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ORIGINAL PAPER

Filler and mobility of rubber matrix molecules

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Abstract Filler surfaces in elastomers influence mobility of rubber matrix molecules. Mobility of rubber matrix molecules then determines elastomer properties and behaviour of rubber products in applications. Effect of filler in elastomer–filler system is usually characterized by different properties: Modulus seem to depend mainly on filler cluster size and filler network behaviour but effect of mobility of rubber matrix molecules is also evident. Bound rubber characterize fraction of rubber immobilized on filler particle surfaces, however, can be obtained only for uncured rubber–filler compounds. As it is shown in this paper, the permeability coefficient of permanent gas in rubber–filler system could characterize mobility of rubber matrix molecules around the filler particles and the activation energy of its permeation could characterize strength of physical bonds between the rubber matrix molecules and surface of filler particles.

Keywords Adsorption of polymer segments · Mobility of rubber molecules · Modulus of filled systems · Bound rubber · Gas permeability coefficient · Activation energy of gas permeation

Introduction

The use of fillers—especially, carbon black—together with accelerated sulphur vulcanisation, has remained the fundamental technique for achieving the incredible range of mechanical properties required for a great variety of modern rubber products. The relationship between filler structure and the reinforcement of

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elastomers is discussed mainly for the static and dynamic (shear or tensile) modulus [1].

Modulus

With the assumption of dilute suspensions of rigid spherical particles in incompressible matrix, the increase of the shear modulus of filled rubbers f_G would be described by Einstein–Smallwood equation [2]

$$f_G = G/G_0 = 1 + 2.5\varphi \tag{1}$$

where shear modulus G holds for filled compound, shear modulus G_0 for polymer matrix, and φ is the volume fraction of filler in the compound.

Guth and Gold modified Eq. 1 for higher concentrations of filler and obtained [3]

$$f_G = G/G_0 = 1 + 2.5\varphi + 14.1\varphi^2 \tag{2}$$

The most important active fillers for elastomers are now carbon black and precipitated silica. Carbon black consists of spherical primary particles with a rough and energetically disordered surface forming rigid aggregates in the ~50–100 nm range with a fractal like structure. These aggregates are the smallest entities in the rubber matrix. Agglomeration of the aggregates in the rubber matrix leads to the formation of filler clusters and even filler network at high enough concentration. Cluster size and filler network properties are strain dependent [1, 4]. Very similar behaviour is observed also for elastomers filled with precipitated silica.

If the hypothesis of spherical particles is released the presented equations do not have anymore a univocal formulation. For active fillers f_G no longer depends on the simple filler volume fraction φ but on some effective volume fraction φ_{eff}. Medalia added 'occluded rubber' volume to the actual carbon black filler volume to obtain the effective volume of the rigid phase. 'Occluded rubber' was defined as the rubber part of the elastomeric matrix, which penetrated the void space of individual aggregates, partially shielding it from deformation [1, 5, 6]. Such effective volume fraction φ_{eff} is strain dependent [7].

In carbon black filled elastomers, the polymer adsorption on the filler surfaces and formation of an immobilized polymer layer is substantial as there is a strong binding of the chains, leading to the layer of localized polymers [1].

The effect of a hard, glassy immobilized rubber layer around the filler particles leads to the dependency of the elastic modulus of filled rubber not only on the volume fraction of filler φ but also on size of primary particles and on immobilized rubber layer thickness [4].

Bound rubber

Physical adsorption and chemisorption of polymer on filler surface from bulk is known to result in a partial loss of polymer solubility [1]. The filler–bound rubber was defined as the total polymer adsorbed on all filler particles, including those dispersed by the solvent. 'Bound rubber' is the fraction of rubber defying extraction by a solvent in an uncured rubber–filler compound. The statistical theory of bound rubber treats the effect as a random adsorption of polymer segments on active sites assumed to exist on the filler particle surface, which are sufficiently strong to resist the desorptive action of a good solvent at room temperature [8–11].

Bound rubber often serves as a practical measure of filler surface activity. Thus, for carbon blacks with comparable surface areas, higher bound rubber content in the uncured rubber compound is an indication of higher polymer–filler interaction. With storage, rheological properties of rubber–filler compounds change as a result of an increase in interaction between the rubber and filler (bound rubber increases as well) [12]. The bound rubber variation during storage can be understood by considering a slow replacement of short rubber chains initially adsorbed on filler particles by larger ones [1, 13].

Permeation

In the glassy state, a polymer is hard and may be brittle, these properties being intimately related to restricted polymer chain mobility. Hence, it is not surprising that penetrant diffusivities through such a structure are low. In contrast, polymers in the rubbery state typically are tough and flexible, with such properties associated with freer chain motion [14]. Penetrant diffusivities of rubber compounds might therefore be sensitive to the presence of hard, glassy immobilized rubber layer around the filler particles.

The use of small molecules as microstructural probes is being more and more adopted in research on polymeric materials. In the permeation of non-condensable gases in polymeric membranes, equilibrium levels of gas sorption in the solid are low and diffusion constants are independent of penetrant concentration in the membrane. Application of Fick's law and Henry's law results in a transport equation in which flux rate at the steady state is given by the product of permeability and partial pressure gradient across the membrane [14]:

$$J = P_{\mathrm{e}} \frac{(P_1 - P_2)}{l} \tag{3}$$

where J is unidirectional flux of gas, P_{e} is permeability coefficient, $(P_1 - P_2)$ refers to pressures at the sample surfaces, and l is thickness of the membrane.

It has been found that the permeability of gases through polymeric materials varies with temperature according to an Arrhenius-type equation [14]:

$$P_{\mathrm{e}} = P_{\mathrm{e0}} \mathrm{e}^{-E_{\mathrm{p}}/RT} \tag{4}$$

where P_{e0} is a pre-exponential factor, E_{p} is activation energy of permeation, R is gas constant, and T is thermodynamical temperature.

Filler and gas permeability

Value of gas permeability of filled elastomers depends on type of matrix polymer, on volume fraction of filler, on interaction between rubber and filler, and on shape and dimensions of filler particles. The lowest gas permeability would have elastomer filled by active filler with platelet particles oriented perpendicularly to the gas flow [15].

Physically, reduced gas permeation in filled polymers is attributed to the increase in diffusion path length and decrease in effective cross-sectional area available for transport. The large difference in permeability reduction between carbon black filled SBR and SBR nanocomposite is mainly result of tortuous diffusional path effects [16]. Nanocomposites show a several-fold reduction in the permeability of gases with small molecules [17], but presence of defects or voids in the matrix–filler interfaces might facilitate gas transport [18].

The gas permeability of nano and micro rubber composites with platelet like morphology has been extensively studied for polymeric membranes used for gas separation processes [19].

Aim of this work

The aim of this work was to use the small permanent gas molecules as microstructural probes in filled vulcanised rubber systems and try to characterize the effect of immobilized rubber layer around the filler particles.

This aim was achieved by measurement of nitrogen permeability for vulcanised SBR samples filled with carbon black of different activity and with precipitated silica. The influence of filler and temperature was then evaluated.

Experimental

Sample preparation

Compounds of styrene-butadiene rubber (SBR 1500 from Synthos) with 30 parts of filler for hundred parts of rubber (i.e., with 21.4 wt% of filler) were used. Compounds with carbon black N220, N330, and N550 (from Cabot), and with precipitated silica KS 408 (from Grace) were prepared according to ISO 2322-1985. An unfilled compound of similar composition served for comparison.

The prepared compounds were compression moulded at 150 °C for $t_{90} + 5$ min to 1 mm sheets and specimens from these sheets were used for permeability testing.

Permeability testing

Gas transport was studied using a laboratory-made apparatus based on a constant volume method. The apparatus for constant volume method consists of a metal cell having two cavities separated by the test piece [20].

The high pressure cavity is filled with nitrogen at constant pressure P_1. The low pressure cavity is initially evacuated to high vacuum. When the steady state of gas flow through the membrane is reached, the linear increase of pressure P_2 with time (i.e., $\Delta P_2/\Delta t$) in low pressure cavity is measured and permeability coefficient P_e is calculated from relation [21]:

$$P_e = \frac{\Delta P_2}{\Delta t} \cdot \frac{V}{A} \cdot \frac{l}{P_1} \cdot \frac{1}{RT} \tag{5}$$

where V is calibrated volume of low pressure cavity, A is area of measured membrane, l is measured membrane thickness, R is gas constant, and T is temperature. The apparatus, method and results are described in detail elsewhere [22].

Results and discussion

Permeability

The permeability coefficient P_e of filled and unfilled vulcanised SBR samples at different temperatures is presented in Table 1:

In Table 1, the permeability coefficient for unfilled vulcanised SBR at each temperature is the highest and the permeability coefficients of filled vulcanised SBR samples at given temperature depend on type of filler. These results qualitatively agree with contemporary concept of filler action on permeability in polymer systems.

Activation energy

The activation energy of permeation E_p for filled and unfilled vulcanised SBR samples calculated from permeability coefficients in Table 1 is apparent from Table 2:

The activation energies of permeation E_p from Table 2 ordered from the highest to the lowest value are presented in Fig. 1.

As we can see from Fig. 1, the activation energy of permeation for unfilled sample is the lowest. In unfilled sample the movements of molecules are not restricted by presence of filler surfaces and activation energy of permeation E_p depends mainly on change in fractional free volume f_v [23]

$$f_v = \frac{V_f}{V_0 + V_f} \tag{6}$$

Table 1 Permeability coefficient $P_e \times 10^{15}$ (mol/m s Pa)

Sample	Temperature (°C)			
	35	50	65	80
Unfilled	2.41	4.74	8.26	12.90
N220	1.74	3.57	6.41	10.44
N330	1.77	3.48	6.11	10.10
N550	1.83	3.69	6.51	10.35
Silica	1.72	3.68	6.49	10.52

Table 2 Activation energy of permeation E_p (kJ/mol)

Sample	E_p
Unfilled	33.793
N220	36.037
N330	34.963
N550	34.867
Silica	36.302

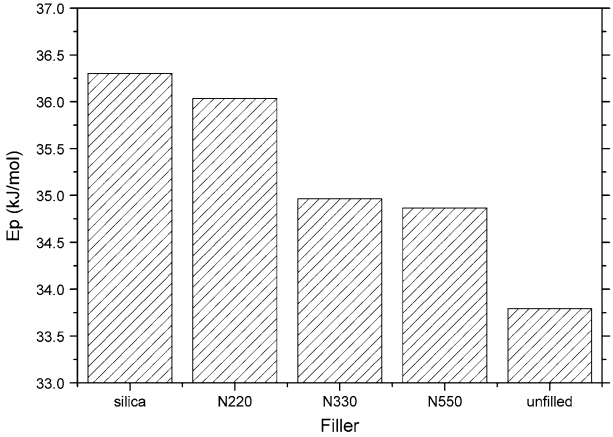

Fig. 1 Activation energy of permeation E_p (kJ/mol) for filled and unfilled samples

where V_0 and V_f is the occupied and the free volume of polymer, respectively.

The activation energies of permeation for filled vulcanized SBR samples in Fig. 1 are higher than that for unfilled sample and depend on type of filler. Diameter of primary particles in carbon blacks increases as the first number in their name increases, i.e., in succession N220, N330, and N550. With increasing diameter of primary particles the specific surface area of carbon blacks (i.e., the area of polymer–filler interaction) decreases and decreases also activation energy of permeation for carbon black filled rubber samples in Fig. 1.

Comparison of fillers

Figure 1 qualitatively agree with our expectations, but we supposed that the activation energy for sample filled with carbon black N330 would be nearer to activation energy for sample filled with carbon black N220 (in agreement with permeability coefficients for filled samples at temperature 35 °C shown in Fig. 2).

The too low activation energy for sample filled with carbon black N330 in Fig. 1 might be consequence of the different temperature dependence of permeability coefficient for samples with different fillers. Let us try to test this hypothesis.

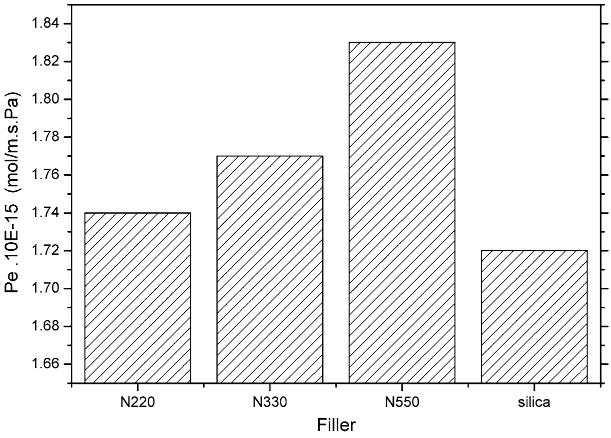

Fig. 2 Permeability coefficient $P_e \times 10^{15}$ (mol/m s Pa) at temperature 35 °C

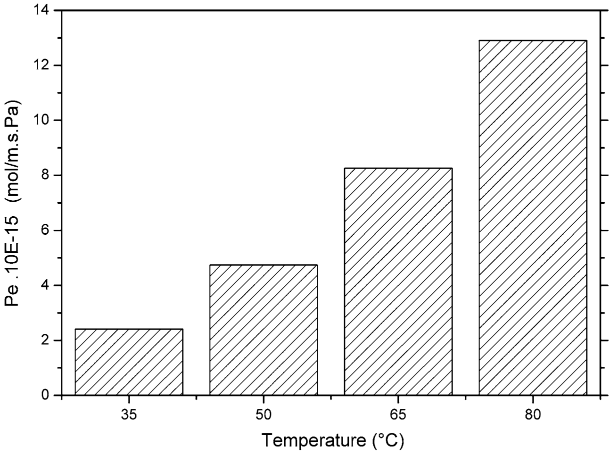

Fig. 3 Permeability coefficient $P_e \times 10^{15}$ (mol/m s Pa) for unfilled sample

Because the permeability coefficient of sample increases with temperature (as in Fig. 3), the decrease in permeability of rubber by presence of filler is in this paper characterized also by the ratio of permeability coefficients (i.e., by the permeability ratio) f_P

$$f_P = P_{\mathrm{eF}}/P_{\mathrm{eU}} \tag{7}$$

where P_{eF} is permeability coefficient of filled rubber at given conditions and P_{eU} is permeability coefficient of unfilled rubber at the same conditions.

Ratios of permeability coefficients f_P obtained from Table 1 are presented in Fig. 4 and there is also the temperature dependence of permeability ratio f_P for filled samples.

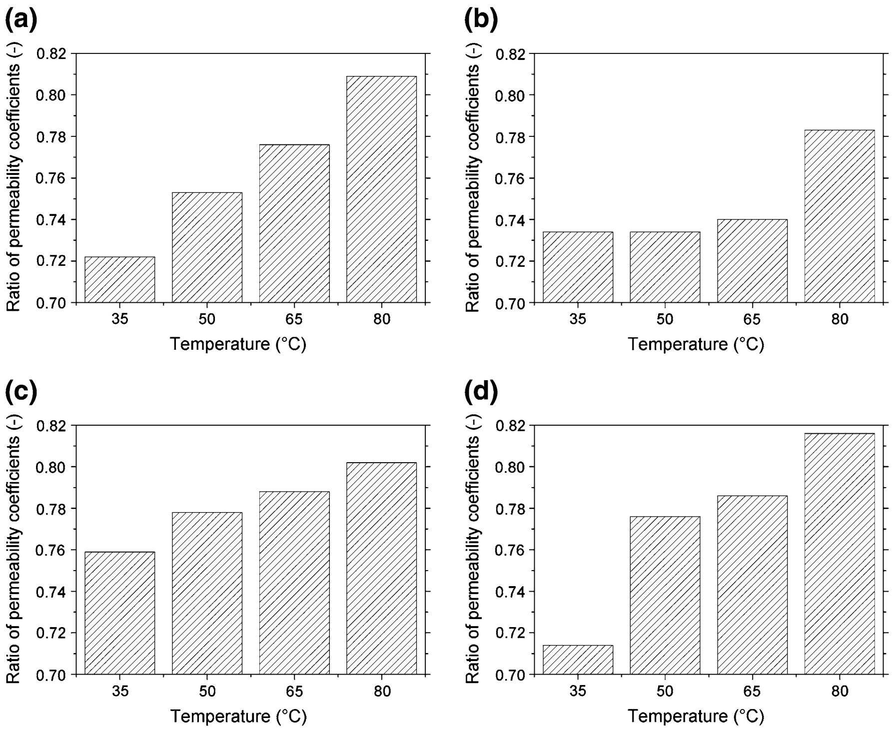

Fig. 4 Ratio of permeability coefficients $f_P = P_{\mathrm{eF}}/P_{\mathrm{eU}}$ for samples filled with: **a** carbon black N220, **b** carbon black N330, **c** carbon black N550, and **d** with silica

From comparison of results in Fig. 4 we can see that ratio of permeability coefficients f_P for samples filled by carbon black N220 and N550 is regularly increasing with temperature whereas the increase for samples filled by carbon black N330 and with silica is irregular. The effect of fillers in elastomer matrix so might be more complicated then it is usually supposed.

Activity of filler

In all filled vulcanised SBR samples we used the same weight concentration of fillers. As density of all carbon black primary particles is practically the same, practically the same is also the carbon black volume fraction φ in all our carbon black filled compounds at each temperature.

Because the volume fraction φ of all our carbon black filled compounds at each temperature is the same, the permeability coefficient P_{e} for samples filled with different types of carbon black evidently depend not only on volume fraction of filler φ but also on activity of filler and on mobility of rubber matrix molecules around the filler particles.

The permeability coefficient P_{e} at given temperature (or the ratio of permeability coefficients f_P at different temperatures) of samples filled with carbon blacks therefore might be used as a value indicating activity of carbon black and characterizing mobility of rubber matrix molecules around the filler particles.

With increasing filler activity the energy needed for unblocking of rubber molecule movements near the filler surface probably increases and therefore increases also the activation energy of permeation E_{p}. The activation energy of permeation (or ratio of activation energies for filled and unfilled sample) might so indicate activity of fillers and characterize strength of physical bonds between rubber matrix molecules and surfaces of filler particles.

The same could be valid for rubber compounds filled with other fillers. However, density of silica is higher than that of carbon black and volume fraction φ of silica in our filled sample is therefore lower than that for carbon black filled samples. Direct comparison of permeability results for carbon black and silica is in this case difficult.

Conclusions

The ratio of modulus for filled and unfilled samples can be used for both rubber compounds and vulcanised rubber samples. Modulus seem to depend mainly on filler cluster size and filler network behaviour but influence of occluded and adsorbed rubber is also evident.

Bound rubber characterize fraction of rubber adsorbed by filler particles, however, can be obtained only for uncured rubber–filler compounds. Bound rubber values apparently depend also on type of solvent and on temperature of extraction.

As it is shown in this paper, the mobility of rubber matrix molecules near the filler particle surfaces could be characterized using mass transport phenomena of permanent gases in rubber–filler systems. The main advantage of mass transport measuring in comparison with bound rubber method is that the permeability coefficients of permanent gases can be obtained also for vulcanized rubbers and at different temperatures.

The permeability coefficient of permanent gases in rubber–filler systems could characterize mobility of rubber matrix molecules around the filler particles. The activation energy of permeation could characterize strength of physical bonds between rubber matrix molecules and surfaces of filler particles.

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