

## The Effects of Plasticizer and Filler on the Curing Characteristic and Mechanical Properties of (SBR) Styrene Butadiene Rubber and (CR) Chloroprene Rubber Blends

MAHMOOD IQBAL\* TEHZEEB AKHTER, ZIA-UL-HAQ FAROOQUI AND KHALID MAHMOOD  
*Materials Science Research Centre PCSIR Labs Complex Karachi. 75280*

(Received 6<sup>th</sup> March 2007, revised 26<sup>th</sup> October 2007)

**Summary:** Curing characteristics and mechanical properties of styrene butadiene rubber and chloroprene rubber blends have been studied. Carbon black loading in the range of 50-70 phr and plasticizer in the range of 7.5-12 phr was used. Minimum torque (ML), maximum torque (MH), cure time ( $T_c_{90}$ ) and hardness was found to increase, while reduction in scorch time was observed by increasing the carbon black loading in the rubber matrix. Increasing the carbon black quantity in the rubber blends resulted in an enhancement of the tensile strength and tear strength up to 60 phr and then gradually decreased as the filler quantity was increased. The curing characteristics indicate that the rubber filler interaction increases the cure time with increasing filler loading. Tensile strength, tear strength and hardness were found to increase with the increasing plasticizer concentration up to 9 phr in the rubber blends. This property gradually decreases as the plasticizer concentration is increased up to 12 phr while elongation at break increases.

### Introduction

Fillers play an important role in enhancing the physical properties of elastomers. Elastomers in their original state are macromolecules with essentially no strength or useful physical properties. These properties can be improved by the addition of various types of fillers. Filler such as carbon black, silica, talc,  $\text{CaCO}_3$  and clay are used in large quantities in rubber, where as the last three act mainly as extenders for reducing the cost, while carbon black and silica act as reinforcing filler. In fact the physical properties of many rubber compounds are not very significant without an adequate level of such reinforcing filler. The effect of carbon black loading on physical performance of rubbers has been discussed by Corrish and Palmer [1] and Bulgin and Walker [2]. They have found that different rubber have different responses to filler loading with respect to certain properties. Hence, their fair distribution among the different components in an elastomer blends is very important for better performance of the rubber compounds. Ayala, Hess *et al.*, [3] have studied carbon black- elastomer interaction for four elastomers namely styrene-butadiene rubber (SBR), natural rubber (NR), butyl rubber and nitrile rubber. They also subjected the carbon black to high temperature to study the effect of graphitization on mixing. They carried out the cross linking reaction and consequently, the properties, like, stiffness, compressive strength, controlled shrinkage and

thermal expansion were affected [4]. The action of particulate fillers on an elastomer is dependent on the total amount of surface area, physical and chemical nature of the filler surface in relation to the elastomers and structures [5-8]. Major properties used for characterizing reinforcing fillers are surface area and structure. The commercial carbon blacks are classified according to ASTM D1765 [9]. The surface area is the measure of primary aggregate of carbon black, which are in the size range of 10-100nm. The aggregate are made of "fused" spherical particles, size of which determines the surface area [10]. The surface area and structure are selected to characterize carbon black due to the fact that they control reinforcement by the filler in the rubber products. Commercial carbon blacks are supplied as pellets. The pellets easily break up into pieces of the size which range between 10-100  $\mu\text{m}$ , which are called as agglomerate. In mixing of gum rubber with carbon black, the first stage is incorporation, by which the agglomerates are taken up inside of aggregate in order to provide sufficient reinforcement.

Rubber blends have gained wide acceptance in industry due to ability to customize their properties to fit particular needs [11]. The mechanical properties are influenced by the crosslinking density of each phase and at the interface of blend components. Sulphur vulcanization process is the predominant

\*To whom all correspondence should be addressed.

method employed in the cross linking of unsaturated elastomers. This system is composed of sulphur, metal oxide (ZnO) and one or more organic accelerators. Natural rubber (NR) has been studied and reported extensively because of its superior performance in tire applications [12]. Any one of the wide choices of available fillers for the rubber industry can be used in styrene butadiene and EPDM rubber compounding. The addition of these fillers in small quantities with respect to raw rubber can affect the mechanical properties [13].

The objective of the present work is to evaluate the effect of carbon black as reinforcing filler and plasticizer on the curing characteristics and mechanical properties of styrene butadiene rubber and chloroprene rubber blends.

### Results and Discussion

The physical properties are responsible for the quality of rubber goods for commercial uses. They also modify processing characteristics and reduce the cost of rubber compounds. To determine the effect of carbon black, it is necessary to study the rheological properties of uncured investigated rubber compounds using moving die rheometer. Table-1 and Fig. 1 illustrate the rheometric characteristics of SBR/ CR formulation containing 50 phr, 55 phr, 60 phr, 65 phr, 70 phr carbon black. It is observed that the carbon black increases the minimum torque (ML), maximum torque (MH) and cure time  $t_{c90}$  with the increase of filler loading in rubber matrix while scorch time ( $t_s$ )

Table-1: Rheometric Characteristics of SBR/CR Rubber blends at 160 °C.

Sr. No.	Test Performed	Carbon black 50 phr	Carbon black 55 phr	Carbon black 60 phr	Carbon black 65 phr	Carbon black 70 phr
1	MH Torque	6.09	8.22	12.86	18.95	22.23
2	ML Torque	2.79	2.92	3.02	3.13	3.45
3	Cure Time ( $t_{c90}$ min)	2.52	4.78	7.34	7.75	8.68
4	Scorch time( $t_s$ min)	1.73	1.65	1.56	1.40	1.28

was found to decrease. The enhancements of these properties were attributed to the higher time the rubber compounds remain in the mill during mixing. As the filler loading increases, the time of incorporation also increases. According to Nando and De [14], the addition of lignin into rubber compounds makes the stocks scorchy and effect becomes more pronounced as one moves towards the efficient reinforcing filler. Bhattacharyya *et al* [15] in their work on short pineapple leaf fiber-reinforced rubber composites also found that there were gradual increase in the torque and decrease in scorch time with increasing maximum fiber concentration. Bateman [16] reported that the amount of active sulfurating agent increases with increasing accelerator concentration, thus, more cross links are formed and a shorter scorch time is observed. Table-2 shows the effect of carbon black loading on physicochemical properties. It was found that tensile strength and tear strength increase with increase of filler loading, up to 60 phr and sharply decrease as the filler loading is increased, while modulus at 100 % elongation decreases. Moreover, hardness and compression set

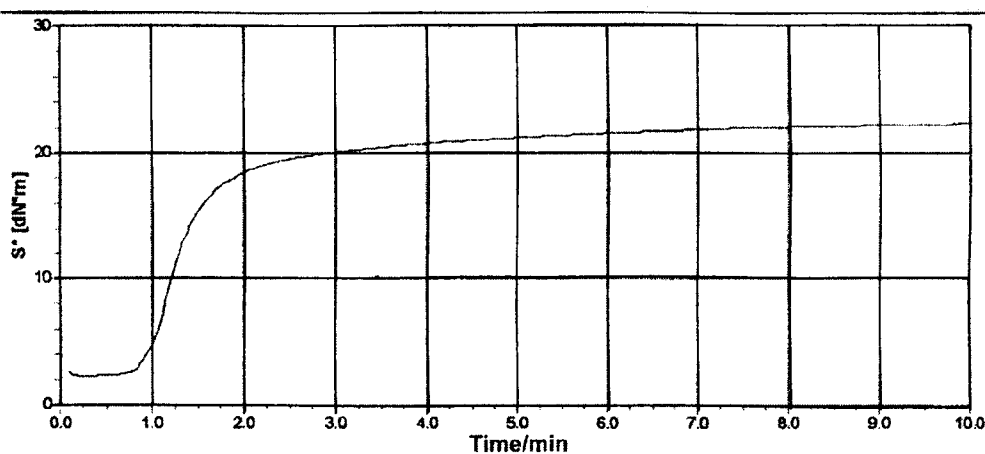


Fig.1. Rheometric characteristics of MDR Curve.

Table-2: Physico-Mechanical Properties of SBR/CR Blend Vulcanizates at Optimum Cure Time before Aging.

Sr. No.	Test Performed	SBR/CR 30/70				
		Carbon black 50 phr	Carbon black 55 phr	Carbon black 60 phr	Carbon black 65 phr	Carbon black 70 phr
1	T.S kg/cm <sup>2</sup>	178	212	235	192	170
2	Elongation (%)	305	348	365	287	242
3	Tear S. (kg/cm)	63	64	72	79	85
4	Hardness	70	75	80	81	82
5	Abrasion	142.9	146.54	154.14	163.04	174.31
6	Rebound resilience (%)	39.8	39.4	34.5	35.9	39.5
7	Compression	20	22	22	27	29

increase with the enhancement of the filler content in rubber matrix. This indicates that the incorporation of carbon black reduces the mobility of macromolecular chains of the rubber and consequently increases the rubber stiffness. From the results it is clear that rebound resilience increases with increasing filler loading while abrasion resistance decreases gradually by increasing the carbon black loading.

#### Effect of Plasticizer

To check the effect of plasticizer on SBR/CR blends, it is necessary to study the physico-mechanical properties of rubber blends. The results are reported in Table-3. It is obvious from these results that the tensile strength, tear strength and hardness increase with the increase of plasticizer concentration up to 9 phr. This property gradually decreases as the concentration of plasticizer is increased up to 12 phr while elongation at break increases.

Table-3: Effect of Plasticizer on Physico-Mechanical Properties of SBR/CR Rubber Blends Vulcanizates at Optimum Cure Time.

Sr. No.	Test Performed	SBR/CR 30/70			
		Plasticizer 7.5 phr	Plasticizer 9 phr	Plasticizer 10.5 phr	Plasticizer 12 phr
1	T.S (kg/cm <sup>2</sup> )	183	230	187	161.31
2	Elongation (%)	313	359	373.36	406.5
3	Tear S. (kg/cm)	53	76	55	54
4	Hardness Shore-A (pts)	75	82	80	70

Table-3 also shows the relationship between the tensile strength and aging time of carbon black. It was found that significant tensile strength and aging

properties were observed as the carbon black loading is increased. The results illustrate that the carbon black filled rubber blends can tolerate thermal oxidative aging more than that of rubber blends containing carbon black of larger particle size. Excellent retention values of modules and tensile strength were observed.

#### Effect of Thermal Oxidative Aging

SBR and CR blends vulcanizates containing carbon black with 50, 55, 60, 65 and 70 phr were subjected to thermal oxidative aging at 100°C for 70 hours. The changes of the physico-mechanical properties were monitored as a function of aging time and the percentage of retained value were calculated and plotted against aging time as illustrated in Table-4. Which shows the relationship between the tensile strength and aging time of carbon black. It was found that good tensile strength and aging properties were observed as the carbon black loading is increased. The results illustrate that the carbon black filled rubber blends can tolerate thermal oxidative aging more than rubber blends containing carbon black of larger particle size.

Table-4: Physico-Mechanical Properties of SBR/CR Blend Vulcanizates after Aging.

Sr. No.	Test Performed	SBR/CR 30/70				
		Carbon black 50 phr	Carbon black 55 phr	Carbon black 60 phr	Carbon black 65 phr	Carbon black 70 phr
1	T.S kg/cm <sup>2</sup>	133	169	208	149	89
2	Elongation %	321	326	355	197	180
3	Hardness Shore-A (pts)	72	76	81	82	82

Excellent retention values of modules and tensile strength were observed. The presence of an appreciable quantity of the investigated fillers carbon black can protect SBR/CR rubber blends aging thermal oxidative agent at 100 °C for more than 4 days. Therefore, the retained physical properties of vulcanizates are good and responsible for the quality of rubber products for commercial uses.

#### Experimental

##### Rubbers

The chloroprene rubber (Bayprene) 320 Moony viscosity ML (1+4) 100 at 100 °C.

SBR 1502 with Specific gravity 0.94 and Moony Viscosity 52 at 100 °C.

The full recipes of the rubber blends are shown in Table-5.

Table-5: Formulation of Rubber.

Sr. No.	Material	Phr ( part per hundred rubber)
1	SBR	30
2	CR	70
3	Stearic acid	2.5
4	Zinc oxide	4.5
5	Antioxidant	1
6	Ranacit	1
7	Antioxidant sp	0.5
8	MBTS	0.75
9	TMTD	0.5
10	Aromatic oil	9
11	Dicumylperoxide	0.75
12	Carbon Black	60

#### Filler

Carbon Black N330 was purchased from Awami Chemical Ltd Karachi (Iran origin). Other ingredients such as zinc oxide, stearic acid, tetramethylthiuram disulfide (TMTD) and aromatic oil were made available from Bayer Ltd and sulphur from (BDH) were used.

#### Techniques

Preparation of Rubber Blends and Determination of Cure Characteristic Mixing were carried out on conventional laboratory two roll mill size (160 x 320 mm) according to ASTM designation D3184-80. Nip gap, roll mill speed time of mixing and sequence of addition of the ingredient were kept the same for all the rubber blends. The total mixing time was kept to a minimum to avoid sticking of the rubber compound to the mill rolls. The cure time at 160 °C, indicated by respective  $t_{c90}$ , was then assessed by using Rheocheck Profile -MD Model MDR 2000 (Moving die Rheometer). Gibitre Italy. Vulcanizates were conditioned for 24 hrs before testing. All properties were measured along the grain direction.

#### Vulcanization

Vulcanization was carried out in heated platen Laboratory press under pressure of about 100 bars and temperature 160 °C for 20 min.

#### Measurement of Mechanical Properties

Physico-mechanical properties (tensile strength, tear strength, modulus) were measured on (Instron) Universal Testing Machine Model 4301 according to ASTM D412-98 (a). All samples were tested in the mill direction for the measurement of mechanical properties. Dumbbell and crescent test pieces, according to ASTM D624, were then cut out. The test for hardness was carried out by using the shore type A Durometer according to ASTM 2240. All tests were conducted at room temperature (25 °C). Abrasion resistance, rebound resilience properties were measured using Abrasion Tester Model 2002016, Rebound Check Model REB2002040.

#### Conclusion

From the above data it is concluded that the carbon black has good effect on the rheometric characteristics. The incorporation of carbon black in rubber blends decreases the scorch time while cure time was found to increase and improves the mechanical properties. An appreciable quantity of the investigated fillers can help the rubber vulcanizates to tolerate the thermal oxidative agent at 100 °C for 4 days. The stiffness of rubber increases as the carbon black loading is increased. In this investigation the use of 9 phr and 60 phr of plasticizer carbon black for SBR/ CR Blends were found most suitable.

#### References

- 1 P. J. Corrish and M. J. Palmer, Advance in Polymer Blends Inst. Rubber Ind. Conference, Laughborough, England (1969).
- 2 D. Bulgin, D. L. Walker (to Dunlop ltd) Br. *J. App. Phys.*, 1, 061, 017 (1965).
- 3 J. A. Ayla, W. M. Hess, F. O. Kistler and G. A. Joyce, *Rubber Chem. Technol.*, 64, 19 (1992)
- 4 F. M. Helaly, A. A. Ahmad and M. A. Abd-EL-Ghaffar, 4th Arab *International Conference on Polymer Science and Technology*, Parts Sept 8-11 p79 (1997).
- 5 M. J. Folkaes and P. S. Hope, *Polymer and Alloys*, Chamman & Hall p.176 (1993).
- 6 G. R. Cotton, B. B. Boonstra, D. Rivin and F. R. Williama, U. *Kauchi, K. Gummi*, 22, 477 (1969).
- 7 D. H. Solemon and D. G. Hawthorne, *Chemistry of pigments and filler*, John Wiley and Sons, New

- York. pp 51 (1983).
- 8 Kirk-Othmer. *Encyclopedia of Chemical Technology*, Carbon Black, Wiley, New York., 4<sup>th</sup> (Eds).Vol.,pp1061(1991)
  - 9 C. R. Herd, Mc Doonaled, G. C. and Hess, W. M, *Rubber Chem. Technology*, **65**, 107 (1992).
  - 10 E. T. McDoneled, K. C. Baranwal and J. C. Andries, In C. D. R. Paul and S. Newman, (Eds), *Polymer Blends*, 2, Chap.19, Acedemic Press, New York (1978).
  - 11 P. Maronteaux, C. Faure, C. Fessared and P. Rigualt, J. B. Lippincolt Company, Philadephia, Torontos Copyright (C). Thanatophoric Dysplasia: A Case study-Griffis **10**, 24 (1979).
  - 12 M. Nakamura, Y. Takagishi and K. Noguchi, *Rubber World*, **218**, 30 (1998).
  - 13 F. F. Hanna., A. A. Yehia and A. Abou Bakr, *Ind. J. Phy.*, **44**, 514 (1970).
  - 14 G. B. Nando and S. K. De., *J. Appl. Polym. Scien.*, **25**, 1249 (1980).
  - 15 T. B. Bhattacharyya, A. K. Biswas, J. Chatterjee and D. Pramanick. *Plast. Rubb. Process. Appl.*, **6**, 119 (1986).
  - 16 L. Bateman, *the Chemistry and Physics of Rubber like Substances*, *Applied Science*, London, p 449 (1963).