	Kilo watt
min	-	Minute
kg	-	Kilogram
mm	-	Millimeter
μm	-	Micrometer
Tm	-	Meliting Temperature
Tc	-	Crystallization Temperature
s	-	Second
nm	-	Nanometer
g	-	gram
Hz	-	hertz

CHAPTER 1

INTRODUCTION

1.1   Background

Engineered thermoplastic elastomers (TPEs), are one of the most versatile plastics available today. The TPEs combine the performance of thermoset rubber with the processing ease of plastic. Thermoplastic elastomers (TPEs) belong to a class of materials that have the combined physical properties of thermoplastics and elastomers (Suryadiansyah 2001).They exhibit properties typical of rubber materials but can be processed like thermoplastics. Therefore, it provides various design options and greater cost-reduction opportunities. TPEs offer a wide range of performance attributes including heat and oil resistance, improved adhesion, test resistance, surface appearance and low permeability. In addition, TPEs are colourable and can be specified in a variety of hardness grades. TPEs give better material utilization because scrap and rejects can be recycled (Suryadiansyah 2001).

TPEs consist of at least two polymeric phases. A hard thermoplastic phase combined with a softer elastomer phase, and the properties of the resultant TPEs will be derived

from the properties of each of the two phases individually and from the extent of interaction between these phases (Arnold and Rader 1992). Currently Malaysian Rubber Board produces ENR with the trade name Epoxyprene. Two grades are available, namely ENR-25 and ENR-50, with 25, and 50 mol % epoxidation, respectively. However the market and applications for ENR found to be very limited. Thus attempts are being made through this research project to diversify the usage and application of this rubber, especially in advanced engineering field. As mention earlier, blending with other polymer is the easiest and the cheapest way to tailor the properties of ENR and at the same time reduces the material cost (Kallitsis and Kalfoglou 1989).The importance of recycling of waste materials (reclaimed rubber) generated from industries worldwide has become significantly important in the recent past mainly due to environmental reasons. The rubber manufacturing industry also faces a major challenge in this regard. Effort to find the satisfactory ways and means to deal with the enormous quantity of waste rubber goods generated by the industry is crucial since it may lead to severe environmental problems unless they are disposed properly (Kallitsis and Kalfoglou 1989). Reclaimed rubber wastes are usually generated during the processing of the products and from the disposal of post-consumer products.

Nowadays, the awareness of recycling waste materials is increasing for all industries worldwide. For rubber products, the automotive and transportation industries are the biggest consumers of raw rubber. Rubber waste is usually generated during the manufacturing process of products for these industries and by disposal of post-consumer (retired) products, mainly including scrap tires. As we can see, in Japan, about one million tons of scrap tires are generated annually. Blending the reclaimed rubber with other polymeric material to form a blend is one of the most effective methods of utilizing the reclaimed rubber for any industrial applications. Among various thermoplastic elastomers (TPEs), blends based on polypropylene are an important class of engineering materials (Rajalekshmi 2005). Therefore this study is focused on the development of a new class of TPEs material by blending PP, ENR and reclaimed rubber with different composition ratio generating from rubber manufacturing industry. It is hopeful at the end the final product developed would find useful applications in the automotive and rubber industries. The blending of PP,

ENR and reclaimed rubber looks to be a very attractive as a way to obtain new TPEs with good mechanical properties and easy processability, these blends are found to be highly compatible. To improve the properties of TPEs blends is to introduce crosslinks in the rubber phase of the blend. This can be done by vulcanisation of the rubber phase through dynamic vulcanisation.

1.2   Problem Statement

Nowadays, thermoplastic elastomers are getting encouraging response due to its unique properties, combining individual properties of plastic and elastomer. They exhibit the properties of both vulcanized elastomer and thermoplastic properties. The unique properties of both materials exist because TPES materials are created only by physical mixing of a thermoplastic and elastomer and no chemical or covalent bonding exists between the two. Thermoplastic elastomers have become a significant part of the polymer industry. Further research of thermoplastic currently lies on the polypropylene (PP), epoxidised natural rubber (ENR) filled reclaimed rubber (RR) involving the effort to reuse the reclaimed rubber that had been vulcanized. This kind of rubber could reduce the manufacturing cost and contribute to a greener environment due to the reclaimed rubbers used. The effectiveness of the TPEs blend also could contribute to reduce waste of epoxidised natural rubber (ENR). However, our country is exposed to ever changing weather with fluctuating temperature and humidity. Sinceenvironments are likely to influence the properties of materials, this study is trying to address the effect of temperature and exposure time to the degradation of blend properties: especially towards tensile properties. The properties will be correlated with the morphology and thermal properties of PP/ENR/RR.

1.3   Objectives

The main focus of this study is to develop a new thermoplastic elastomer (TPEs) using polypropylene (PP), epoxidised natural rubber (ENR) and reclaimed rubber

(RR) which to find a suitable solution to an existing problem of disposing the reclaimed rubber waste material generated from rubber based product industries.

The objectives of this study are:-

   a) To prepare PP/ENR filled reclaimed rubber (PP/ENR/RR) using melt compounding and dynamic vulcanisation technique

   b) To study the effect of temperature and exposure time to the tensile properties of PP/ENR/RR blend

   c) To correlate the tensile properties with morphological characteristic of PP/ENR/RR blend

1.4   Scope of Project

This study focuses on to produce the new thermoplastic elastomer material with material from the blend of polypropylene (PP), epoxidised natural rubber (ENR) and reclaimed rubber (RR). The study also focuses on the effect of temperature and exposure time to the tensile properties of PP/ENR/RR blend. The effect of temperature that will be set on sample will be evaluated the tensile properties of PP/ENR/RR blend. Zinc oxide and stearic acid will be used as an activator, and then sulphur acts as a curing agent. The process melt compounding involve is the materials in form of pallet will blend together in an internal mixer to produce compound materials on operating temperature at $180^{o}C$, rotor speed is 60 rpm. Crusher machine is used to produce small particle size before is placed into a mold (Hydraulic hot molding machine) for the compression molding process. Lastly, the sample materials will be cut into specific size to be stored in the fridge by the time and temperature that has been set. After that the sample will be tested formechanical testing, physical testing, thermal testing and morphology analysis.

CHAPTER 2
LITERATURE REVIEW

This chapter is a literature reviewonpolymer blends, its types and properties as well as recent development in polypropylene and epoxidised natural rubber based blends. Since blending of polymers is an effective way to obtain materials with specific properties. Few processing and fabrication techniques are also discussed in this chapter.This review is based on previous and current research.

2.1   Polymer Blends

The definition of polymer blends has been described in various ways from a brief explanation to a specific one. Work (1987) defines polymer blends as a mixture of two or more different species of polymer. Dean (2006) stated in the 70's defined polymer blends as mixture of two or more polymers intimately in single continuous solid phase. Wiley (2006) noted the polymer blend has two definitions which are the broad definition includes any finely divided combination of two or more polymers and the narrow definition specifies that there be no chemical bonding between the various polymers making up the blends. Utracki and Favis (1989) defined polymer blend as mixture of two or more polymer or copolymer materials. Kumar and Gupta (1998) stated that polymer blends are physical mixture of two or more polymers that are commercially prepared by mechanical mixing which can be achieved through rotor-cam and compounder and screw extruder. Then, Utracki (2002) noted that polymer blend as a mixture of two or more macromolecular species.

Principles of polymer blends include homogeneous and heterogeneous (Gabriel and George 1999). In homogeneous blends, the mobility is averaged, consequently glass transition temperature are averaged. In heterogeneous blends, the mobility of original phases present, consequently glass transition temperatures of original phases are present. When two polymers are miscible down to segmental level, single homogeneous phase are formed, it will exhibit a single glass transition temperature, Tg from the compound and shows thermodynamically miscible. This will give compounder quick economical control over balance of properties for different applications. On the other hand, in practical, plastic technologists were also developed large number of polymer blends that are immiscible but very useful, combining some of the best practical properties of each polymer in the blend; they tended to use the term compatible blend (Gabriel and George 1999). However, there are also a lot of blends which are totally immiscible and incompatible when blended together, due to differences in material characteristic (polarity, molecular weight, crystalline and etc). These incompatible blends will eventually exhibit poor properties in physically and mechanically.

In the development of new multiphase polymeric materials, the goal of combining the favourable properties from each of individual material is not an easy task. This is because of low combinatorial of entropy of mixing, immiscible of blend and etc will give rise to two-phase system, which is mostly characterised by a coarse and unstable phase morphology and poor interfacial adhesion between the phases (Dedecker and Groeninckx 1998). The poor interfacial adhesions could also be affected by differences in material characteristic such as polar-polar and non-polar attraction. The vast difference in molecular weight, amorphous or crystalline of material phase as well as the suitable blend ratio of blend composition will resulted in different compounded properties (Cahn 2000).There is number of polymer pairs that were found completely miscible to give homogeneous single phase, with properties proportional to the ratio of the two polymer in the blend and several of these blends were exhibited commercially importance (Gabriel and George 1999). There are two types of existing polymer blends which are classified based on their matrix either thermoset or thermoplastic.

2.1.1 Thermoset Elastomer (TSE)

Thermosetting elastomers gain their strength from an irreversible cross linking process that occurs when the compound is subjected to pressure and heat. During this process, or "cure", special chemical agents within the compound react to the heat and pressure to vulcanize the molecules together. Once cured, thermoset compounds obtain the necessary physical properties needed to function in fluid sealing applications. Reheating thermoset compounds will not cause them to melt as thermoplastics do.

Callister (2007) stated that thermosetting polymers are network polymers. They become permanently hard during their formation, and do not soften upon heating. Network polymers have covalent crosslinks between adjacent molecular chains. During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, phenolic and some polyester resins, are thermosetting(Callister 2007).

Pospisil *et al.* (1999) defined that the thermosetting elastomer cannot be remelted. Furthermore, the thermosetting elastomer (TPE) has a good abrasion resistance, fatigue resistance, high heat resistance, good thermal stability, good strength and etc (Walsh 1989). The application of thermosetting elastomer (TSE) normally used in automotive applications, flooring, gaskets, wire and cable applications, coating and etc (Roe and Rigby 1987).

2.1.2 Thermoplastic Elastomer (TPE)

Thermoplastic elastomer (TPE) is a new polymer which combine the service properties of elastomer (vulcanized rubber) and also able to be process

asthermoplastic (Holden *et al.* 1998). This combination of properties can be obtained through the simultaneouspresence of soft elastic segments (that have high a high extensibility and low glasstransition temperature, Tg) and hard segments (which have a lower extensibility, a highTg) and there are susceptible association to crosslinking (Holden *et al.* 1998). Santen (2003) stated since the 1940's, many industrial research groups from all over the world have been looking for materials that can be used as an alternative for natural rubber. This led to the discovery of several types of thermoplastic elastomers (TPE). TPE's possess many of the physical properties of rubbers, i.e. softness, flexibility, and elasticity but in contrast to conventional rubbers, they can be processed as thermoplastic materials. Conventional elastomer/rubber are covalently (irreversibly) crosslinked and they cannot be processed once the material is shaped and vulcanized. In contrast, the crosslinks in thermoplastic elastomers are reversible in nature, allowing a processing applying conventional technique for thermoplastics, e.g. injection molding and extrusion. Another advantage is the possibility to recycle scrap.

Thermoplastic elastomers (TPEs) can be produced from polymer blends consisting of non-vulcanized virgin rubber and thermoplastic polymers such as polyolefin (Grigoryeva 2003). The TPE properties can be much improved by a dynamic or in situ curing. During dynamic vulcanisation, carried out by intense mixing above the melt temperature of the thermoplastic polymer, the rubber phase will be crosslinked (vulcanized) and finely dispersed (mean particle size of a few microns) in the thermoplastic (Grigoryeva 2003). The latter takes the role of the matrix. The resulting TPE exhibits rubbery characteristics while maintaining the thermoplasticity of the matrix (Grigoryeva 2003).

Thermoplastic elastomers are known as two-phase system consisting of rubbery elastomeric (soft) component and rigid (hard) component. The soft phase can be polybutadiene, polyethylene, polyisobutylene, polyoxyethylene, polyester, polysiloxane or any of the typical elastomers while the hard phase are polystyrene, polymethyl methacrylate, urethane, ionomer – polyethylene-co-acrylic acid (sodium, Mg, Zn salt), ethylene propylene diene monomer, and fluro polymers(Jasen *et*