Natural rubber Permeability Filler Mica Clay Silica Graphite HAF-carbon black

Studies on the Effect of Fillers on Air Permeability of Natural Rubber Vulcanizates

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Compounds of natural rubber containing different fillers were evaluated for their air permeability. The results indicated that incorporation of filler generally reduce the permeability, but certain fillers such as mica, graphite and clay produced substantial reduction which was attributed to the particular morphology of these fillers as evidenced from photomicrographs. Physical properties were mostly lowered, with exception of carbon black.

Untersuchung des Füllstoffeinflusses auf die Luftdurchlässigkeit von NR-Vulkanisaten

Naturkautschuk Permeabilität Füllstoff Glimmer Kreide Silica Graphit HAF-Ruß

Mischungen von NR mit verschiedenen Füllern wurden auf ihre Luftpermeation hin geprüft. Die Ergebnisse deuten an, daß der Einbau von Füllern allgemein die Permeabilität reduziert, aber bestimmte Füllstoffe wie Glimmer, Graphit und Kreide erzeugten eine beträchtliche Abnahme, die auf die besondere Morphologie dieser Füllstoffe hindeutete, wie aus den Mikroaufnahmen hervorging. Die physikalischen Eigenschaften wurden mit Ausnahme bei Ruß verschlechtert.

In a wide variety of rubber products the gas retaining capacity of elastomers is made into use. Automobile tyre inner tubes, bladders, play balls and balloons are a few among them, but one drawback of elastomers is that the pressurised gas slowly escapes through the membrane to the atmosphere due to permeation. Permeation occurs whenever a pressure gradient exists across the membrane and it is governed by the solubility and diffusivity of gas in the elastomer under consideration.

Permeability measurements of various elastomers to hydrogen has been carried out by *Van Amerongen* [1]. The results showed that synthetic rubbers such as nitrile, polychloroprene and butyl rubber are having permeability values from one third to one eighth of natural rubber(NR). Because of the superior performance of these synthetic rubbers to impermeability, most of the earlier research work carried out were exclusively on synthetic rubbers. Earlier investigations showed that permeability of polymers to gases increased as the size of penetrant molecule reduced [2–4]. Presence of polar and bulky groups in the molecular chain hinders permeation of gas molecules[1]. Very low gas permeability of methyl and butyl rubber is in agreement with this. High internal mobility of unsaturated molecular chain is the reason for high permeability of NR and polybutadiene[5].

Low gas permeability for rubber products can be achieved by two ways. One method is to use special purpose synthetic rubbers like butyl and nitrile rubber or chemically modified NR. Epoxidised natural rubber(ENR) is a good example for chemically modified NR having very low permeability [6]. Butyl rubber and ENR are very expensive compared to NR. A more cost-effective method to reduce permeability would be the use of selected fillers in rubber compounding. Very little work has so far appeared in the literature regarding the effect of fillers on air permeability of NR. Van Amerongen [7] has evaluated the effect of carbon black at 50 phr and mineral filler at 20 vol-% on gas permeability of NR. The results showed that incorporation of filler reduced permeability of the base-polymer. The objective of the present work is to identify the filler and its dosage in NR compounds which will reduce the permeability to a considerable level. The effect of such fillers on other technologically important properties are also studied. Such compounds can find application in cycle tubes, bladders, diaphragms, air pillows, play balls etc. which are not so critical as automobile tyre inner tubes.

1 Experimental

NR used for this study was ISNR 5, the raw rubber properties of which are given in *Tab. 1*. Fillers evaluated were mica powder (200 mesh), HAF black(N330), precipitated silica, precipitated calcium carbonate, china clay and graphite powder. These were fine particle size commercially available rubber grade materials. All other ingredients were of commercial grade.

Tab. 1. Properties of ISNR 5

Dirt content,	%	0.02
Volatile matter,	%	0.52
Ash content,	%	0.15
Nitrogen content,	%	0.40
Wallace plasticity,	%	43.00
PRI		72.00

1.1 Preparation of compounds and test specimen

Compound formulations are given in *Tab. 2* and were prepared using a laboratory model two-roll mixing mill (15 cm × 30 cm) conforming to ASTM D 3182. Each compound was blended to homogenise the additive and give adequate dispersion of the ingredients. After complete mixing, the stock was sheeted out at a nip gap of 3 mm. Test samples were moulded by heating to their respective cure times as obtained from Monsanto Rheometer, in a 45 cm × 45 cm hydraulic press having electrically heated platens at 150 °C.

1.2 Testing of vulcanizates

In the present work permeability measurements were carried out using the air permeability tester, CEAST Dow Cell CODE 6210/000, according to ASTM D 1434-75. Moulded test specimens of diameter 8.6 cm and thickness 0.25 mm were used for measurements. The sample was mounted in a gas transmission cell to form a sealed semi-barrier between two chambers. One chamber contained air at 1.013×10^5 Pa pressure and the other at a very low pressure (good vacuum) of nearly 26 Pa, which receives the permeating gas. Transmission of gas through the test specimen is indicated by an increase in pressure at the low pressure side.

All other vulcanizate properties were determined by the relevant ASTM procedures. In order to assess the ageing resistance of vulcanizates, tensile specimens were kept in an air oven maintained at 70 °C for 7 days. After that period, samples were conditioned for 24 h at a relative humidity of 50 % and tested for tensile properties.

2 Results and discussion

Fillers containing active groups like hydroxyl groups were reported to adsorb accelerators, causing an increase in the time required for the compound to attain a particular level of vulcanization than that required for gum compounds [8]. Optimum cure time at 150 °C obtained for silica filled compounds is in agreement with this (*Fig. 1*). An increase in cure time was obtained with higher loading of this filler. Fillers such as graphite, mica and calcium carbonate also showed slight increases in cure time as their loading was increased. HAF and clay showed least variations in cure time with loading.

Air permeability plots of the vulcanizates are given in *Fig. 2*. It depicts the rate of volume flow of air under steady state conditions refered to standard temperature and pressure, between unit pressure difference and controlled temperature. HAF black was found to reduce permeability by 31 to 43 % as the filler loading was increased from 10 to 40 vol-%. Non-black fillers like precipitated calcium carbonate and silica were also found to reduce the permeability. Reduction of about 47 % on permeability of the gum vulcanizate was obtained for a loading of 30 vol-% of silica. Permeability values obtained with different loadings of calcium carbonate point to the fact that there is no characteristic difference between reinforcing and non-reinforcing fillers as far as permeability is concerned. For HAF black and silica it was found that as the loading was changed from

Fig. 1. Cure time as a function of filler loading for NR compounds filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

30 to 40 vol-%, permeability values reached a steady level and even increased slightly in the case of silica [9]. This was not observed with calcium carbonate. The non-reinforcing character of calcium carbonate causes to retain properties like elongation at break, resilience and flexibility of the polymer chain even at higher loadings so that rupture of the matrix may not start with the same volume of filler in the case of HAF black and silica filled vulcanizates [9].

Tab. 2. Formulation of the mixes (plec, except fillers)

Natural rubber ISNR 5	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Phenyl-β-naphthyl amine	1	1	1	1	1
Filler B, C, D, E, F, G (Volume %)	0	10	20	30	40
Naphthenic oil	–	2	4	6	8
Diethylene glycol[2]	–	0.5	1	1.5	2
CBS	0.6	0.6	0.6	0.6	0.6
Sulfur	2.5	2.5	2.5	2.5	2.5

B – Mica powder (200 mesh)
C – HAF black (N330, 26 - 30 nm)
D – Precipitated calcium carbonate
E – Precipitated silica
F – China clay
G – Graphite powder
1 – Used only for compounds E and F

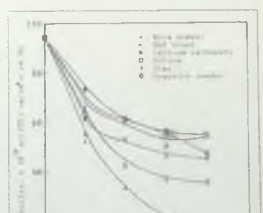

Fig. 2. Air permeability as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

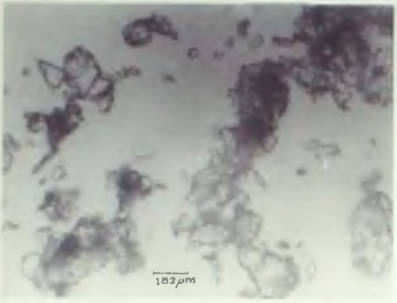

Fig. 3. Photomicrograph of mica powder

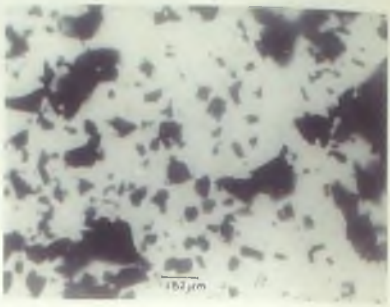

Fig. 4. Photomicrograph of graphite powder

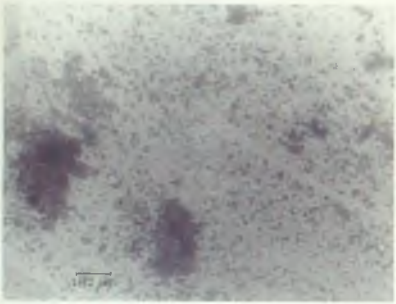

Fig. 5. Photomicrograph of china clay

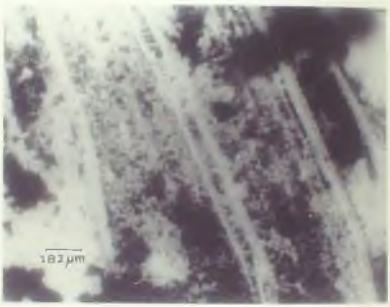

Fig. 6. Photomicrograph of HAF black

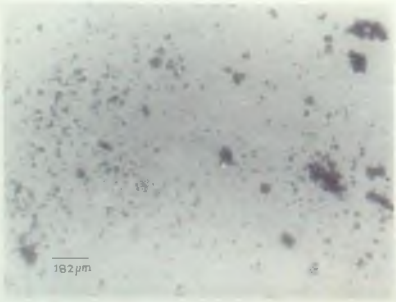

Fig. 7. Photomicrograph of precipitated calcium carbonate

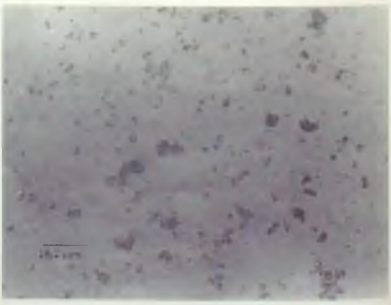

Fig. 8. Photomicrograph of precipitated silica

Fillers like mica, graphite and china clay were found to produce vulcanizates of lower air permeability. Among these mica showed a severe reduction of about 80 % in permeability with a volume loading of 30 %. Reduction in permeability by 61 and 52 % with graphite and china clay, respectively, clearly shows that these fillers can be considered as a separate class. These fillers also showed a levelling off effect beyond 30 vol-% loading.

Fig. 3 to 8 are the photomicrographs of the uncompounded fillers that were used for this study. Mica (Fig. 3) and graphite (Fig. 4) powder have a laminar structure not clearly detectable in the pictures. Clay particles are seen to be in a more associated state even though the clustures formed are not larger in size. This particular morphology may be responsible for the relatively higher reduction in permeability with these fillers. Mica (Fig. 3) and graphite particles (Fig. 4) are comparatively larger in size compared with clay particles (Fig. 8). Even though the clusters of particles may be broken during compounding the shape of the particles may be retained in the vulcanizate. Mica particles are found to have less sharp corners compared with graphite particles. Bonding between the sharp edges and matrix may not be as efficient as with round corners. This may be another reason for the marked difference between the permeability of mica and graphite filled vulcanizates. During moulding ,laminar fillers tend to orient uniformally in response to shear flow stresses in a manner which enhances the planar reinforcement [10]. This necessitates the air to travel a longer path to pass around the filler particles than in the case of normal isotropic filler particles.

In this study it was observed that generally all fillers lead to lower properties except carbon black. Failure properties like tensile strength, tear strength and resistance to abrasion loss were improved by incorporation of HAF black which is characteristic of a reinforcing filler. Tensile strength (*Fig. 9*) and tear strength (*Fig 10*) increase initially and pass through a maximum and then decrease with further increase in loading. The range of filler loadings at which maximum strength is attained depends on the type of filler. In general, the reinforcing fillers require only less quantity of filler (20–25 vol-%) compared with the non-reinforcing ones. The decrease in properties at high loadings is a simple dilution effect, general to all fillers, nearly due to a diminishing volume fraction of polymer in the compound [11]. Optimum strength was observed at 30 vol-% of HAF black. The silica filler used was of the ordinary type and the cure system did not contain a secondary accelerator which is normally included in silica filled mixes for optimisation of technological properties[12, 13]. Hence the properties of silica filled vulcanizates do not represent the characteristic values obtainable for reinforcing fillers. The decrease in properties with loading of calcium carbonate, clay, mica and graphite was gradual. The decrease in tensile strength observed is maximum for graphite filled vulcanizates.

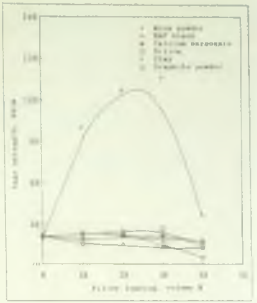

Fig. 10. Tear strength as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

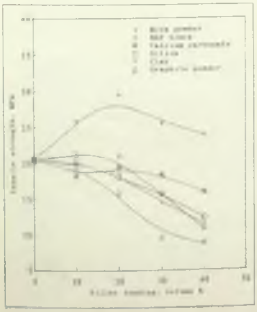

Fig. 9. Tensile strength as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

Tab. 3. Physical properties of vulcanizates

Mixes	Hardness, Shore A	Heat build-up, ΔT °C	Compression set, %	E.B, %	Resilience, %
A	35	6	39.1	1153	79.1
B10	45	9	43.0	829	78.4
B20	52	16	50.8	650	74.6
B30	57	23	60.9	560	73.1
B40	63	35	63.4	461	70.9
C10	40	10	51.2	854	71.7
C20	50	21	52.6	825	58.4
C30	60	34	52.9	638	50.0
C40	70	49	55.6	449	42.2
D10	36	8	46.7	1053	73.9
D20	43	9	47.4	978	70.9
D30	49	14	48.5	951	70.2
D40	52	18	52.6	860	66.6
E10	40	10	39.6	952	66.6
E20	42	20	49.5	845	63.8
E30	48	29	52.8	721	55.1
E40	54	59	59.9	609	41.1
F10	39	8	48.4	924	73.9
F20	43	14	53.9	831	68.9
F30	47	24	55.0	750	63.1
F40	48	40	61.2	604	53.2
G10	40	9	42.5	1132	76.8
G20	46	17	59.7	875	73.9
G30	52	23	61.6	777	71.7
G40	55	27	73.4	646	68.0

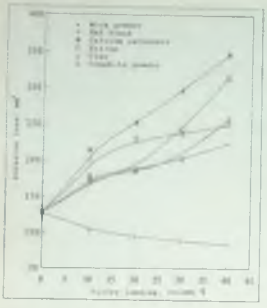

Fig. 11. DIN abrasion loss as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

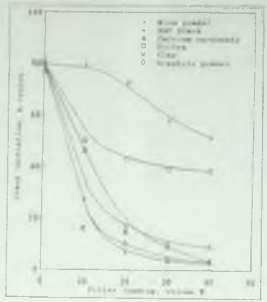

Fig. 12. De Mattia flex crack initiation as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

The very high drop in tensile properties with increased quantity of mica and graphite is due to the large particle size of these fillers.

With the exception of HAF black filled vulcanizates the tear strength progressively decreased with filler content for all the fillers studied. HAF black in turn improved tear strength up to 30 vol-% loading. As elastic properties of the vulcanizates are dependent on the free movement of rubber molecules, fillers are supposed to reduce elastic properties. The progressive increase in the properties such as hardness, heat build up, compression set and decrease in elongation at break, and rebound resilience with higher loading of filler supports this (*Tab. 3*). With the exception of HAF black all other fillers showed an increase in abrasion loss with filler loading (*Fig. 11*). The poorest abrasion resistance noticed was for calcium carbonate.

Fatigue resistance as evidenced from De Mattia flex crack initiation were found to decrease with increased filler loading for all vulcanizates (*Fig. 12*). Maximum flex cracking resistance observed was for HAF black. Flex crack resistance of mica, graphite and clay were considerably lower than others. This large variation is due to the large size and laminar nature of these fillers, by virtue of which these fillers cannot maintain the same level of bonding to the matrix at high degrees of deformation.

Retention of tensile properties after ageing for 7 days at 70 C was found to be gradually decreasing for all the fillers with higher loadings (*Fig. 13*). For HAF black the drop was somewhat higher than expected. The reason may be due to the tendency of carbon black to promote the oxidation of sulfur cured vulcanizates as reported by earlier investigators [14].

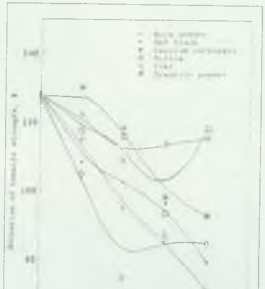

Fig. 13. Retention of tensile strength as a function of filler loading for NR vulcanizates filled with mica powder, HAF black, calcium carbonate, silica, clay and graphite powder

3 Conclusions

All fillers used in this study, viz. HAF carbon black, silica, calcium carbonate, china clay, mica powder and graphite powder were found to reduce the air permeability of NR. No remarkable difference is observed between reinforcing and non-reinforcing fillers as far as permeability is concerned.

The substantial decrease in permeability imparted by fillers like mica, graphite and clay may be attributed to their particular morphology

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