# The properties of composites based on NR/CSM rubber blend and waste rubber powder

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Keywords: composites, elastomer, waste rubber powder, gamma irradiation. The use of reclaiming scrap waste rubber is of great ecological interest due to its significant influence to the environment. Powdered waste rubber (WRP) can be used as a filler in mixtures with rubbers, thermoplastics, and as modifiers for asphalt. In this work the composites based on natural rubber (NR) and chlorosufonated polyethylene (CSM) filled with different content of WRP were prepared on a laboratory-size two-roll mixing mill. The curing by sulfur was done at 160° C. The mechanical properties, namely tensile strength, tensile modulus at 100% elongation, elongation at break and hardness have been followed up as a function of irradiation dose (100; 200; 300; 400 kGy), as well as waste rubber powder content (0; 20; 40; 60; 80; 100 phr). It was assessed that the addition of 20 phr waste rubber has improved the properties of obtained elastomeric materials. The improvement of composites mechanical properties is in correlation with homogeneous WRP distribution which has been assigned by scanning electron microscopy (SEM).

#### **INTRODUCTION**

Technological development of reclaiming scrap waste rubber process is of great interest due to its significant influence to the environment. A normal disposal method of waste rubber such as incineration or landfilled is not a desirable approach as it caused environmental problems such as air and water pollution. The recyclization of waste rubber by mechanical or chemical methods is the ultimate approach to solve the problems (Ismail at al., 2003). Transforming bulk rubber to powders using mechanical process is the most preferable procedure of reclaiming rubber and it is more economical compared to chemical process. Powdered waste rubber (WRP) can be used as a filler for elastomeric materials, thermoplastics, and as modifiers for asphalt. The effect of WRP addition (a waste product from mechanical process of rubber ball and artificial eggs) on the properties of natural rubber (NR) compounds has been studied (Ismail & Yusof, 2004). Blending of two or more types of rubber is a useful

technique for preparing and developing elastomeric material with properties superior to those of individual constituents. Moreover, each kind of rubber in the blend has their own advantages and specific application due to their chemical configuration and composition. Hence, it is economically easier to blend more than one type of rubber having the desired properties rather than chemically creating of a new elastomer. Elastomer based on two or more rubbers is used for many reasons such as lowering the compound cost, for ease of fabrication and for improvement of the performance of the industrial rubber (Sombatsompop & Kumnuantip, 2003). Natural rubber (NR) was blended for a long time for these reasons. Figure 1 shows the chemical structure of cis-polyisoprene, which is the main constituent of NR. Synthetic cispolyisoprene and natural cis-polyisoprene are derived from different precursors (isopentenyl pyrophosphate and isoprene). NR is an elastic hydrocarbon polymer that naturally occurs as a milky colloidal suspension, or latex, in the sap of some plants. Natural rubber is categorized as a radiation crosslinking type of polymer as it contains a double bond in its basic cis-1,4-polyisoprene units.

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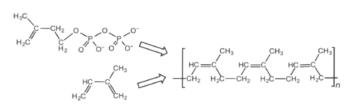


Figure 1. Chemical structure of cis-polyisoprene, the main constituent of natural rubber. Synthetic cis-polyisoprene and natural cis-polyisoprene are derived from different precursors.

Due to these properties, it would be expected that NR attains higher tensile strength than other elastomers like chlorosulphonated polyethylene rubber (CSM). The introduction of chlorine and sulfur dioxide onto the polyethylene linking via condensation or substitution reactions molecule destroys the crystallinity, thereby changing the thermoplastic material into an amorphous polymer chlorosulphonated polyethylene, which contains 25-43% by weight of chlorine and 1-1.5% by weight of sulfur as SO<sub>2</sub>Cl units. The high reactivity of this rubber is due to the SO<sub>2</sub>Cl groups. Elastomeric materials based on CSM are superior to other rubbers in their resistance to the effects of ozone and inorganic acids, such as chromic, nitric, sulfuric, and phosphoric acids, as well as to the effects of concentrated alkalies, chlorine dioxide, and hydrogen peroxide (Marković at al., 2009). Elastomers based on CSM are used for cable jacketing materials and have excellent radiation resistance needed in nuclear power stations. The temperature region for its most efficient use is from -60° to 180°C. Rubber waste is usually generated during the manufacturing process of product of these industries and by disposal of postconsumer (retired) products mainly including scrap tires (Salleh at al., 2016). High-energy radiation is a well-known technique for modification of polymers. Radiochemical studies on crosslinking or degradation of polymers are important for designing new materials (Alex at al., 1989; Zhang at al. 2012). The focus of the present work was to study the gamma irradiation resistance of composites based on two network precursors, nonpolar natural rubber and polar CSM, and different content of WRP.

#### MATERIAL AND METHODS

Natural rubber was supplied by Dow chemical, USA. Its cis-1,4 content was 97%. Mooney viscosity, ML 1+4 was 48. Chlorosufonated polyethylene (CSM, Hypalon 40S) with sulphur content 1 mol% was obtained from DuPont. The rubbers were used as delivered. The recycled rubber waste powder was supplied by Watas holding Sdn. Bhd, Penang Malaysia (250–500 mm particle size). The network precursor ratio in all samples was 50:50 (w/w). The content of waste rubber powder was varied (0; 20; 40; 60; 80; 100 phr). Other ingredients were: tetramethyl thiuramdisulfide, TMTD (1 phr); N-cyclohexyl-2-

benzothiazolesulfonamide, CBS (1 phr); magnesium oxide (4 phr); sulfur (1.5 phr); zinc oxide 5 phr; stearic acid (2 phr); naphthenic oil (10 phr). The rubbers were separately pre-masticated for about 1 min each, keeping a tight nip gap. The mixing of the rubbers and fillers was performed on a two roll mill. The gear friction of the mill is 1:1.4. The hollow rolls were cooled by using flushing water in order to regulate the temperature not exceeding at 40° C during the different stages of mixing according to ASTM D-15-627. The rubber mixes obtained were sheeted and left for a period of at least 6 hours before testing. The addition of ingredients during mixing was carried out following the same order and conditions of mixing. The applied hydraulic force during crosslinking attained 6.7MPa. The vulcanization characteristics of compounds were carried out using an oscillating disc rheometer (Monsanto 100). The scorch time (ts2), the optimum cure time (tc90), the curing rate index (CRI), and maximum torque (Mh) were determined from the obtained curves. The crosslinking was carried out at 160° C in an electrically heated hydraulic press. Tensile tests were performed on dumbbell samples that were cut from sheets (2 mm thick). The tensile strength and the elongation at break were determined at room temperature using a universal tensile testing machine (Zwick 1425). Samples with flat surface were cut for hardness test (Durometer Model 306L Type A). Gamma irradiation was performed in air in the Co 60 radiation sterilization unit with the dose rate of 10 kGyh-1 and total absorbed dose of 100, 200, 300 and 400 kGy. Radiation dose of 400 kGy can be considered as a relatively high dose. The scanning electron microscopy images of the rubber blends fractured surfaces were taken by a JEOL JSM-5400 model of the microscope. The samples were sputter coated with gold for 3 min under high vacuum with image magnifications of 7500X.

#### **RESULTS AND DISCUSSION**

NR/CSM rubber blend were found to be compatible, hence the partial compatibility might be due to the interaction of nonpolar phase of NR and polar phase of CSM phase occurs with the strain induced crystallization of NR rubber. The curing characteristics of the rubber blend filled with WRP are summarized in Table 1. It can be seen that the values for MI and Mh increase with the WRP content in the rubber compounds. The addition of WRP reduces the flow of rubber blend compounds, which resulted in an increase of minimum torque.

It can be seen that the curing time, tc90 increases with increasing WRP content. Various researchers who studied the curing of the rubber compounds containing recycled rubber powder reported that sulfur migrates from rubber matrix into the rubber powder. The increased scorch time indicates higher scorch safety of the rubber blend.

In the Figure 2. the effect of waster rubber powder on tensile strength for the prepared composites irradiated

WRP content _ (phr)	Curing characteristics					
	M <sub>ı</sub> , dNm	M <sub>h</sub> , dNm	ΔM, dNm	t <sub>s2</sub> , min	t <sub>c90</sub> , min	CRI
0	4	40	36	6	15	11.0
20	5	42	37	8	16	12.5
40	5	45	40	9	16	14.3
60	7	46	39	9	17	12.5
80	7	47	40	10	17	14.3
100	7	47	40	10	17	14.3

Table 1. The curing data for NR/CSM rubber blend compounds with different content of waste rubber powder

with different doses is given. It is obvious that the tensile strength increases with increasing irradiation dose reaching its maximum value at 200 kGy. Due to the strain induced crystallization behavior of both network precursor in elastomeric material (Toki at al., 2000) the rubbers reinforced each other when subjected to extension (Bandyopadhyay at al., 1995). Gamma irradiation is a powerful means for crosslink elastomers, however, exposure to higher dosage of it degrades the polymer. It is well known that during irradiation several detrimental processes take place, such as main chain scission, crosslink formation and crosslink breakage (Dubey at al., 2006; Marković at al., 2007; Marković at al., 2010). The extent of crosslinking and chain scission depends on network precursor structural characteristics and the presence of initiators. Based on its chemical structure, the tertiary substituted carbon atom on the main rubber chain represents the most susceptible carbon atoms and during irradiation breakage of this bond takes place favorably, leading to the formation of the hydrogen atoms and chloride radical. When it happened that such radicals stand favorably to each other then they may react with each other with the result of formation of a

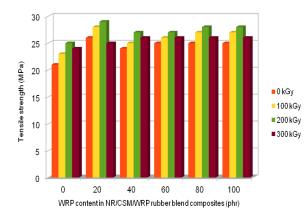


Figure 2. The effect of waste rubber powder content on tensile strength for the NR/CSM/WRP composites irradiated with different doses.

covalent bond, i.e., crosslink between two adjacent macromolecules.

The influence of WRP content on tensile modulus at 100% elongation (M100) for the composites irradiated with different doses is shown in Figure 3. It can be seen that the M100 of all samples increases with increasing the irradiation dose, whereby NR/CSM/WRP rubber blends composites has attained higher value than pure NR/CSM rubber blend. The M100 value increases with content of WRP rubber increase up to 20 phr and it decreases after 20 phr of WRP content in blends. The influence of WRP content on elongation for the rubber blend composites irradiated with different doses is shown in Figure 4. And, the influence of WRP on hardness for prepared composites irradiated with different doses is shown in Figure 5. The hardness of the rubber blends increases with irradiation dose. A higher amount WRP would result in an increased hardness of the vulcanizates. The SEM micrograph of composites with 20 phr WRP is shown in Figure 6. The mechanical properties improvement of prepared composites is in correlation with homogenous WRP distribution which has been assigned by SEM.

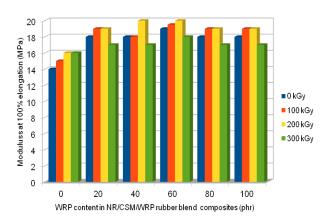


Figure 3. The effect of waste rubber powder content on tensile modulus at 100% elongation (M100) for the NR/CSM/WRP composites irradiated with different doses.

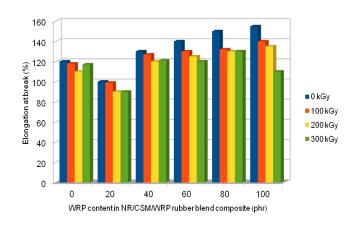


Figure 4. The effect of waste rubber powder content on elongation at break (Eb%) for the NR/CSM/WRP composites gamma irradiated with different doses.

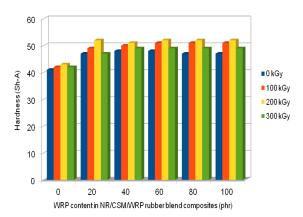


Figure 5. The effect of waste rubber powder content on hardness values for the NR/CSM/WRP composites gamma irradiated with different doses.

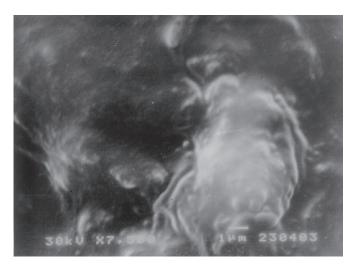


Figure 6. The SEM micrograph of NR/CSM/WRP composites filled with 20 phr waste rubber powder at 7500X magnification.

#### CONCLUSIONS

The purpose of this work was to investigate the vulcanization behavior and gamma irradiation ageing of elastomers based on two network precursors, nonpolar natural rubber and polar CSM and different content of waste rubber powder. The characteristics ts2, tc90 and curing rate index of rubber blend compounds increase with increasing WRP content. The incorporation of WRP reduces the flow of rubber blend compounds, which resulted in an increase of minimum torque. The improvement attained in mechanical properties has been certified by assessment of physical properties of the prepared rubber blend composites. The magnitude of improvement is a function of the gamma irradiation dose as well as the content of WRP in rubber blend. It was estimated that the tensile strength for all prepared elastomeric materials increased with increasing gamma irradiation dose reaching its maximum value at 200 kGy, as a consequence that the crosslinking process was the dominating one up to 200 kGy, whereas the degradation process has apparently prevailed for higher doses. The improvement in mechanical properties of prepared composites is in correlation with homogenous WRP distribution which has been assigned by scanning electron microscopy.

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## Svojstva kompozita na osnovu NR/CSM blendi kaučuka i recikliranog gumenog praha

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Ključne riječi: NR/CSM, kompoziti, prah reciklirane gume, elastomeri, ozračivanje. Upotreba recikliranog gumenog praha predstavlja veliki ekološki interes zbog njegovog značajnog uticaja na životnu sredinu. Uobičajeni način zbrinjavanja gumenog otpada kao što je spaljivanje ili odlaganje na otpad nije poželjan pristup jer je prouzrokovao probleme sa zagađenjem zemljišta i vode. Recikliranje hemijskim ili mehaničkim postupkom predstavlja adekvatno rešenje, pri čemu se mehaničkom rešenju mlevenja otpadne gume u prah daje prednost zbog ekonomičnosti postupka. Reciklirani gumeni prah može da se upotrebi kao punilo u mešavini sa kaučucima, termoplasitma ili kao modifikator za asfalt. U ovom radu sintetizovani su kompozitni materijali na bazi blendi poliizoprenskog kaučuka (NR) i hlorosulfonovanog polietilena (CSM) sa različitim udelima praha reciklirane gume (WRP), koristeći laboratorijski dvovaljak na 40°C. Umrežavanje sa sumporom je ostvareno na 160°C. Praćena su mehanička svojstva vulkanizata kao što su prekidna jačina, modul pri 100% istezanja, prekidno izduženje i tvrdoća u zavisnosti od doze gama zračenja (100, 200, 300 i 400 kGy) kao i sadržaja gumenog praha izraženo u phr jedinicama, što znači delova na 100 delova kaučuka (20; 40; 60; 80; 100). Ustanovljeno je da udeo recikliranog gumenog praha od 20 phr poboljšava mehanička svojstva kompozita rezultat su ravnomerne raspodele praha reciklirane gume, što je i potvrđeno SEM mikroskopijom.