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Effect of sulfur and Nano- carbon black on the mechanical properties of hard rubber

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Abstract

To improve the properties of hard rubber(Ebonite) from natural rubber, added Nano-Carbon black, where measured the properties of tensile, density, hardness and the properties of the vulcanization of a group of samples with different amount of sulfur from 18-36 pphr and different of carbon black (18-26-30) pphr. The results showed that the best carbon black ratio is 30 pphr, where it gives a balance between tensile properties of hand and toughness and flexibility of on the other hand and reduce brittleness in hard rubber.

Keyword: Natural rubber, Nano-Carbon black, Ebonite, Hard Rubber and Sulphur.

الخلاصة

لتحسين خصائص المطاط الصلب (ايبونايت) من المطاط الطبيعي، تم اضافة اسود الكربون النانوي وتم قياس خصائص الشد والكثافة والصلابة وخصائص الفلكنة لمجموعة من العينات مع كميات مختلفة من الكبريت من 18–36 pphr و كميات مختلفه من اسود الكاربون (18–26–30) pphr. وأظهرت النتائج أن أفضل نسبة للكاربون هي 30 pphr، حيث يعطي التوازن بين خصائص الشد من ناحية والمتانة والمرونة من ناحية أخرى وتقليل هشاشة في المطاط الصلب.

الكلمات المفتاحية: المطاط الطبيعي، اسود الكاربون النانوي، ايبونايت ، المطاط الصلب ، الكبريت.

Introduction

Ebonite also called hard rubber was vulcanization rubber processed with high content of sulphur (30-50 pphr) and has a glass transition temperature (*Tg*) higher than the room temperature. It has structured network and high hardness but it is brittle, flammable, non-toxic, high resistant to chemicals, good electrical insulating properties, excellent strength properties, and ease to manufacture. The hard rubber is used as storage tanks, reaction vessels, and pump linings (Kemp and Malm 1935; Lo and Chu 2011; Winya and Pittayaprasertkul ,2015) However, hard rubber is produced from natural rubber (NR), styrene-butadiene rubber (SBR), and nitrile-butadiene rubber (NBR).

The natural rubber or Para rubber is very important to the economy of Iraq in (rubber products). It is Cheap and easy to manufacture have good properties, (Winya and Pittayaprasertkul, 2015) the mechanical and chemical properties of natural rubber vulcanized are important factors that affects the efficiency of the rubber products used in applications requiring high modulus of elasticity, high strength, high hardness and suitable toughness, (Andrew, 1999) such as rubber used in body armor. The rubber must have high mechanical properties and high impact strength.

As the sulphur content increases, the mechanical properties such as the modulus, the tensile strength and the hardness will increase. However, it will become brittle and low toughness. Therefore, it should additional additives to improve the chemical composition of the rubber in order to improve the properties of toughness and reduce brittleness, a wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, the reduction in materials costs and improvements in processing (Abou-Kandil and Gaafar, 2010).

The most commonly-used fillers in the rubber industry are carbon black, silica, clay, carbon nano-fiber, and mica (Li *et.al.,* 2014; Pal *et.al.,* 2010; Pan *et.al.,* 2013; Samaržija-Jovanović *et.al.,* 2011; Sengloyluan *et.al.,* 2014).

Meltzer studied the influence of fillers and degree of vulcanization on the mechanical properties of hard styrene-butadiene rubber (SBR) – butyl rubber. He found that the Tg increasing with the degree of vulcanization (Meltzer and Dermody, 1964). Meltzer also reported the fraction of sulphur atoms effective in crosslinking is 0.04-0.07 and 0.10-0.13 in hard rubber for natural rubber and SBR, respectively (Meltzer and Dermody , 1964; Meltzer *et.al.,* 1963). For cis-polybutadiene rubber, the fraction turns from 0.06 to 0.17 and for trans-polybutadiene rubber it turns from 0.07 to 0.16 (Meltzer and Dermody , 1965).

Sung-Seen Choi investigated the influence of the modification of silica on the retraction behaviors of natural rubber vulcanizates reinforced with silica and carbon black. The vulcanizates containing the silane coupling agent recovered faster than those without the silane coupling agent (Choi , 2006). Rattanasom et al. examined the mechanical properties of natural rubber reinforced with silica/carbon black hybrid filler at various ratios in order to determine the optimum silica/carbon black ratio. The results revealed that the vulcanizates containing 20 and 30 pphr of silica in hybrid filler exhibit the better overall mechanical properties *et.al.,* 2007).

Chi-Fang Chu studied Influence of clay, silicate and carbon black on the environmental resistance properties of hard rubber. The result the carbon black has the best hardness and resistivity stability after the immersion test (Rattanasom, Saowapark, and Deeprasertkul , 2007). Rattanasom et al. studied the mechanical properties, heat ageing resistance, cut growth behavior and morphology of natural rubber which had been prepared by a partial replacement of the calcined clay with different amounts of various types of carbon black. At similar hardness, the compounds containing both clay and carbon black give the better tensile strength, edge-cut tensile strength, tear strength and thermal ageing resistance compared to the control (Rattanasom and Prasertsri , 2009).

Liangliang Qu et al. studied the synergistic reinforcement of nanoclay and carbon black in natural rubber. A synergistic effect in reinforcement between nanoclay and carbon black was proven by the marked enhancement in tensile strength from 11.4MPa for neat natural rubber to 28.2MPa for natural rubber nanocomposite with 5wt% nanoclay and 20wt% carbon black. Jia et al. found that the mechanical properties of natural rubber filled with both clay and carbon black were greatly superior than those of either natural rubber/ clay nanocomposites or natural rubber/carbon black nanocomposites (Qu *et.al.,* 2010).

Nattawat W. and Narupon P. studied reinforce the mechanical properties of the rubber compounds when added sulphur and silica were varied from 45 to 60 pphr and 5 to15 pphr, respectively. The experimental results showed that the addition of 10 pphr silica provides the maximum tensile strength and hardness. However, for the amount of silica higher than 10 pphr, the tensile strength tended to decrease. They observe that the amount of sulphur 60 pphr with 10 pphr silica gives the maximum hardness (Winya and Pittayaprasertkul , 2015)

The objective of this paper is the study the effect of increasing the amount on the sulphur properties of the rubber compound. The composite rubber contains 18-36 pphr of sulphur and (18-26- 30)pphr of carbon black (N-115) in particle size 17-23 nm.

Experimental Section

Materials

NR (natural rubber, 500g), Carbon black (N-115), Stearic Acid, Sulphur, Oxide Zinc, and Accelerators MBT (2-Mercaptobenzothiazole), MBTS (Dibenzothiazole disulfide).

Instrumentation

The mechanical properties were measured by Universal Testing Machine (WDW-5). The hardness (Shore D) was measured by TH210 according to ASTM D2240. The density measured by GP-120S. The curing times and vulcanization behavior were obtained by Micro Vision Enterprises at 150 ˚C. The compounds were subsequently compression molded Thermal –Electrical Hydraulic press at 180 ˚C.

Preparation of Compound Rubber

Preparation of compound formulations was achieved by mixing natural rubber at a temperature of 30 °C. Ebonite composite containing oxide zinc, stearic acid, Nano carbon black and Accelerators MBT and MBTS given in Table 1. The composite rubber investigated contains 18-36 pphr of Sulphur and leave for 24 hours. After that will study curing characteristics and mechanical properties.

Table 1 The Compound Formulations.

Materials (pphr)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
NR	100	100	100	100	100	100	100	100	100	100
Oxide Zinc	3.63	3.93	4.235	4.53	4.84	5.14	5.44	5.74	6.05	6.35
Sulphur	18	20	22	24	26	28	30	32	34	36
Stearic Acid	1.81	1.96	2.11	2.26	2.41	2.56	2.715	2.86	3	3.16
Carbon black (N-115)	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30	18, 26,30
MBT	0.42	0.455	0.49	0.52	0.56	0.59	0.63	0.66	0.7	0.73
MBTS	0.42	0.455	0.49	0.52	0.56	0.59	0.63	0.66	0.7	0.73

Results And Discussion

In general, it is known that increasing the sulphur content in rubber leads to increased rubber hardness and greatly increase the mechanical properties of rubber, but leads to the formation of Hard rubber and increase the brittleness of rubber, but when the addition of Nano-carbon black to Hard rubber leads to giving flexibility to chains, for rubber without affecting the mechanical properties of Hard rubber, because carbon acts as a lubricant for chains, which will allow it to move. Therefore, a balance is achieved between the resulting adhesion of the tangles of the hand and the movement given by the carbon on the other hand.

Figs.1 and 2 shows that the value of the tensile strength and modulus increases with the percentage amount of sulphur due to increase the amount of cross linking in rubber and that the value of the tensile strength and modulus also increases with the period time because of sulphur continued to produce cross linking within the rubber depending on the amount of sulphur content big.

And reduced the tensile strength and modulus of elasticity with increase the nano carbon black because the nano carbon black is working on the lubrication of the chains thus reducing the friction between the chains and facilitates the movement of chains even with the cross link, which leads to the reduction of tensile properties

Through Figs. 3 and 4, show the elongation and toughness decrease when increasing the sulphur ratio, depending on the restriction of the movement of chains and through the formation of crosslinking within the rubber, but that the decrease in the above two characteristics is not large due to the presence of Nano-carbon black, , but when increasing Nano carbon black at the same proportion of sulphur, the properties of toughness and elongation increase, depending on that the nano carbon black works on the lubrication of rubber chains reduces the friction between chains, which allows for the movement of molecular chains and increases the same properties which acts as a lubricant of the series, giving little flexibility to chains.

The best ratio of nanocarbon black added to the natural rubber is 30 pphr, where it gives the results of its approximate to the Hsueh-huan(Lo and Chu , 2011). Therfore, will study the hardness and curing charcteristics for natural rubber have 30 pphr only.

Nano-carbon black increase the hardness values of the rubber significantly and this is evident in the Fig.5, depending on the agglomeration of carbon on the surface of the rubber, the hardness values are increase with the increase in the amount of sulphur depending on the increase in the percentage of cross linking within the rubber.

Table 2 shows that the curing characteristics of all hard rubber samples have nano carbon black (30 pphr). The experimental results show that amount of sulpher have no significant effect on M_L (minimum torque), Ts_2 (scorch time) and Tc_{90} (optimum cure time). Regular variations in the maximum torque (M_H) and optimum curing time (Tc_{90}) were observed for the samples". The samples have Sulphur (28-30 pphr) system demonstrated an optimal curing time .

Figure 6 displays the maximum torque (M_H) of hard rubber compounds filled with Carbon black. The initial decrease in torque is due to the softening of the matrix. The torque then increased due to the crosslinking between the molecular chains. Crosslinks are formed between the unsaturated sites and molecules during vulcanization. The maximum torque increases proportional to the Sulphur content, indicating crosslink density enhancement and optimum curing time (Tc_{90}) were observed for the samples". The apparent change in the values of irregular inductance is due to the heterogeneity of the ratio of large carbonated rubber impregnation that hinders the formation of entanglements in rubber.

Table 2 Curing Characteristics of Hard Rubber

Sample	M_L (Kg cm)	M_H (Kg cm)	Ts_2 (min)	Tc_{90} (min)
S1	9	55.4	1.33	4.7
S2	10.7	67.2	1.73	11.7
S3	7.3	68.2	1.45	9.38
S4	7.3	59.5	1.75	10.28
S5	7.4	62.2	0.97	8.35
S6	6.2	50.8	1.92	7.45
S7	6.4	51.9	1.93	6.9
S8	7.1	52.8	1.92	6.13
S9	7.9	75.4	2.22	7.58
S10	16.3	66.3	2.35	8.15

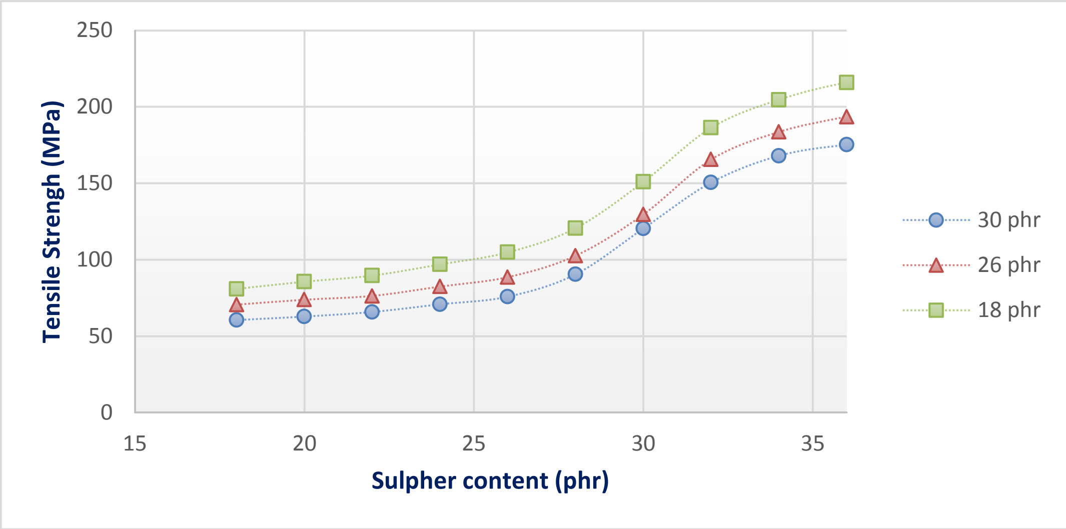

Figure 1. Effect of sulpher and nano carbon black content on tensile strength.

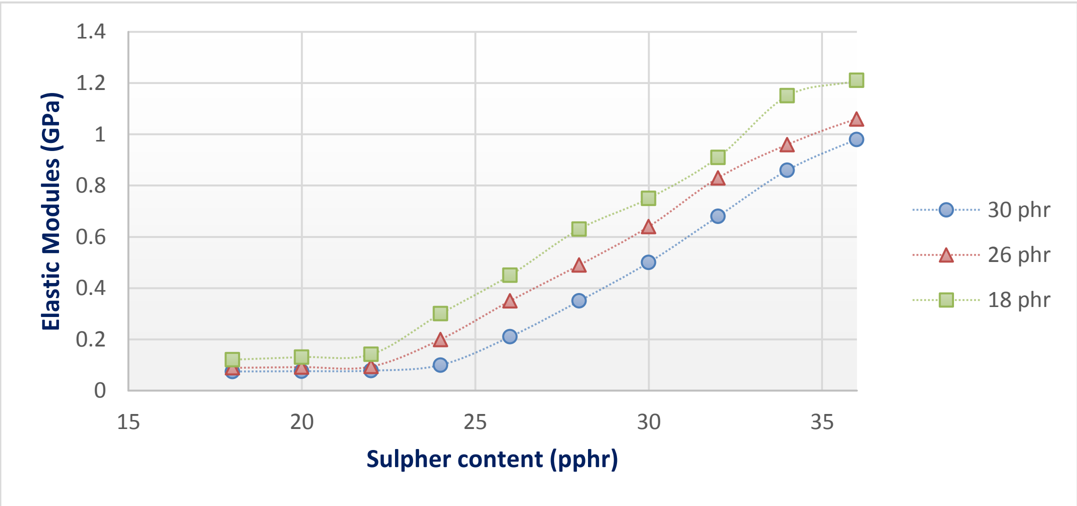

Figure 2. Effect of sulpher and nano carbon black content on elastic modulus.

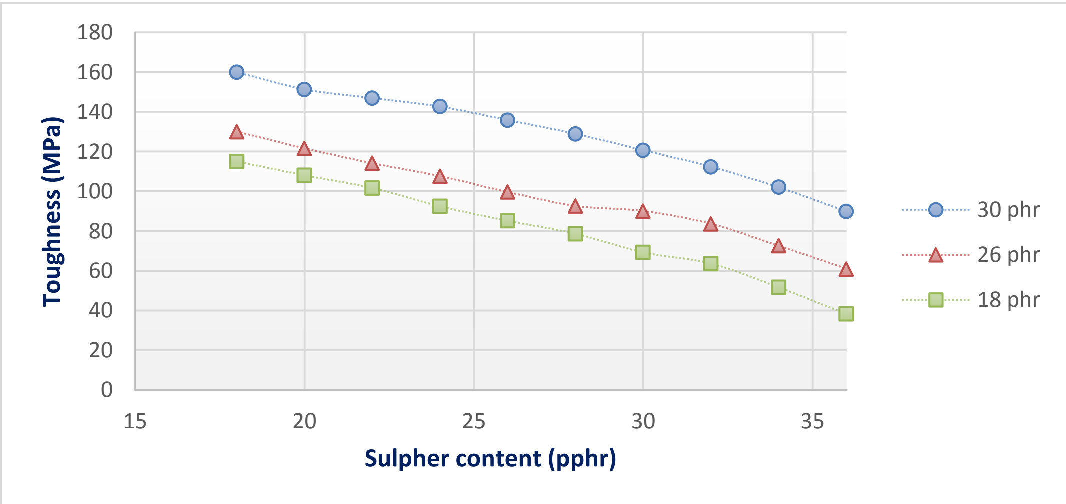

Figure 3. Effect of sulpher and nano carbon black content on elongation.

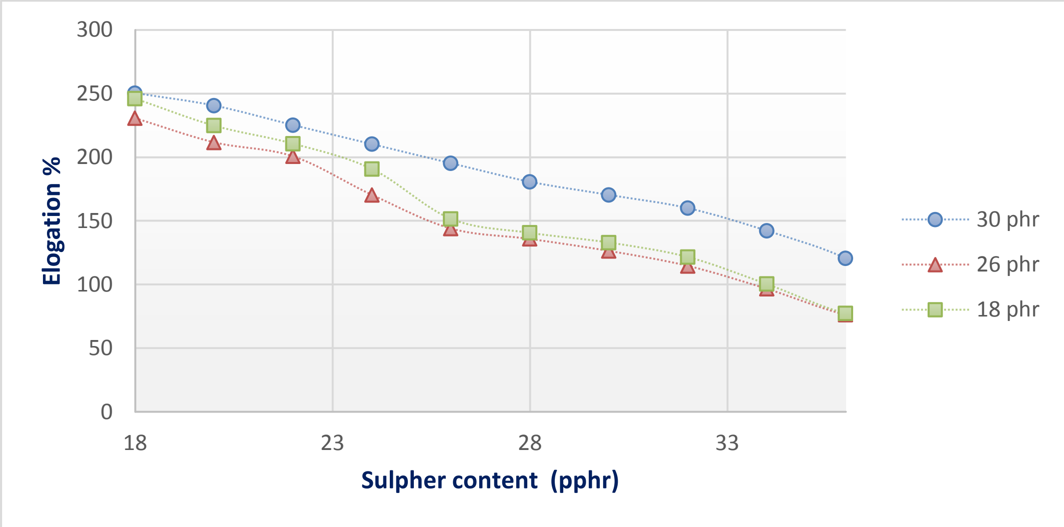

Figure 4. Effect of sulpher and nano carbon black content on toughness.

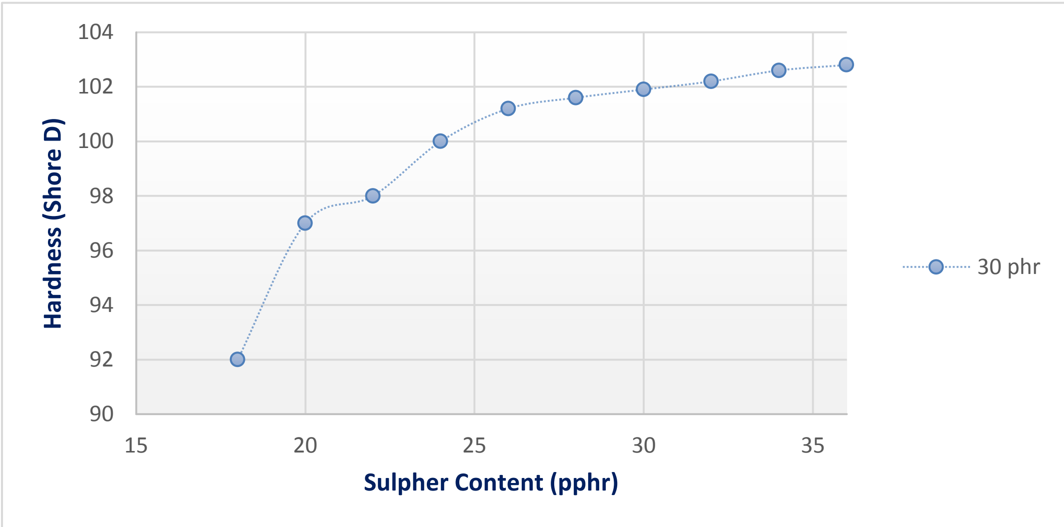

Figure 5. Effect of sulpher content on hardness.

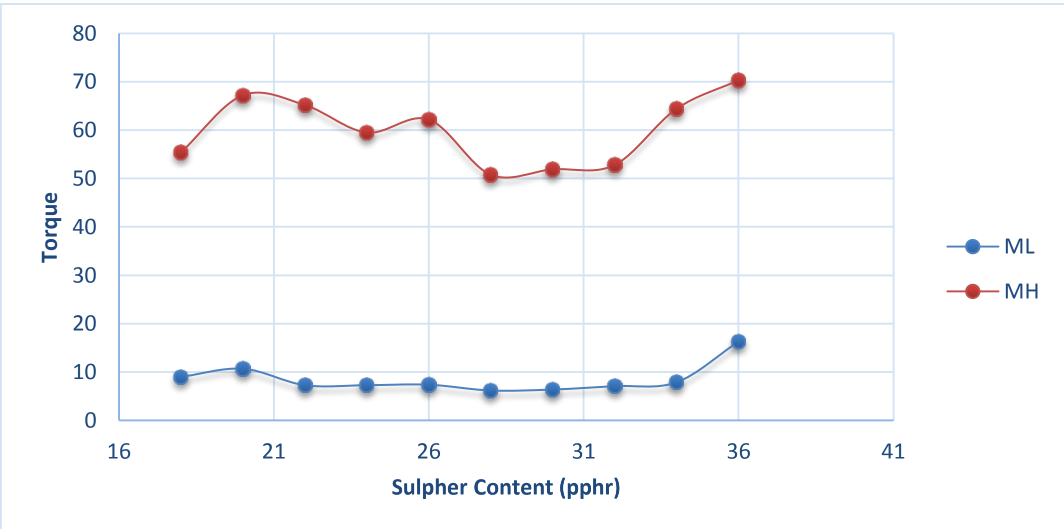

Figure 6 Effect of sulpher content on torques.

Conclusion

These results showed that the addition of Nano carbon black 30 pphr to ebonite (natural rubber) is given flexible and give toughness also increase the hardness and reduce the brittleness. This allows the use of ebonite in wide applications including shock absorption in armor to the tensile strength and hardness highest.

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