EFFECT OF CARBON BLACK LOADING ON THE MECHANICAL PROPERTIES OF RUBBER VULCANIZATES

MOHD FAISAL BIN AHMAD SHAFAWI

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Faculty of Chemical & Natural Resource Engineering
Universiti Malaysia Pahang

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ABSTRACT

The effects of filler loading on the tensile and elongation at break of SMR 10 using a sulphur vulcanization system was studied. Carbon black (N220) was used as the fillers and the loading range was from 10 to 40 phr. Two Roll Mill (Model LS-22005) and 25 Ton Hot Cold Molding Press (Model LS22025) used for mixing and molding press. Both equipments were supplied by Lotus Scientific. Tensile and elongation at break were determined using a Universal Testing Machine (Model 133004600771) operating at 20 mm/min. Results show that, elongation at break decreases, but tensile strength, increase with filler loading. This observation is attributed to the rubber–filler interphase interaction of carbon black and rubber.

ABSTRAK

Kesan-kesan pengisian yang berbeza pada pemanjangan dan ketegangan pada waktu putus SMR 10 menggunakan sistem pemvulkanan sulfur telah dikaji. Karbon hitam (N220) telah digunakan sebagai pengisi dan julat pemuatan ialah dari 10 hingga 40 phr. Two Roll Mill (Model LS-22005) dan 25 Ton Hot Cold Molding Press (Model LS22025) digunakan untuk penyebatian dan membentuk. Kedua-dua peralatan-peralatan telah dibekalkan oleh Lotus Scientific. Pemanjangan dan ketegangan ditentukan menggunakan Mesin Ujian Universal (Model 133004600771) beroperasi pada 20 mm / min. Keputusan menunjukkan bahawa, pemanjangan di waktu putus berkurangan, akan tetapi kekuatan ketegangan, meningkatkan dengan pengisian karbon hitam. Pemerhatian ini boleh dijelaskan kerana wujudnya kesan interaksi interfasa diantara karbon hitam dan getah.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

NR	Natural Rubber
SBR	Styrene Butadiene Rubber
NBR	Acrylonitrile Butadiene Rubber
Phr	Part per hundred rubber
CB	Carbon black
SMR	Standard Malaysia Rubber
IPPD	N-isopropyl-N’-phenyl paraphenylenediamine
CBS	N-Cyclohexyl-2- benzothiazole sulfonamide
rpm	Rotation per minute

LIST OF SYMBOL

%	Percent
^{O}C	Degree Celsius
g/mol	Gram per mole
Mpa	Mega Pascal
N/mm	Newton per millimeter
mm	millimeter
psi	Pound per square inch
s	Second

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Rubber is one of the most important products to come out of the rainforest. Natural rubber (NR) is an elastomer (an elastic hydrocarbon polymer) that was originally derived from a milky colloidal suspension, or latex, found in the sap of some plants. NR is one of the important elastomer and widely used to prepare many rubber products. NR exhibits outstanding properties such as green strength and tensile strength because it can crystallize spontaneously when it is strained. Beside that, it also has the ability to stick to itself and to other material which make it easier to fabricate.

However, in rubber formulation, NR usually blends together with synthetic or manmade rubber like Styrene Butadiene Rubber (SBR), Polybutadiene Rubber (BR) and Acrylonitrile Butadiene Rubber (NBR) which can undergo much more elastic deformation under stress, than most materials and still return to its previous size without permanent deformation.

Rubber products are composed of many different mechanistic materials, e.g. steel belt, nylon fibers, gas barrier layers, to form an overall product. This paper will focus on the effect of the filler loading on the tensile strength of rubber compound, emphasizing carbon and silica elastomer pounds. The elastomers are solution and emulsion polybutadiene rubber, styrene butadiene rubber, acrynitrile butadiene rubber, natural rubber, and blends. Additives are used to increase the rubber’s strength, wear resistance, performance and processing.

These additives consist of fillers like carbon black and silica, curatives to promote cross-linking, mixing aids such as aromatic oil to aid the dispersion of fillers, and anti-degradants such as anti- oxidants and anti-ozonents. Already it can be seen that combining all of these materials together results in a complex composite with end properties depending on the formulation used.

The processing of these materials also affects the end properties. The resulting properties desired for filled rubbers include good mechanical properties, both static and dynamic. Typically these properties are obtained through a series of experiments that vary the ratios of filler and measure the effects of the tensile. Recently however, efforts have been directed at understanding the mechanistic role of fillers loading in order to predict their effect on reinforcement.

The reinforcement of elastomer by fillers loading has been reviewed by other researcher. They considered that the effect of filler loading is to increase the number of chains, which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. There include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix.

1.2 PROBLEM STATEMENT

The choice of filler to the any given rubber formulation must take into account the desired physical properties like tensile. This is because the different grade of filler will give different value of tensile even though the loading is same. Now days a lot of rubber product produced which prefer different value of tensile, depend on the product purpose.

Filler loading is a critical factor in achieving the degree of elastomer modification desired to give a rubber compound properties suitable for a given end-use application. A rubber compounder must select the right formulation, the right carbon black grade/loading level combination and the right vulcanization system to give to give a rubber compound with the desired properties at the lowest possible cost.

Besides that, overload of filler can give rubber compounds become useless product. This is because the compound will become too hard to process .When the rubber specimen too tough, slippage and tearing may occur. That compound will become waste which can give bad effect to environment especially when carbon black used as filler.

1.3 OBJECTIVE

The objective of this research is to study the effect of the carbon black loading on the tensile of rubber vulcanizates.

1.4 SCOPE OF STUDY

The scope of study in this research is to measure the tensile and elongation at break of rubber compound filled with 10, 30, and 50 phr of N220 carbon black loading by using 2.5kN force.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber is the prototype of all elastomer. It is extracted in the form of latex from the bark of the Para rubber tree (*Hevea brasiliensis*), a member of the spurge family, Euphorbiaceae. Because of it natural derivation it is sold at variety of grades based on purity, viscosity, oxidation resistance and rate of cure. The natural rubber polymer is nearly 100% *cis*-1, 4 polyisoprene with the molecular weight ranging from 1 to 1 x 10^6 (Peter, 1999). The formula of the repeating unit is C_5H_8 with the molecular weight of repeat unit 68.12 g/mol.

Natural rubber tends to crystallize spontaneously at low temperature or when it stretch. The other unique properties of natural rubber such as follows:

1. Natural rubber combines high strength (tensile and tear) with outstanding resistance to fatigue.
2. It has excellent green strength and tack which means that it has the ability to stick to itself and to other materials which makes it easier to fabricate.
3. It has moderate resistance to environmental damage by heat, light and ozone which are one of its drawbacks.

4. The natural rubber has excellent adhesion to brass-plated steel cord, which is ideal in rubber tyre.
5. It has low hysteresis which leads to low heat generation, and this in turn maintains new tyre service integrity and extends retreadability.
6. The natural rubber has low rolling resistance with enhanced fuel economy.
7. It has high resistance to cutting, chipping and tearing.

2.2 Future of Natural Rubber

The future for natural rubber looks bright. Ever increasing volumes are being produced. At 5.92 million tons per annum, natural rubber has 39% of the world rubber consumption of 15.14 million tons per annum. The earthquake-bearing market will take off when people realize that such systems not only save lives, but also the contents of the buildings. Powder-free surgical gloves are on the way and this, achieved by polymer coatings both on the inside and out, will eliminate the protein allergy problem. All predictions of future cars see them continuing to use rubber tyres. The space shuttle lands on all natural rubber tyres because of the superb performance of this 500 year old polymer. With space travel around the corner, surely natural rubber has a guaranteed future.

2.3 Filler

A rubber compound contains, on average, less than 5 lbs. of chemical additive per 100 lbs. of elastomer. Filler loading is typically 10-15 times higher. Of the ingredient used to modify of properties of rubber product, the filler plays a dominant role. It acts as cheap diluents of more costly elastomer. The characteristic which determine the properties filler will impart to a rubber compound are particle size, surface are, and surface activity.

2.3.1 Filler Morphology and Characterization

Fillers are made up of primary particles at the smallest size-scale, Angstrom to micron, which are strongly bonded to other primary particles to form an aggregated structure (Kohls *et al*., 2002). The aggregates range from the nanometer to micron size-range and these can interact with other aggregates through weaker secondary bonding to form agglomerates. Tables 2.1 and 2.2 show the methods commonly used to determine filler morphology and how the morphologies relate to filler properties. These methods give information about the filler primary particle size, surface area, surface structure and energy aggregate size / structure, and agglomerate size /structure.

Table 2.1: Filler characterization methods and information obtained

Method	Information
Scanning electron microscopy (SEM) Transmission electron microscopy (TEM)	Primary particle, aggregate and agglomerate structure, fractal geometry
Nitrogen gas absorption (N SA) Dibutyl phthalate absorption (DBPA) Cetyltrimethyl ammonium bromide absorption (CTAB)	Specific surface area, aggregate shape, particle size, pore size
X-Ray diffraction (XRD) Small angle X-ray scattering (SAXS) Small angle neutron scattering (SANS)	Primary particle, aggregate and agglomerate structure, surface area, fractal dimension
Infrared spectroscopy (IR) Nuclear magnetic resonance imaging (NMR) X-ray photo-spectroscopy (XPS) Inverse gas chromatography (IGC)	Filler surface structure and chemistry

Table 2.2: Filler morphology and properties

Morphology	Filler Effect	Filler Characterization
Surface chemistry	Filler–filler Filler–polymer	Surface functional groups
Primary particle Volume, shape	Hydrodynamic/mechanical Reinforcement	Size, shape, Structure Surface area
Branched aggregate	Hydrodynamic Occluded rubber	Structure, Surface area Fractal dimension; branching coefficient
Agglomerated Aggregates	Filler networking Trapped rubber	Structure Surface area Fractal dimension

2.4 Carbon Black

Carbon black is widely used as filler in elastomer, plastic and paint to modify the mechanical, electrical and the optical properties of the material in which they are dispersed and consequently determine their applications in a given market segment (Donnet *et al.*, 1993). When it used as fillers in rubber, it change fracture behavior and improve abrasion and failure properties. There are four main processes to produce carbon black, furnace process which is widely used, thermal process, Channel or impingement process and Lampblack process.

The primary carbon black characteristic that influence the properties of carbon black compounds with elastomer are the particle size, aggregate size, the morphology of the carbon black aggregate and its structure.

2.4.1 Specific Surface Area

The primary particle size or specific surface area is characterized by different adsorption methods of specified molecules (Donnet *et al*., 1993). The most widely used adsorption methods are:

1. The iodine number, which reflects a ‘not true’ surface area, because it is affected by porosity, surface impurities and surface oxidation.
2. The cetyltrimethyl ammonium bromide (CTAB) method, which analyzes the so-called external surface area which corresponds to the accessible surface area of carbon black for an elastomer.
3. The BET nitrogen adsorption surface area, which provides the ‘total’ surface area including porosity.
4. The Statistical Thickness Surface Area (STSA), which is an alternative technique for the determination of the external surface area.

All these measures surface areas are affected in different ways by the nature of the carbon black surface and have not to correlate exactly with the actual occupied surface by an elastomer in a mixture. This should be kept in mind when physical properties are deduced from the surface.

2.4.2 Structure

The primary particles formed during the initial carbon black formation stage fuse together building up three dimensional branched clusters called aggregates. High structure blacks exhibit a high number of primary particles per aggregate (Frohlich *et al*., 2005), which is called a strong aggregation low structure blacks show only a weak aggregation. These aggregates again may form loose agglomerates linked by van der Waals interactions.

2.4.3 Surface Activity

In a physical sense, variations in surface energy determine the capacity and energy of adsorption. The surface chemistry of carbon blacks has a significant effect only on the vulcanization behavior of filled compounds. No direct correlation has been demonstrated between chemical groups on the carbon black surface and rubber related properties (Donnet *et al*., 1993).

2.5 Filler and Rubber Interaction

Interactions between fillers and rubbers have a significant effect on reinforcement properties of a filled rubber. The chemical and physical properties of the rubber and filler as well as the amount of each present in a compound influence these interactions. Rubber–rubber interactions mainly occur when blends of rubber are used in compounds and are considered to be not as significant as filler–rubber and filler–filler interactions. Filler–rubber interactions are described by the compatibility of the filler with the rubber while filler–filler interactions are described by the attraction of filler to itself and the ability to form a network. The most important effect of filler–rubber interactions has to do with the occlusion of rubber. So called ‘bound rubber’ is trapped between or within aggregates where it is no longer part of the elastically active rubber matrix. Instead, bound rubber acts as part of the filler network and increases the ‘effective’ filler volume.

Filler–filler interactions are a primary mechanism in reinforcement, especially at high filler loading. These interactions depend on chemical interactions between the filler particle surfaces (filler–filler, filler–rubber), physical interactions (van der Waals forces, hydrogen bonding), morphology of the filler network, and filler volume fraction. The surface energy of the filler influences how compatible it is with the rubber. Silica for example is highly polar and doesn’t interact well with a non-polar elastomer like styrene–butadiene (SBR) but does have good interaction with polar elastomers like poly-dimethyl siloxane (PDMS). The filler structure also determines how compatible it is with the rubber. As the surface area of the filler increases it has more sites available to interact with the rubber or other filler particles. A highly branched structure also makes it possible for some of the rubber matrix to become mechanically interlocked between aggregates.

Filler–rubber interactions have been studied by Wolff and Wang in a series of papers on both carbon black and silica fillers. Those studies looked at the effect of surface energy, distance between filler aggregates, and the effect of filler–rubber interactions on dynamic mechanical properties.

2.6 Bound Rubber

Bound rubber is the rubber that is trapped by the filler aggregates after mixing (Kohls *et al.*, 2002). There are several models that explain the different ways in which rubber is excluded from the matrix and incorporated in with the filler. Figure 2.1 illustrates these models.

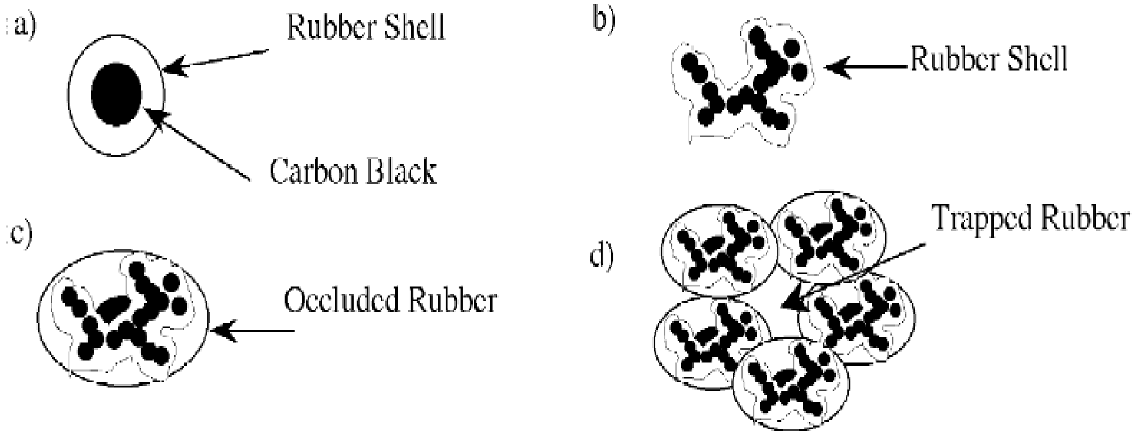

Figure 2.1: Model of rubber exclude from the rubber matrix

In case (a), the rubber chains are attracted either physically or chemically to form a rubber shell on the surface of the carbon black particle. The rubber that is attached closest to the carbon black molecule is much stiffer than the rubber molecules that are further away. In case (b), the rubber shell that is shown for the individual particle in (a) is seen throughout the filler aggregate. As in (a), the rubber chains closest to the aggregate are the stiffest. In this shell model bridging of the bound rubber in the aggregate leads to a higher bound rubber fraction. In case (c), rubber collects around the aggregate and the rubber shell to form an outer layer of occluded rubber. This layer is not as tightly bound to the filler aggregate but does experience decreased mobility near the surface of the aggregate. In case (d) rubber is trapped between aggregates which have formed agglomerates. This rubber experiences little stiffness increase and becomes 'free' once the aggregate structure breaks apart during deformation

These bound rubber models give an explanation of what happen when a filler network develops in the rubber. As the amount of carbon black is increased the bound rubber content also increases (Datta *et al*., 1994).Processing of rubber compounds also affects the bound rubber content. When the mixing time in increased during filler addition and when the storage time of the compound before curing is increased the bound rubber content also increases (Leblanc *et al*., 1997)

2.7 Filler and Reinforcement

The basic purpose of fillers is to 'fill' a plastics that is increase the bulk at low cost, to improve the economics. With good adhesion between filler ad polymer, consequently the filler begins to play a role in improving mechanical properties (Murphy, 2001). Therefore, fillers are not only for reducing cost but also to modify properties such as stiffness, hardness, thermal stability and shrinkage. In this case, the fillers function as the non-reinforcing fillers in the composites. Non-reinforcing fillers are addictive to improve the hardness strength of composite but reduce the tensile strength and tear strength.

The effect of fillers on the composite properties are largely dependent on the mean particle size, particle shape, particle size distribution of filler and the strength of the bond between filler particle and polymer matrix(Wypych, 1999). Most filler do not consist of particles which are all the same size and the same shape. The shape of the particles affects the modulus and the other mechanical properties significantly. Spherical particles are less likely to initiate cracking than more slender particles. However, flat platelet-type particles tend to produce stronger bond between the filler particle and matrix, due to increased surface area available for bonding. One measurement of shape is the aspect ratio. The greater aspect ratio, the greater the increase in bonding area is available which usually improved mechanical properties (Miller, 1996).

2.8 Internal Mixer

An internal mixer is a closed mixing device that can be used to produce compounds with short mixing cycles of 5-10 minutes at volumes of up to 500 kg. The internal mixer, a relatively expensive machine, consists of an enclosed mixing chamber with cooling channels. The mixing chamber contains two rotating kneader rotors to ensure high-speed mixing. A filling chute with a ram is connected to the top of the mixing chamber for adding ingredients and at the bottom of the chamber is a discharge opening for dumping the mixed batch on a cooling mill. In practice, two different mixing rotors are used, the tangential (old) and the intermeshing (new) mixing rotors. Intermeshing rotors have a higher fill capacity so the mixing efficiency is greater.

2.9 Tensile Strength

Tensile strength is indicated by the maxima of a stress-strain curve and, in general, indicates when necking will occur. As it is an intensive property, its value does not depend on the size of the test specimen. It is, however, dependent on the preparation of the specimen and the temperature of the test environment and material.

Tensile strength, along with elastic modulus and corrosion resistance, is an important parameter of engineering materials used in structures and mechanical devices. It is specified for materials such as alloys, composite materials, ceramics, plastics and wood.

The ability of rubber to stretch to several times its original length is one of its chief characteristics, but it is worth noting that at least as many rubber products are used in compression or shear as are used in tension. Essentially, dumb-bell shaped or, less often, ring-shaped test pieces are strained at a constant rate of traverse and force with the corresponding extension recorded. It is usual in rubber testing to calculate tensile stresses, including those at break, on the initial cross-sectional area of the test piece, and these stresses are sometimes called *nominal stresses.* Extension is always recorded as percentage of elongation, which is the increase in length as a percentage of original gauge length.

Physical testing of the rubber vulcanized is necessary to trace out the short falls in processing methods, to control and maintain the quality of the products and to undertake research and development work. The quality of the finished products depends not only on the quality of the starting materials but also on the correct operation of the various processing steps. Processing errors committed during the manufacture can seriously affect the properties of the final product. For example, too much milling of the rubber in the mixing mill or in the internal mixer can give a product of low strength. Errors made in weighing or the omission of any one of the ingredients during mixing can