Polymer Testing 53 (2016) 257–266

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material characterisation

Mechanical properties of carbon black filled hydrogenated acrylonitrile butadiene rubber for packer compounds

Xiaozhen He [a], Xinyan Shi [a, *], Martin Hoch [b], Christoph Gögelein [c]

[a] Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber and Plastics, Qingdao University of Science and Technology, Qingdao, 266042, People's Republic of China
[b] Arlanxeo, High Performance Rubber Research Center, Qingdao, 266042, People's Republic of China
[c] Arlanxeo, Deutschland GmbH, Kaiser-Wilhelm-Allee 40, 51369, Leverkusen, Germany

ARTICLE INFO

Article history:
Received 19 April 2016
Accepted 15 June 2016
Available online 16 June 2016

Keywords:
HNBR
Carbon black
Packer compounds
Mechanical properties

ABSTRACT

Hydrogenated acrylonitrile butadiene rubber (HNBR) was chosen to develop peroxide cured and carbon black N220 (CB) reinforced high modulus vulcanizates with possible applications in packers for oil exploration. HNBR vulcanizates are investigated by Rubber Processing Analyzer RPA 2000 and stress-strain tests conducted both in elongation and compression mode. All the mechanicals properties were tested both at room temperature (RT) and 150 °C in order to reflect application of packers. The results show that the modulus of CB filled HNBR vulcanizates increases with the increase of CB loadings in shear, tensile and compression mode. The physical interactions resulting from CB reinforcements show a stronger temperature-dependence than chemical crosslinks formed by curing agent. So the addition of reinforcing carbon black will have limited benefit for producing packer compounds with high enough modulus at high temperature, but more amount of curing agent will contribute to a stable high enough modulus. It is testified the filler-filler interaction is more temperature dependent than filler-rubber interaction and more chemical crosslinks increase the filler-rubber bonding and slightly decrease the filler-filler interaction, which is confirmed by the reinforcement factors. Compression tests show a strong dependence on the geometry of the samples and the compressive Payne Effect is examined by the multiple compression cycles. It gets stronger as the CB loading is increased.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Packers are rubber sealing element used in the oil field [1]. Its service environment is very harsh: high depth-high temperature such as 150 °C to 175 °C, high pressures such as >70 MPa, exposure to crude oil and drilling fluids. Although air is generally absent and therefore oxidative aging will not take place, but crude oil can contain hydrogen sulfide which can attack double bond containing polymer causing severe embrittlement. So far, technical information on packers is mainly related to patent literature [2–5] focusing on design aspect, so only few reports on packer recipes and their effect on mechanical properties can be found. There are many types of packer assemblies which include constructions with reinforcing fibers [3] and metal sleeves [5]. This included inflatable packers. Packers are also used in fracking operation to separate formations [2,4] where high pressure is applied. In oil field, NBR and its hydrogenated version HNBR are typical elastomers used in the oil field. In this paper HNBR was chosen due to its excellent properties, such as heat resistance, oil resistance and chemical resistance, especially against H_2S and aging resistance [6,7].

Here carbon black N220 (Particle averaged size is 20–25 nm) is used as the only reinforcing filler with dosage variations up to 80 phr to achieve high modulus of HNBR compounds. The upper dosage limit was set by a limit of the compound viscosity which allows molding operation. Peroxide was chosen as the curing agent due to its higher heat stability than sulfur. The cross-link density was adjusted by two peroxide dosage levels. The geometry of packers is subject to variation in service. The thick sleeves are used to set around a center cylinder where compression by pistons causes bulging out the outer free surfaces to seal a gap to the outer casing the well. To account for the rather complicated deformations samples were measured at shear, tensile and compression model, respectively. Here, high temperature measurements at 150 °C were included as well to come closer to real service conditions. Typical

---

* Corresponding author.
E-mail address: lindashi88@hotmail.com (X. Shi).

http://dx.doi.org/10.1016/j.polymertesting.2016.06.009
0142-9418/© 2016 Elsevier Ltd. All rights reserved.

application challenges are related to creating compounds with high enough modulus at high temperatures to resist deformation under pressure and still be able to seal gaps between casing and drill string.

2. Experimentals

2.1. Materials and formula

Details of the materials and formulations are shown in Table 1.

2.2. Preparation of vulcanizates

HNBR was first mixed in internal mixer at a rotor speed of 40 rpm for 1 min at 50 °C. Then, half of CB and additives except peroxide were added and mixed for 1 min. The rest of CB and additives except peroxide were added and mixed for 3 min. The total mixing time was 5 min. The mixtures were taken out of the mixer and processed into sheets at 50 °C with peroxide on a laboratory two-roll mill (SAGA Instruments Pte Ltd, C0840, USA) with a roller speed ratio of 1:1.2 and temperature below 50 °C and then kept at room temperature for 24 h before curing. Curing time was determined by a Moving Die Rheometer 2000 from Alpha Technologies. Sample curing was carried out on a cure press (VC-150T-FTMO-3RT, Jiaxin Electric Company, China) at pressure of 60 MPa and175 °C and $t_{90} + 5$ min as curing time.

2.3. Measurements

Vulcanization characteristics were determined using a Moving Die Rhometer MDR2000 (Alpha Technologies Company, USA) at 175 °C, according to ASTM D 2084-95.

Dynamic Rheological Measurements of Vulcanized Rubber Compounds was carried out using a Rubber Processing Analyzer RPA 2000 (Alpha Technologies, USA) with strain range of 0.28–100% in shear mode at 60 °C and 150 °C and a frequency of 1 Hz.

Tensile tests were carried out using an Instron 3365, (Instron, USA), at a tensile speed of 500 mm/min according to ASTMD412.

Uniaxial Compression tests were measured by MTS 831.50 Elastomer Testing System (MTS Company, USA), at a compression speed of 2 mm/min with cylindrical samples.

Morphology Analysis was carried out using scanning electron microscopy (SEM; JSM-7500F; Japan Electron, Japan); The cryo-cut surfaces were chosen to be sputtered with thin layers of gold and imaged using SEM.

3. Results and discussion

3.1. Curing characteristics and hardness

The curing characteristics are shown in Fig. 1A–D. It can be seen that the optimum cure time (t_{90}) of the HNBR compounds decreases with increasing carbon black loading from Fig. 1C and curing agent amount from Fig. 1D, indicates more CB and peroxide loadings promoting the peroxide curing. With the increase of carbon black, the interaction between rubber and filler is increased, and then the content of bound rubber increases. As a result, with the same content of curing agent, the content of curing agent in free rubber matrix increases relatively, and then it forms more chemical crosslink density, the optimum cure time (t_{90}) decreases. The cure torque (MH-ML) increases with increasing the carbon black dosage and curing agent content as shown in Fig. 1D. Moreover, the cure torque (MH-ML) makes a linear relationship with carbon black dosage. It is a common sense that more curing agent forms more chemical crosslink density which causes a higher (MH-ML). It should also be concluded that chemical crosslinks increase the physical interactions (either filler-filler or filler-rubber or both) since the (MH-ML) increased with the increase of CB loadings. As a result, the modulus increases, and then the hardness of HNBR vulcanizates increases as shown in Fig. 1E. When filled with 80 phr carbon black, the hardness can reach nearly 90 Shore A, which is the necessary requirement of packer product. Typically, the hardness required for packer products can reach 90 Shore A.

3.2. Dynamic mechanical properties

Fig. 2 shows the strain-dependence of storage modulus G′ of CB filled HNBR vulcanizates at different temperature. It can be seen whether it's 60 °C or 150 °C, the storage modulus of the vulcanizates increases with the increasing content of carbon black. The storage modulus decreased drastically when tested at 150 °C. G′ of vulcanizates with higher CB loading shows stronger strain-dependence indicating a stronger Payne Effect [8–11]. In packer applications applied strains can amount to some 30% in compression resulting also in shear strains and elongation strains.

The same vulcanizates at 150 °C exhibits a weaker Payne effect than at 60 °C, suggesting filler-filler networks getting weaker at higher temperature due to reduced filler-filler interactions. It can also be seen in Fig. 2(A), that there is no dependence of storage modulus at 60 °C on the crosslink density (peroxide dosage). However, we find that the amount of peroxide has an effect on the modulus of the vulcanizates at 150 °C as the G′ of vulcanizates with higher peroxide content is higher, but show the same strain-dependence when CB is the same as shown in Fig. 2B. It is suggested that the physical interactions (filler-filler and filler-polymer interaction) dominate the storage modulus at low temperature while the chemical crosslinking networks dominate it at high temperature since physical interactions are easily destroyed at 150 °C. From that one can infer that added reinforcing carbon black will have limited benefit for producing packer compounds with high enough modulus at high temperature, but more amount of curing agent will contribute to permanent enough modulus.

In order to further investigate the filler-filler (F-F) and filler-rubber (F-R) interactions in CB filled HNBR vulcanizates, five strain sweeps were carried out as shown in Fig. 3 for unfilled and filled vulcanizates. It can be seen after the first sweep to around 40%

Table 1
Materials and formulation.

Materials	Characteristics	Source	Amount (phr)
HNBR	Therban 3627, bound ACN: 36 wt%, residual double bond content 2%, Mooney viscosity ML (1 + 4)100 °C: 70 MU	Arlanxeo GmbH, Germany	100
Carbon black	Corax N220, particle size:20–25 nm	Orion Engineered Carbons Trading, Shanghai	0, 50, 65, 80
Antioxidants	Naugard 445, 4, 4′-Bis (α,α -dimethylbenzyl) diphenylamine	Addivant, USA	1.5
Antioxidants	Vulkanox ZMB2/C5, Zinc-4-and 5-methyl-2- mercaptobenzimidazole	Arlanxeo AG	0.5
Process aid	Struktol WB 222, Alphatic, fatty acide esters and condensation products	Schill + Seilacher "Struktol" GmbH, Germany	1.5
Peroxide	Luperox F40, α, α′ Di (*t*-butyl peroxy)diisopropylbenzenes, 40 wt% of $CaCO_3$ carrier	Arkema, China	4.5, 6

Download English Version:

https://daneshyari.com/en/article/5205734

Download Persian Version:

https://daneshyari.com/article/5205734

Daneshyari.com