PREPARATION AND PROPERTIES OF MICROCRYSTALLINE-CELLULOSE-FIBER FILLED SBR/BR BLENDS

by

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ABSTRACT

Preparation and properties of non-microcrystalline cellulose (non-MCC) and microcrystalline cellulose (MCC) filled SBR/BR blends have been investigated. This research is divided into two main series, and each series undergo ageing test to the samples prepared. For first serie, the effect of different fillers, filler loading and ageing on properties of filled SBR/BR blends were studied. The results for curing characteristics, showed that both scorch time and cure time increased for non-MCC but decreased for MCC, whereas the torque and viscosity increased with incorporation of both filler in SBR/BR blends. MCC filled SBR/BR blends showed shorter scorch time and cure time but higher viscosity and torque value than non-MCC filled SBR/BR blends. The mechanical properties of MCC filled SBR/BR blends shows better tensile properties compared to non-MCC filled SBR/BR blends as filler loading increase up to 6 phr. The SEM result also shows that the fiber are well wetted and the pulled out of fiber from the rubber matrix is minimum up to 6 phr for both non-MCC and MCC filled SBR/BR blends. The thermal stability of MCC filled SBR/BR blends was better enhanced than that of non-MCC filled SBR/BR blends. For second series, the effect of reinforcing efficiency between hybrid MCC/silica (untreated and treated) filled SBR/BR have been investigated. At lower filler ratio of MCC, composite shows better tensile properties, thermal analysis, and resistance to aging, especially in the presence of (3-aminopropyl)trietoxysilane, 3-APE. However, the composites in the presence of coupling 3-APE show lower tensile properties at higher filler ratio of MCC, 10/0. The SEM result of hybrid MCC/untreated silica and MCC/treated silica shows many holes remaining

after the filler are pulled out from the rubber matrix and un-wetted filler on the surface particularly at highest silica content (0/10). From the thermal analysis observation, the MCC/treated silica filled SBR/BR blends show better thermal stability compared than MCC/untreated silica filled SBR/BR blends. Tensile properties for MCC and non-MCC filled SBR/BR blends, hybrid MCC/untreated silica and MCC/treated silica filled SBR/BR blends after ageing shows lower value than before ageing. From the SEM observation, the surfaces of all composites were remarkably changed to rougher surface with continuous crack formation compared than all composites before ageing. The thermal stability for all composites after ageing is lower than composites before ageing.

ABSTRAK

Penyediaan dan sifat-sifat campuran getah stirena-butadiena (SBR)/getah butadiene (BR) terisi bukan-mikroberhablur selulosa (bukan-MCC) dan mikroberhablur selulosa (MCC) telah dikaji. Ujikaji ini terbahagi kepada dua bahagian, dan setiap siri telah dilakukan ujian penuaan ke atas sampel yang disediakan. Bagi siri pertama, kesan pengisi yang berbeza, pembebanan pengisi dan penuaan terhadap sifat-sifat campuran SBR/BR berpengisi telah dikaji. Keputusan-keputusan bagi sifat-sifat pematangan telah menunjukkan bahawa kedua-dua masa skorj dan masa pematangan bertambah bagi bukan-MCC tetapi menurun bagi MCC, manakala tork dan kelikatan meningkat dengan penambahan kedua-dua pengisi ke dalam campuran SBR/BR. Campuran SBR/BR menunjukkan masa skorj dan masa pematangan yang lebih pendek tetapi nilai tork dan kelikatan yang lebih tinggi daripada campuran SBR/BR terisi bukan-MCC. Sifat-sifat mekanikal campuran SBR/BR terisi MCC menunjukkan sifat-sifat tensil yang lebih baik berbanding campuran SBR/BR terisi bukan-MCC dengan peningkatan pengisi sehingga 6 bsg. Keputusan SEM menunjukkan gentian dibasahi dengan baik dan penarikan keluar gentian daripada matrik adalah minimum sehingga 6 bsg bagi kedua-dua campuran SBR/BR terisi bukan-MCC dan MCC. Kestabilan terma bagi campuran SBR/BR terisi MCC adalah lebih baik berbanding campuran SBR/BR terisi bukan-MCC. Bagi siri kedua, kesan kecekapan pengukuhan antara campuran SBR/BR terisi MCC hibrid/silika (tidak dirawat dan dirawat) dan penuaan terma telah dikaji. Pada nisbah pengisi MCC yang rendah, komposit menunjukkan sifat-sifat tensil, analisis terma, dan ketahanan terhadap penuaan yang lebih baik terutama dengan kehadiran (3-aminopropil)

trietoksilana, 3-APE. Namun, komposit dengan kehadiran 3-APE menunjukkan sifat-sifat tensil yang rendah pada nisbah pembebanan pengisi MCC paling tinggi, 10/0. Keputusan SEM campuran SBR/BR terisi MCC hybrid/silica (tidak dirawat dan dirawat) menunjukkan banyak lubang terbentuk selepas pengisi ditarik keluar dari matriks getah dan pengisi yang tak dibasahi permukaannya terutama pada kandungan silika tertinggi. Daripada pemerhatian kestabilan terma, campuran SBR/BR terisi hibrid MCC/silika dirawat menunjukkan kestabilan terma yang lebih baik berbanding campuran SBR/BR terisi hibrid MCC/silika tidak dirawat. Sifat-sifat tensil bagi campuran SBR/BR terisi MCC dan bukan-MCC, campuran SBR/BR terisi hibrid MCC/silika dirawat dan MCC/silika tidak dirawat selepas penuaan menunjukkan nilai yang lebih rendah berbanding sebelum penuaan. Bagi pemerhatian SEM, permukaan bagi semua komposit menunjukkan perubahan kepada permukaan yang lebih kasar dengan pembentukan retak yang berterusan berbanding komposit sebelum penuaan. Kestabilan terma bagi semua komposit selepas penuaan adalah lebih rendah berbanding dengan sebelum penuaan.

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DECLARATION

I hereby declare that this thesis is based on my original work except for quotations and citations, which has been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UniMAP or other institutions.

(SITI SALWA BINTI MOHAMMAD SHIRAJUDDIN)

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURES

3-APE	(3-aminopropyl)trietoxysilane
6ppd	N-(1,3-dimethyl)-N'-phenyl-ρ-phenylenediamine
BIIR	Bromo Butyl Rubber
BR	Butadiene Rubber
CBS	N-cyclohexyl-2-benzothiazolesulfonamide
CIIR	Chloro Butyl Rubber
CTF	Coconut Trunk Fiber
CV	Conventional Vulcanization
DPG	Diphenylguanidine
DP	Degree of polymerization
DRC	Dry Rubber Content
EV	Efficient Vulcanization
FTIR	Fourier Transform Infrared Spectroscopy
IIR	Butyl Rubber
IR	Isoprene Rubber
MBT	Mercaptobenzothiozole
MCC	Microcrystalline Cellulose
MWD	Molecular Weight Distribution
NBR	Nitrile Rubber
NF	Natural Fiber

NR	Natural Rubber
PRI	Plastic Retention Index
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
SLR	Sri Lanka Rubber
SMR	Standard Malaysian Rubber
StAc	Stearic Acid
TGA	Thermogravimetric Analysis
TMP	Thermomechanical Pulp
TSR	Technically Specified Rubber
TTR	Technically Thailand Rubber
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Micro Cellulose – Reinforced Filler Rubber Vulcanizate

Microcrystalline cellulose (MCC) is a purified, partially depolymerised cellulose that occurs as a white and odourless crystalline powder. It is a highly crystalline particulate cellulose made up of a chain of about 250 glucose molecules. In nature, several microcrystals are hinged together and surrounded by amorphous cellulose to form a cellulose microfibril. If the amorphous cellulose is removed, the resultant product is called level off DP (degree of polymerization) microcrystalline cellulose. MCC can be made from any material that is high in cellulose ranging from pure cellulose, commercial grade cellulose to lignocellulosic materials. (Adel *et al.,* 2010).

Natural fiber (NF) has been investigate as potential sources to produce MCC, since woody plants and cotton were quite expensive. Reports have shown that MCC can be produced from water hyacinth (Gaonkar & Kulkarni, 1987), coconut shells (Gaonkar & Kulkarni, 1989), groundnut shell and rice husks (Okhamafe *et al.,* 1991), cereal straw (Jain *et al.,* 1983), bagasse and corn cob (Okmahafe *et al.,* 1995), soy bean, oath and rice hulls as well as sugar beet pulp (Hanna *et al.,* 2001). Luffa cylindrica (Ohwoavworhua *et* *al.*, 2004) orange mesocarp. (Ejikeme, 2008) and rice and bean hulls (Adel *et al.*, 2010) have also been studied as potential sources of MCC. But, for the best of our knowledge, MCC made from coconut trunk fiber (CTF) has not studied yet.

Since cellulose from different sources differs in properties (crystallinity, moisture content, surface area and porous structure, molecular weight, etc.) different properties of MCC obtained from different sources are expected; and the conditions of hydrolysis also affect the properties of the obtained MCC (El-Sakhawy & Hassan., 2007). The hydrolysis of cellulose to obtain MCC can be accomplished using mineral acid, enzymes or microorganisms. Although enzymatic methods are desirable because glucose, a useful by-product is created, these methods are more expensive and create MCC products having a lower crystallinity. Thus acid hydrolysis or hydrolytic degradation, typically with a strong mineral acid such as hydrogen chloride is the conventional method of choice for manufacturing MCC (Hanna *et al.*, 2001). The acid hydrolysis process produces a MCC of predominantly coarse particulate aggregates, typically having a mean size range of about 15 to 40 microns.

Nowadays, MCC has been widely used especially in food, cosmetic and medical industries as a water-retainer, a suspension stabilizer, a flow characteristics controller in the system used for final products, and as a reinforcing agent for final products such as medical tablets. There have been some studies on MCC as a reinforcing filler in plastic composites in the past few years (Laka *et al.*, 2003; Reinsch & Kelley, 1997; Kubat &

Klason, 1983) However, little has been reported about using MCC as a reinforcing filler in rubber vulcanizates.

1.2 Application and Future Trends

The widespread of the market in natural fiber reinforced composites is that of rubber composites ranging from household to industrial products, such as rubber bands, pencil erasers, ball for sports, aircraft tires and inner tube. Recently, the tire manufacturers is intensely interested in natural fiber composites because of inexpensives, readily available, light in weight and renewable (Bai & Li, 2009). As for rubber industry especially in the rubber tire application, MCC used as a reinforcing filler to replace current fillers in tire application, which are carbon black and silica. Natural fiber reinforced rubber composites combine the elasticity of rubber with the strength and stiffness of the fibre.

Other potential application for natural fiber reinforced rubber composites are door and window profiles, hoses, belts, matting, flooring and dampeners (antivibration mounts) for the automotive industry in what is known as the 'under the bonnet' products. Additionally, natural fiber reinforced composites are also use in textile industry because of its excellent elongation and recovery properties. Gloves (medical, household and industrial) and toy balloons are also other large consumer of rubber composites (Nunes & Visconte, 2000; Haghighat *et al.*, 2005).