

GLASS FLAKE PARTICLES FOR ENHANCED PERMEATION RESISTANCE OF ELASTOMER COMPOUNDS

Dr Christopher A Stevens
David W Mason

NGF EUROPE Limited, Lea Green Road, St Helens, WA9 4PR, UK
Tel: +44 (0)1744 853065 Fax: +44 (0)1744 816417
Email: chris.stevens@ngfeurope.com david.mason@ngfeurope.com

BIOGRAPHICAL NOTE

Chris Stevens (47) has worked in many areas of the rubber industry: seals for nuclear power plant, rubber and plastic developments with carbon black, rubber curemeter and viscoelastic test machine design, with additional expertise in stress analysis, fracture mechanics and ageing properties of elastomers. He has been Technical Manager for NGF EUROPE Limited since 1999, directing pioneering improvements in rubber and glass cord technology.

ABSTRACT

Many high performance elastomer compounds are used in sealing and barrier applications that require low permeation. Two examples are nitrile rubber for fuel containment and chloroprene rubber for plant lining application. New experiments have examined the properties of such rubber compounds incorporating glass flake. These particles are disc shaped, with a very high plate area and a very thin thickness. Two thicknesses of flakes have been studied: 2 μ and 5 μ . The experiments progressively replaced carbon black with glass flake. Very significant reductions in permeation were observed for relatively low loadings of glass flake. The mechanism that provides this increase in permeation resistance will be discussed. The changes in physical properties of the compound that accompany the incorporation of glass flake have also been studied, and provide the full picture for the reinforcement of these rubber compounds. The novel use of this filler can offer significant performance gains and significant cost reductions by utilising thinner barrier layers and/or by extending barrier service life.

INTRODUCTION

PERMEATION

Elastomer compounds are often used for their barrier properties. In such applications the requirements are often for the elastomers to be flexible, impermeable and abrasion resistant. This paper discusses the use of novel filler materials to improve the permeation resistance of elastomers while maintaining or improving the other desirable properties.

The permeation of a fluid through an elastomer membrane is given by the integrated form of Fick's law¹:

$$q = P (p_1 - p_2) At/L \quad (1)$$

where q is the mass of fluid permeating through a membrane of thickness L and area A in time t . The driving force for the transport is the pressure difference between the fluid side (vapour pressure p_1) and the dry side of the membrane (vapour pressure p_2). The interaction of the fluid and the membrane determines the permeability coefficient, P . Often a simpler form for permeation is used by rearranging equation (1) by defining the permeation rate Q :

$$Q = qL/(At) = P(p_1 - p_2) \quad (2)$$

The permeability coefficient is determined by two material properties; the solubility coefficient, S and the diffusion coefficient, D :

$$P = D S \quad (3)$$

The (unsimplified) units of P are kg.m/m².s.N.m⁻², D : m²/s, S : kg/(m³Mm⁻²). The permeation of fluid therefore depends upon the solubility of the fluid in the rubber, and the ease with which it can pass through the elastomer.

GLASS FLAKE

Glass flake as a permeation resistance enhancer of the bulk material is novel. Previously such fillers have only been used for coatings and paints. With such systems there is always a long term durability question

about the interface between coating and bulk. The aim of this paper is to introduce glass flake into the bulk material, without altering the tried and trusted properties that make the elastomers the materials of choice.

Glass flakes are small platelets of glass with a high aspect ratio. These platelets are typically 5 μ or 2 μ thick, and 100 to 1000 μ across. These particles are created by inflating an extruded annular parison of molten glass until the desired thickness is obtained. The glass is solidified, then milled and sieved in order to obtain different area to thickness grades. These particles have high surface areas due to the high aspect ratio.

Different glass formulations can be used for different environments. For general purpose use, E glass is used. C glass is used when additional resistance is required against acids.

LOW PERMEATION APPLICATIONS

This paper presents the examination of permeation of water through chloroprene rubber, as might be used for a tank lining, and of fuel through acrylonitrile-butadiene (NBR) rubber as might be typical for a gasoline hose.

Laminating CR with EPDM has been presented as one route to increasing the permeation resistance of chloroprene to water. The permeation of water was demonstrated² to be higher for the polar elastomer (CR) than for non-polar EPDM. The permeation of water through a laminate was then explained in terms of the changes in partial pressure due to the solubility and diffusion of the first layer before each interface. The addition of glass flake into CR is seen as a simpler method, that will avoid the complication of multiple layers, and concerns about adhesion of interfaces.

NBR is the general purpose fuel resistant elastomer. Improvements in permeation resistance can be gained by using^{3,4} high acrylonitrile content NBR, carboxylated NBR, and blends with PVC.

This study used two model formulations to look at the impact of addition of glass flake upon water permeation through CR and fuel permeation through NBR.

TABLE I
CHEMICAL COMPOSITION RANGES OF GLASSES

| Component | E Glass | C Glass |
|---------------------------------------|---------|---------|
| SiO ₂ | 52-56% | 65-72% |
| Al ₂ O ₃ | 12-16% | 1-7% |
| CaO | 16-25% | 4-11% |
| MgO | 0-6% | 0-5% |
| B ₂ O ₃ | 5-13% | 0-8% |
| Na ₂ O or K ₂ O | 0-0.8% | 9-13 |
| ZnO | - | 0-6% |

EXPERIMENTAL

COMPOUNDS

The model CR compound was the same as used by Cassidy et al². The model NBR formulation was that presented by Morton⁵ as an automotive fuel hose compound. In both compounds, carbon black was increasingly replaced by glass flake. Two grades of glass flake manufactured by Nippon Sheet Glass, Glass Fiber Company of Japan* were used:

RCF-600N. The glass flakes are 5 μ thick with a mean diameter of 600 μ . The glass surface is treated with an acryl-silane adhesive.

RCF-2300N. The glass flakes are 2 μ thick with a mean diameter of 300 μ . The glass surface is treated with an acryl-silane adhesive.

* North America: contact NGF Canada (www.ngfcanada.com), Europe: contact NGF Europe (www.ngfeurope.com)

The ingredients were mixed in an internal mixer. The glass flake was added with the carbon black. The glass flake was completely dispersed through the mix. No ingredients fell out when each mix was dumped. The mixes were further refined by 6 passes on a two roll mill. The sheets were taken off with a very tight nip (about 0.5 mm). This high shear was effective in aligning the flakes within the plane of the sheet. 2 mm sheets were cured and moulded.

PERMEATION TESTING

Triplicate circular sheets were die stamped from the cured compounds. The cell method was used to assess permeation⁶. This method was similar to that used by Dunn et al⁴. About 50 cm³ of water was used in the cell for the water permeation with the CR sheets. The cells were stored at 60°C, and weighed daily at room temperature. The NBR sheets were tested at room temperature, with 50 cm³ of ASTM fuel B in the cells. The gradient of the weight loss from days 2 to 7 was used to evaluate the permeation of the fluids to each rubber. At the end of the fuel permeation testing, the NBR swelling was assessed by weight gain.

TABLE II
CR COMPOUND FORMULATIONS

| | Parts by weight, phr | | | |
|-------------------------|----------------------|-----|-----|-----|
| Chloroprene, Neoprene W | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 |
| Magnesium oxide | 4 | 4 | 4 | 4 |
| Accelerator ETU | 0.5 | 0.5 | 0.5 | 0.5 |
| Stearic acid | 0.5 | 0.5 | 0.5 | 0.5 |
| Antioxidant PPD | 2 | 2 | 2 | 2 |
| Carbon black, N550 | 50 | 45 | 40 | 35 |
| Glass flake RCF-600N | 0 | 5 | 10 | 15 |

TABLE III
NBR COMPOUND FORMULATIONS

| | Parts by weight, phr | | | | | |
|-----------------------|----------------------|-----|-----|-----|-----|-----|
| NBR, ACN 40% | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 1 | 1 | 1 | 1 | 1 | 1 |
| Antioxidant PPD | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Plasticiser | 5 | 5 | 5 | 5 | 5 | 5 |
| Sulphur | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator MBTS | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Carbon black, N762 | 90 | 85 | 80 | 70 | 80 | 70 |
| Glass flake RCF-2300N | 0 | 5 | 10 | 20 | 30 | |
| Glass flake RCF-600N | | | | | | 20 |

PHYSICAL PROPERTIES

Additional sheets of the compounds were used to obtain the tensile properties of dumbbells. Trouser tear specimens were used to obtain the tearing energy. The NBR compounds were tested with and without exposure to the fuel to evaluate any changes due to degradation by the fuel. The fuel ageing was the same duration as the permeation test: 7 days at room temperature.

RESULTS

PERMEATION

The permeation test results for water and CR are shown in Figure 1. There are several different ways in which the permeation can be expressed. For simplicity, the water vapour transmission rate data are reported. The alternative results are tabulated in Table IV. The fuel permeation results are shown in Figure 6 and Table V. Some of the data were not analysed at time of writing.

TABLE IV
WATER PERMEATION THROUGH CR COMPOUNDS

| | | | | | |
|--------------------------------|----------------------|----------------------|----------------------|----------------------|-----------------------------|
| Carbon black N550 | 50 | 45 | 40 | 35 | |
| Glass flake RCF-600N | 0 | 5 | 10 | 15 | |
| Permeability | $3.4 \cdot 10^{-11}$ | $5.1 \cdot 10^{-11}$ | $1.3 \cdot 10^{-11}$ | $4.2 \cdot 10^{-12}$ | g/(sec.m.Nm ⁻²) |
| Permeance | 0.007 | 0.011 | 0.003 | 0.001 | g/(m ² .hr.torr) |
| Water vapour transmission rate | 25.4 | 38.0 | 9.9 | 3.2 | g/(m ² .day) |
| Resistance | $6.7 \cdot 10^7$ | $5.5 \cdot 10^7$ | $5.8 \cdot 10^8$ | $8.3 \cdot 10^8$ | N.sec/g |

TABLE V
WATER PERMEATION THROUGH NBR COMPOUNDS

| | | | | | | |
|--------------------------|----|----|------|------|-----|-------------------------|
| Carbon black N774 | 90 | 85 | 80 | 70 | 80 | 70 |
| Glass flake RCF-2300N | 0 | 5 | 10 | 20 | 30 | |
| Glass flake RCF-600N | | | | | | 20 |
| Fuel vapour transm. rate | | | 18.6 | 18.9 | 5.0 | 7.3 |
| | | | | | | g/(m ² .day) |

PHYSICAL PROPERTIES

The tensile, modulus and tear properties for the CR compounds with glass flake are shown in Figures 3 to 5. These are presented for NBR in Figures 7 to 9, together with the measurements taken after ageing by the fuel. Additionally, the volume swell of the NBR by the ASTM B fuel is shown in Figure 10.

DISCUSSION

GLASS FLAKE IN CHLORPRENE RUBBER

The permeation of water through CR showed a drastic decrease as increasing amounts above 8 phr (5%) of glass flake were added to the compound. When the loading was about 10% of the compound (15 phr), the permeation of water had been reduced ten-fold.

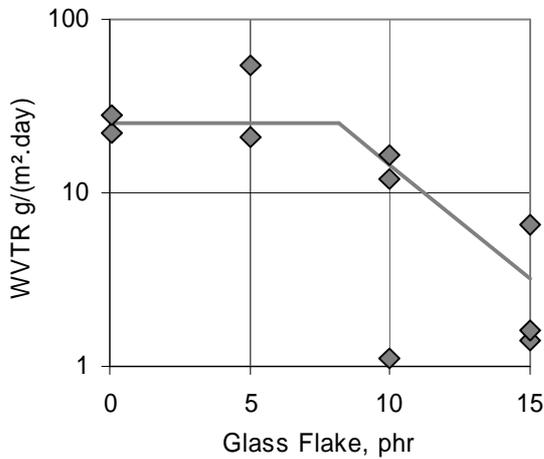


FIG. 1. Water vapour transmission rate dependence upon loading of CR with glass flake.

The glass flakes are aligned parallel to the direction of the sheet. When there is no flake in the compound, the water permeates through the rubber at a rate of 24 g/(m².day). This is the rate through the 2 mm sheet of rubber. If a disc is placed across the diffusion path, the path is lengthened as the water is required to go around the flake particle (horizontally) before it can continue (vertically) through the rubber. If there is a low concentration of flake particles, there is sufficient open rubber for the water to continue to pass directly through. However, once a critical loading is reached (8 phr), there is no longer a direct path through the 2 mm thickness. The route becomes more labyrinthine with increased amounts of flake. This is illustrated in Figure 2.

The effect of flake upon the cured compound properties is to increase the flexibility. The modulus slowly reduces with the increase in flake addition. The rupture properties slightly decrease with flake addition. These reflect the removal of carbon black from the formulation. In applications where high stiffness is important, the flake can be added in addition to, rather in replacement for, the carbon black. The tear strength of the CR compound rose when the flake loading was above 8 phr. When the flake loading is high enough to reduce permeation, the flake becomes more reinforcing than carbon black.

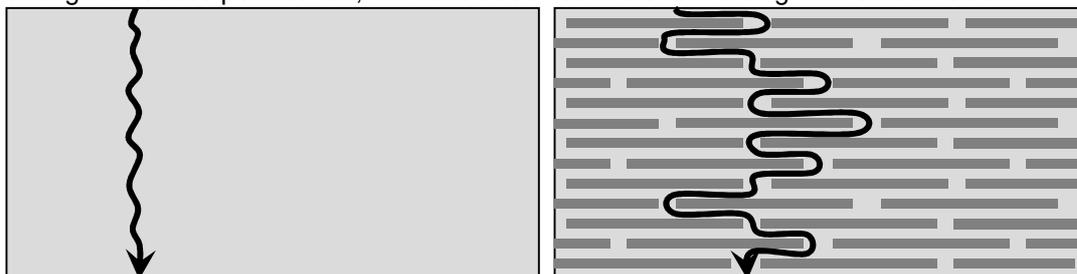


FIG. 2. Mechanism for increasing diffusion path length in a labyrinthine manner with glass flakes.

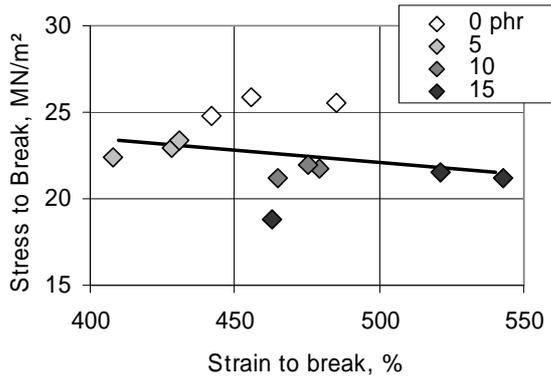


FIG. 3. Dependence of tensile properties compounds upon flake loading for CR compounds.

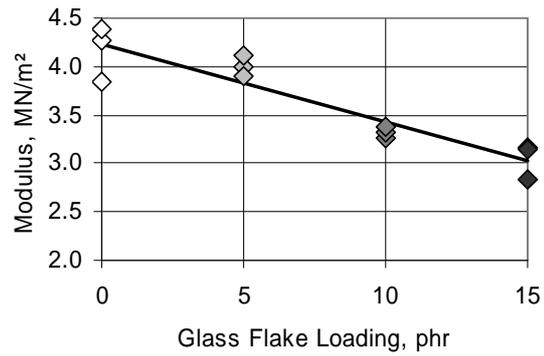


FIG. 4. Modulus dependence of CR upon flake loading.

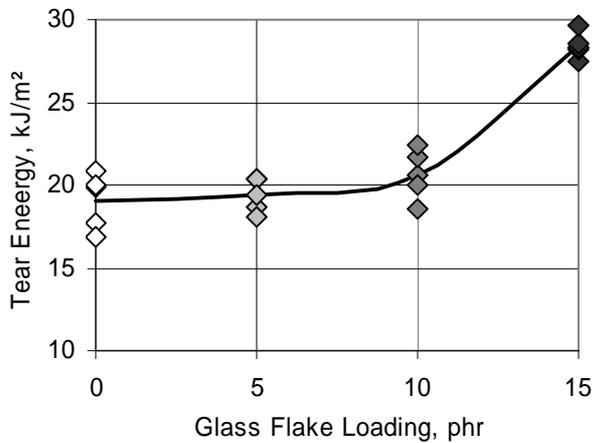


FIG. 5. Tear strength dependence upon loading of CR with glass flake.

Overall, the CR experiment gives favourable properties once the flake loading is over 8 phr (5%). When the flake is present as 10% of the compound, the permeation is only one tenth of the starting compound, the rubber is 25% softer with 50% more tear resistance. High elongation and high tensile strength are retained, although slightly lower than the starting compound.

GLASS FLAKE IN ACRYLONITRILE-BUTADIENE RUBBER

The NBR formulations were not as regular as the CR experiment. At the high loading of glass flake, extra carbon black was also added. The CR experiment achieved loadings up to 15 phr, 10%. The NBR experiment went up to 30 phr, but due to the high amount of carbon black, this was only 13% of the total compound. The NBR data are therefore presented as % rather than phr loading in Figs 6 onwards.

When analysed in a similar manner to the CR data, the glass flakes are seen to improve the permeation resistance of the NBR to fuel. The effect is not as strong for the fuel/NBR combination as the water/CR. The critical loading of flake before permeation drops is above 10%. In NBR, the 13% loading has a four-fold reduction in permeation compared with the 5% loaded compound. This is not as impressive as the ten-fold reduction observed for water/CR.

The relatively poorer performance of the fuel/NBR system may be due to the choice of glass flake. Large flakes (600µ) were used for the CR experiment than the 300µ size flakes used in NBR. The 600µ flakes at 20 phr (10% marked Δ and * in Fig. 6) in NBR performed better than the 300µ flakes with a fuel transmission rate 60% lower. More of the smaller particles are required to increase the labyrinthine diffusion path in comparison with the large flakes.

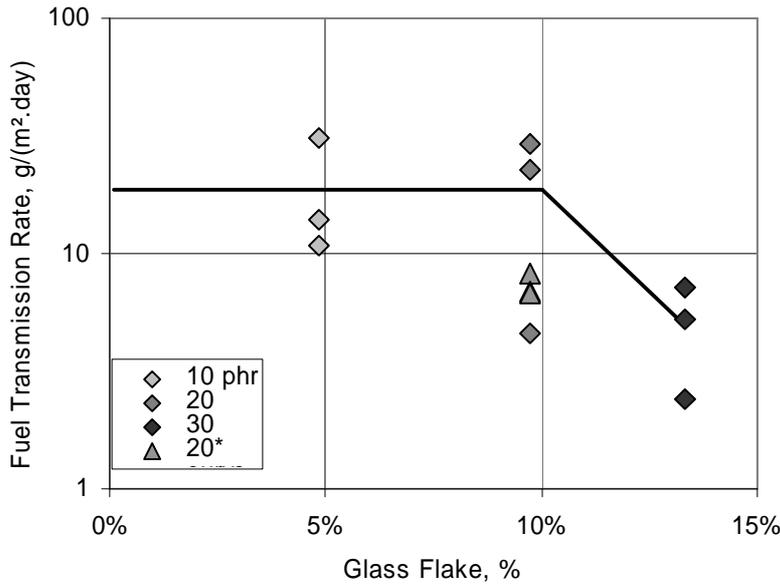


FIG. 6. Fuel vapour transmission rate dependence upon loading of NBR with glass flake. (RCF-2300N \diamond and RCF-600N Δ and *).

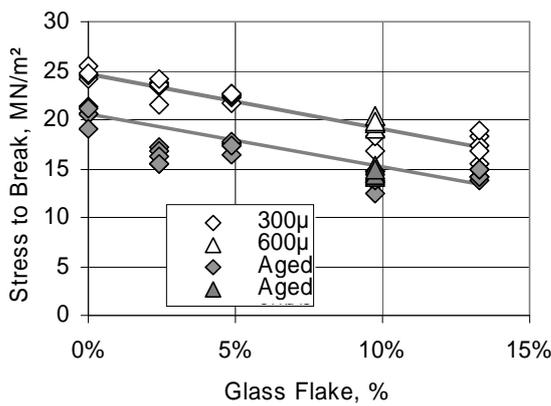


FIG. 7. Dependence of tensile stress of NBR upon flake loading .

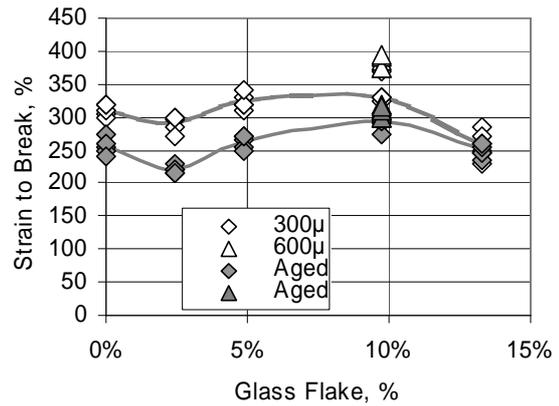


FIG. 8. Dependence of tensile strain of NBR upon flake loading.

The addition of glass flake decreased the tensile stress to break of the NBR compounds. As with CR, this is consistent with the removal of carbon black. The tensile strength of the NBR that had been aged in fuel was reduced by about 20%. This drop was consistent for the compound without and those with glass flake. The glass flake neither increased nor decreased the strength of the rubber with respect to fuel resistance. The strain to break data suggested that the fuel aged most highly loaded compound (13% flake) was as flexible as the new compound.

The tensile properties showed slightly better tensile performance (higher strength and higher strain to break) for the larger flake particles. The fuel ageing was similar for the different sizes of flakes, again evidence that the ageing is independent of the glass flakes.

The tear strength of the NBR compounds, like the CR compounds, showed an increase in tear strength as carbon black was replaced by glass flake. There was no loss of tear strength for the base compound after ageing in Fuel B. After ageing in Fuel B, the glass flake still gave an increase in tear strength above the base compound. However, the increase is lower for the aged in Fuel B specimens than for the unaged specimens.

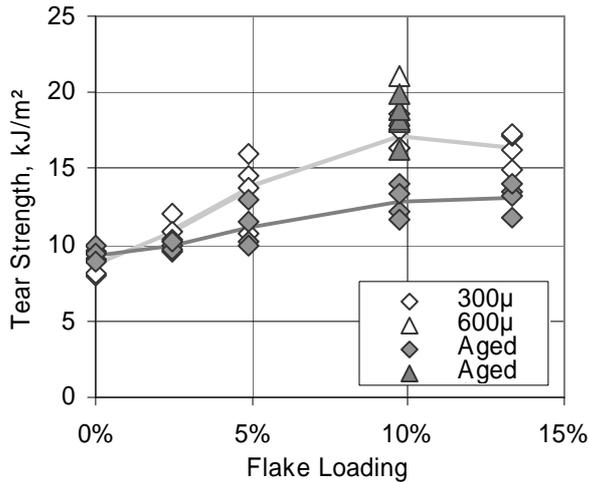


FIG. 9. Tear strength dependence upon loading of NBR with glass flake.

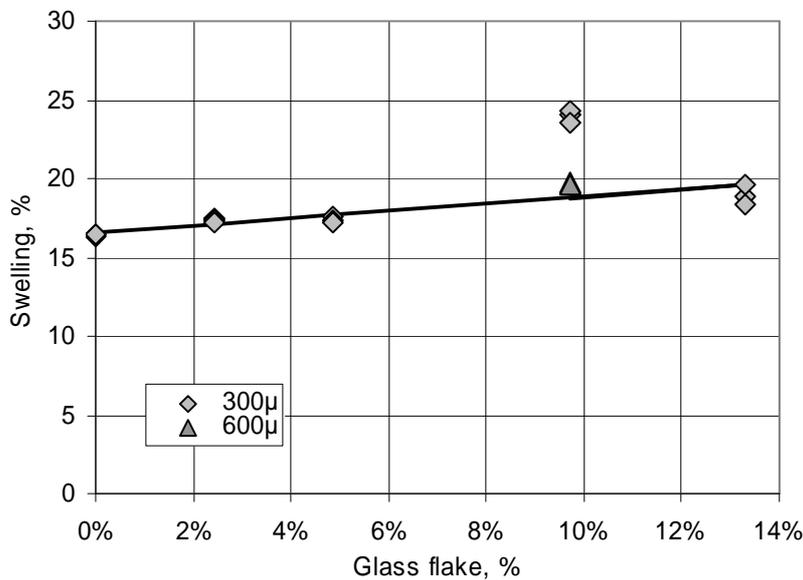


FIG. 10. Swelling dependence upon loading of NBR with glass flake. Weight gain after 7 days in ASTM Fuel B.

The swelling data increased with loading of glass flake. This is consistent with the removal of carbon black and consequent reduction in modulus. It is interesting that the compound most highly loaded with glass flake absorbed the highest quantity of solvent. This compound gave significantly reduced permeation. This demonstrates that although the solubility component may increase, the very large effect of increased diffusion path length will still dominate.

CONCLUSIONS

Addition of 10% of glass flake in chloroprene rubber gave a ten-fold reduction in water vapour transmission rate. Addition of 13% of glass flake in acrylonitrile-butadiene gave a four-fold reduction in fuel transmission rate. By replacing carbon black with glass flake, the CR compound became more 25% flexible in conjunction with a 50% increase in tear strength. Glass flake has the potential to significantly improve the permeation resistance of rubber components such as tank linings and fuel hoses.

REFERENCES

1. J. Crank and G.S. Parks, "Diffusion in Polymers", Academic Press, New York, 1968, Ch.8
2. P.E. Cassidy, T.M. Aminabhavi, and J. C. Brunson, "Water Permeation Through Elastomer Laminates I Neoprene/EPDM", RUBBER CHEM. TECHNOL., **56**, 357, (1983)
3. H. A. Pfisterer, and J.R. Dunn, "New Factors Affecting the Performance of Automotive Fuel Hose", RUBBER CHEM. TECHNOL., **53**, 357, (1980)
4. J.R. Dunn, H.A. Pfisterer, J.J. Ridland, "NBR Vulcanizates Resistant to High Temperature and 'Sour' Gasoline", RUBBER CHEM. TECHNOL., **52**, 331, (1979)
5. M. Morton (ed), "Rubber Technology", Third Edition, 1987, Van Nostrand Reinhold, New York
6. BS EN ISO 6719:2001 method b
7. ASTM D471 Fuel B (30% toluene, 70% iso-octane by volume)