NITRILE RUBBER COMPOUNDS WITH IMPROVED FLEX-CRACK RESISTANCE

K.S. Mohanadas and Siby Varghese

Rubber Research Institute of India Kottayam – 686009, Kerala,India

Received: 16 September 2014 Accepted: 03 October 2014

Mohanadas, K.S. and Varghese, S. (2014). Nitrile Rubber compounds with improved flex-crack resistance *Rubber Science*, **27**(2): 263-267.

Incorporation of reinforcing fillers is essential for enhancing of technologically important physical properties of elastomers. Various types of carbon black are highly efficient in reinforcing elastomers. Within the family of black fillers, reinforcing efficiency varies widely and this depends mainly on the particle size of the filler. For certain applications, along with reinforcement, resistance to flex-crack also has importance. In this study, conventionally used blacks namely HAF, FEF and GPF were compared for their flex-crack resistance in nitrile rubber vulcanizates. Nitrile rubber was selected since the study was aimed at developing a flex-crack resistant vulcanizate which can perform in hydrocarbon oil medium. By increasing the dosage of carbon black from 40 to 60 phr, flex-crack resistance improved up to 50 phr loading for the three fillers and this decreased thereafter. Among the fillers used, the one with the largest particle size produced the highest flex-crack resistance.

Keywords: Acrylonitrile rubber, Fatigue, Flex-crack resistance, Particle size, Reinforcement

Rubber vulcanizates are well noted for their flexibility in static and dynamic applications. In this respect, resistance to flex-cracking is of significance. The resistance to fatigue failure of polymers is dependent on many factors such as elastomer, type of filler and its particle size and loading, presence of antidegradants, type of cure system and the state of cure of the matrix (Mars, 2004). Flex-crack resistance of polymers has been studied by many investigators (Beaty,1964; Lake,1972). It is largely dependent on the easiness with which the molecular chains in the rubber matrix are flexed. This study aims to develop a flex-crack resistant vulcanizate which can perform in hydrocarbon oil medium. Among the oil resistant elastomers, acrylonitrile butadiene rubber (NBR) is commonly used for oil contact applications. For the improvement of physical properties of elastomers, incorporation of reinforcing filler is essential. The addition of carbon black to rubber compounds can result a pronounced reinforcing effect depending on both the filler type and its volume fraction (Medalia, 1987). The major factor controlling the reinforcement of rubbers by fillers is the size of the filler particles. The type of filler used and its dosage are decided by the end-use specifications. Improvements in various technological properties with filler are a function of the particle size, surface area, structure and the extent of compatibility of the filler to the polymer (Kraus, 1978).

Since the objective of this work is to examined the effect of black fillers on flex-crack resistance of nitrile rubber vulcanizate

Correspondence: K.S. Mohanadas (Email: mohan@rubberboard.org.in)

Table 1. **Formulation of mixes**

	Mixes								
Ingredient	H40	H50	H60	F40	F50	F60	G40	G50	G60
NBR	100	100	100	100	100	100	100	100	100
HAF	40	50	60	-	-	-	-	-	-
FEF	-	-	-	40	50	60	-	-	-
GPF	-	-	-	-	-	-	40	50	60

Other ingredients:-ZnO 5, DOP-Variable, Stearic acid 2, TDQ 1.5, 4020 1.5, MBTS 1, TMTD 0.1 , Sulphur 1.5

for oil contact applications, other properties of relevance to dynamic applications, *viz.* heat build-up, etc as well as the effect of immersion in a hydrocarbon oil were also studied.

Acrylonitrile butadiene rubber used for the study was KNB 35L manufactured by M/s. Kumho Petrochemicals, South Korea. Carbon black was supplied by M/s Adithya Birla Group, India. Other chemicals used were rubber grade.

Mixes were prepared as per the formulations given in Table 1. The dosage of black fillers, *viz.* HAF, FEF and GPF were used at three levels, 40, 50 and 60 phr. Preparation of the mixes were carried out on a two-roll laboratory mixing mill as per ASTM D 3182 .

Cure characterization was performed on a Monsanto rheometer (MDR 2000) as per ASTM D5289. Samples were compression moulded at 150 °C in an electrically heated press to their respective optimum cure times. The stress-strain properties were determined using a universal testing machine (model Zwick Z 500) with dumbbell shaped samples as per ASTM D 412. Heat buildup was determined as per ASTM D 623. Flex-crack resistance was measured using a DeMattia Flexometer as per ASTM D 813. Effect of fuel immersion was found out as per ASTM D 471 and hardness measurements were done using Durometer (ASTM D 2240).

NBR vulcanizates with the three carbon blacks were prepared at three different loadings each *viz.* 40,50, and 60. The dosage of process aid has been increased in proportion to the filler loading. Mixes were designated as H, F and G for HAF, FEF and GPF respectively. The numerical value associated with the letter indicates the filler loading. The cure characteristics of the mixes are given in Table 2.

The optimum cure time of the mixes was determined at 150 °C. It was observed that the cure time of mix with HAF is comparable with FEF. Between FEF and GPF there is a slight variation in cure time as the former recorded the lowest values at all

Table 2. **Cure characteristics of mixes**

Parameters	H40	H50	H60	F40	F50	F60	G40	G50	G60
Cure characteristics on MDR @ 150 °C									
MH-ML, dNm	9.9	10.4	11.3	10.0	10.1	9.8	6	8.5	9.82
ts_2, m:s	2:11	2:11	2:06	2:01	2:14	1:48	3:11	3:23	3:11
t_{90}, m:s	5:24	5:39	5:52	5:25	4:54	4:14	6:11	6:42	6:08

Table. 3. **Physical properties**

Parameters	H40	H50	H60	F40	F50	F60	G40	G50	G60
Tensile strength (MPa)	21.6	22.9	19.0	20.2	21.7	18.7	17.7	18.2	17.5
Tear strength (N/mm)	51.1	54.4	55.1	48.0	49.9	51.7	44.7	46.6	52
Hardness (Shore A)	52	56	60	49	52	54	48	50	52
Heat build-up (ΔT °C)	43	48	60	37	44	46	28	30	32
Effect of oil, decrease in volume (%) (20W40 oil @ 24h/RT)	0.6	1.1	1.3	0.8	1.29	1.5	1	1.4	1.7
Demattia flexing									
Crack initiation, k.cycles	63.9	80	66.3	62.1	72.1	51.1	141	202	163
Change in physical properties after ageing at 70 °C for 72 h									
Tensile strength (%)	+29	+14	+25	+11	+7	+11	+14	+9	+8
Hardness, units	+6	+4	+2	+6	+4	+1	+7	+6	+6

loadings compared to GPF. This is quite expected since heat generated during the preparation of GPF mixes is low, resulting in lower heat history and hence improved safety and a slightly higher cure time. The state of cure as indicated by MH-ML is comparable for mixes containing HAF and FEF. The GPF filled vulcanizates showed progressive improvement in torque as the loading increased from 40 to 60 phr. The mix containing 60 phr of GPF filler has the torque comparable with mixes having HAF and FEF black. It is evident from the ts_2 values, that the scorch safety of HAF and FEF filled mixes were slightly lower than those of the GPF compounds.

The physical properties of the mixes are tabulated in Table.3. As nitrile rubber is non-crystallisable, it requires reinforcing fillers to enhance the stress - strain properties. In the present study also the tensile strength was found to increase with the loading of fillers. The improvement on stress-strain properties were in correlation with the reinforcing properties of the fillers in consideration. The tensile strength increased in the order GPF < FEF < HAF. Tensile strength was found to increase up to 50 phr loading of carbon black and then decreased with further loading. The same trend has been shown by the three fillers used for the study. Properties like tear strength, hardness and heat build-up were found to depend on the reinforcing power of the filler. HAF having the smallest particle size among the three, recorded the highest value for these properties. FEF recorded medium values followed by GPF.

The heat build-up of the vulcanizates was found to increase with filler loading (Fig.1). The filler having the lowest particle size (HAF) showed the highest heat generation and is linear with filler loading.

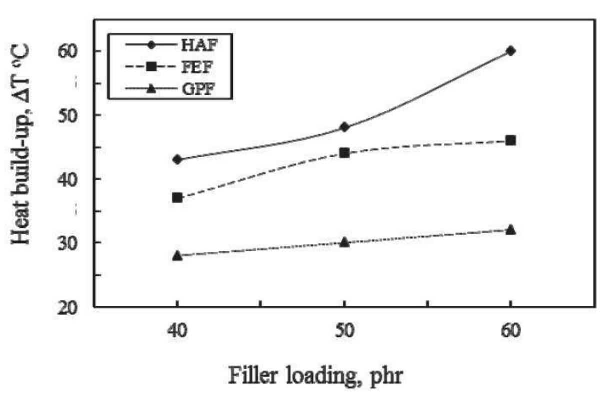

Fig. 1. Heat build-up of vulcanizates

Since particle size is directly related to the reciprocal of surface area of filler, the effect of small particles actually reflects their large interface between polymer and the filler (Boonstra, (1975). The heat build-up was found to decrease in the order, HAF>FEF>GPF, at different loadings of carbon black and the same order is followed in the surface area of the respective fillers.

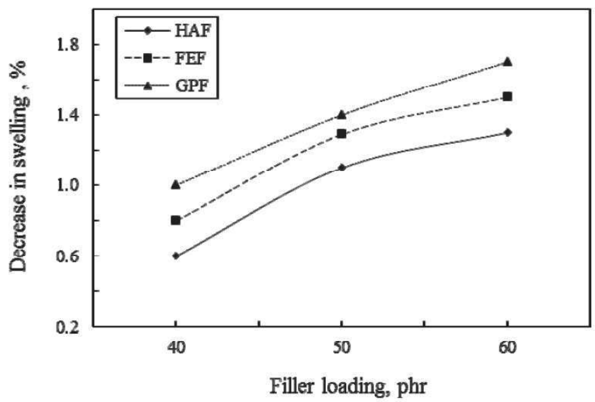

Fig. 2. Effect of oil on vulcanizates

The change in volume of vulcanizates in 20W40 oil filled with different loadings of black is shown in Fig. 2. Progressive decrease in swelling was observed with all the fillers. The lowest change has been observed for HAF filled vulcanizate at all levels of loading. Maximum change was shown by GPF filled vulcanizates whereas FEF recorded values in between HAF and GPF. The surface area of the blacks in consideration is in the order GPF<FEF<HAF. As a result the rubber to polymer interaction decrease from HAF to GPF. When the polymer to filler interaction is weak, lubricant molecules penetrates easilythrough the rubber matrix (Boontrsa *et al.*, (1965).

Flex-crack resistance of the vulcanizates was found to increase with filler loading up to 50 phr, and thereafter it showed a decrease. Interestingly, the filler with the minimum reinforcement (GPF) recorded the highest flex-crack resistance and vulcanizates with HAF black recorded the least. The resistance to flex-cracking is in the order HAF<FEF<GPF. As the particle size of the filler increased, the resistance to flex-cracking also increased progressively (Fig.3). Under constant strain conditions, compounds containing coarse black will have a significantly higher fatigue life than those with fine black (Dizon *et. al*, 1974).

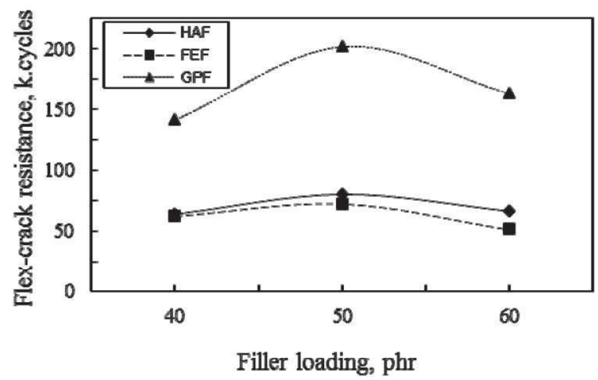

Fig.3. Effect of carbon black loading on the flex-crack resistance

Since the failure properties of nitrile rubber is dependent on the amount of reinforcing fillers present, the tear strength of the vulcanizates was found to increase with loading of filler. HAF being the highest reinforcing filler among the selected fillers, showed the maximum tear strength values at 60 phr loading. The other two fillers recorded tear strength values as per their particle size.

The tensile strength and hardness were found to increase on heat ageing. This is quite natural with rubber mixes having marching cure. The drop in EB with ageing is attributed to the increase in crosslinking on heat ageing.

By the incorporation of carbon black to nitrile rubber, the flex-crack resistance was found to increase up to a loading of 50phr above which it has been decreasing. All the three type of fillers used for this study showed the same trend, but the filler with larger particle size showed better flex-crack resistance than those with smaller particle size. This was in line with the observations made by earlier investigators in styrene butadiene rubber (Dizon *et al*.,1974). The cure time of HAF and FEF filled vulcanizates are almost comparable whereas GPF recorded comparatively lower value. Physical properties like tensile strength, tear strength and hardness are maximum for HAF black, whereas the swelling and flex crack resistance registered the minimum.

REFERENCES

Beaty, J.R.(1964), Fatigue of rubber. *Rubber Chemistry and Technology,* **37**(5):1341-1364.

Boonstra. B.B (1975). Reinforcement by fillers. In: *Rubber Technology and Manufacture.* (Ed. Blow C.M), Newnes Butterworths, London, 7, p 230.

Boonstra, B.B. Taylor G.L. (1965). Swelling of filled rubber vulcanizates. *Rubber Chemistry and Technology,* **38**(4):943 -960.

Dizon, E.S, Hicks, A.E. and Chirico,V.E. (1974). The effect of carbon black parameters on the fatigue life of filled rubber composites. *Rubber Chemistry and Technology,***47**(1):231-249.

Kraus, G. (1978). Reinforcement of elastomers by carbon black.*Rubber Chemistry and Technology,* **51**(2):297-321.

Lake, G.J.(1972). Mechanical fatigue of rubber. *Rubber Chemistry and Technology,* **45**(1):309-328.

Mars, W.A. (2004). Fatigue life of rubber. A literature survey. *Rubber Chemistry and Technology,* **77**(3):391-412.

Medalia, A.I. (1978) Effect of Carbon black on ultimate properties of rubber vulcanizatis. *Rubber Chemistry and Technology,* **60**(1):45-61.