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Erzielen der richtigen Balance zwischen Spezifikation und Verarbeitbarkeit bei ausgewählten Hochleistungselastomeren

Achieving the Right Balance between Specification and Processability on Selected High Performance Elastomers

M. J. Winrow (Sp), A. Müller, I. Watson, C. Wheeler, Clwyd Compounders Ltd, Ruabon (UK)

Rubber compounders today frequently face engineering specification requirements that are challenging in themselves, but in addition to meeting a specification, the compounder must also consider the type, size and method of manufacture of the end product. In order to obtain the specified properties, the formulated compound may be highly viscous, which can in turn limit its processability and its ability to mould well and produce a defect-free part. This study aims to show through selected case studies how holistic analysis of processing and service requirements, coupled with innovative compounding, can produce compounds suitable for the most demanding applications.

Methods

All physical testing was carried out to BS903: A26 1995/ISO48:1994 and ISO37:2005. The dispersion of each batch was tested using a dispegrader to BS ISO 11345.

Study 1 – High-strength HNBR for large packers in the oil and gas industry

Compounds in the oil and gas industry must withstand harsh service conditions – they may be exposed to methane, carbon dioxide, water, saline, and sour crude oil (containing H_2S) at above 150°C and 1,000 bar. HNBR can be compounded to offer an outstanding balance between mechanical, dynamic and abrasion properties as well as resistance to hot air, oils and chemicals.

Formulations

Two compounds were formulated for this study (Table 1). Formulation A is a typical industry standard HNBR for packer elements, designed for high tensile strength and high hardness. It has poor material flow, so processing is difficult and part manufacturing is limited to compression moulding. Formulation B is a bespoke formulation by Clwyd Compounders designed for packer elements. The very high tensile strength of Formulation A is sacrificed for higher elongation at break, which can be more beneficial in service. It also contains non-extractable process additives to aid compound flow and enable transfer moulding of parts.

Ingredient	Formulation A	Formulation B
Polymer	High viscosity HNBR	Medium viscosity HNBR
Filler 1	N330 carbon black	N330 carbon black
Filler 2		Precipitated silica
Coagent	TAIC	Liquid coagent TMPTMA
Curative	Peroxide	Peroxide

Tab. 1: Formulations A and B

Packers are used at elevated temperatures and allowances must be made for the reduction of up to 50% in elongation at break compared to results obtained at ambient temperature (Figure 1).

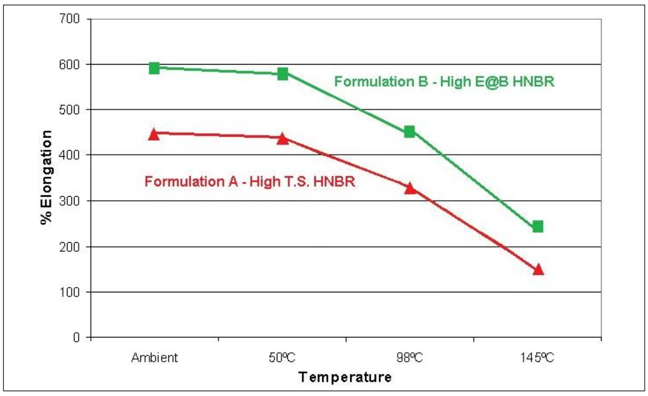

Fig. 1: Elongation at break is reduced at high temperatures

Properties of Formulations A and B

Samples were tested on a MDR at 185°C. The minimum torque of A is considerably higher than B. Both compounds reach a constant maximum torque, indicating full cure and a good compression set.

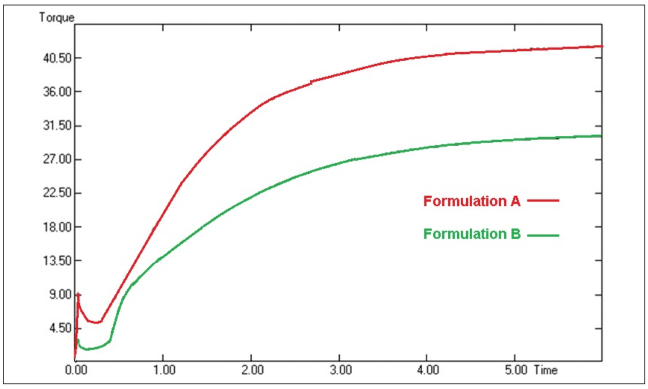

Fig. 2: Rheology of Formulations A and B

Physical testing results are shown in Figure 3. Formulation B shows lower tensile strength than Formulation A, but elongation at break of B is considerably higher than A. This allows for a drop in elongation at high temperature.

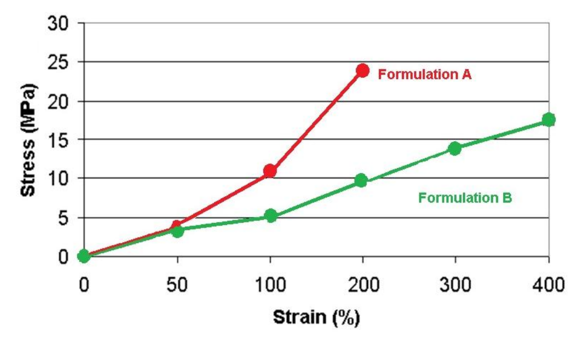

Fig. 3: Stress-strain curve for Formulations A and B

Conclusions

This study shows the need for compromise between high hardness and tensile strength on one hand, and high elongation and good processability on the other. Our aim was to design a bespoke compound suitable for service conditions. Formulation B offers good all-round properties, showing improvement in elongation at break and material flow compared to the industry standard compound. The end result is better flow, improved consolidation during moulding and improved elongation at break, reducing possibility of part failure in the field.

Study 2 – High-strength, high-elongation bladder

A customer required a peroxide-cured EPDM to manufacture two components using transfer moulding – a diaphragm and a thin-walled extended bladder. The compound also had to meet the specification in Table 2.

Property	Specification
Hardness (IRHD)	50 – 60 IRHD
Tensile strength (psi)	≥ 2000 PSI
Elongation at break (E@B)	≥ 600%

Tab. 2: Specification requirements

A blend of low viscosity polymers was selected to ensure good compound flow, and carbon black used to increase physical strength of the compound. Peroxide-cured EPDM is prone to mould fouling, so we investigated novel process aid packages to aid part demoulding.

Process control

Good dispersion results in optimal physical properties in the finished compound. In order to ensure the best possible dispersion was achieved and to eliminate processing variability between test formulations, we used TrendView Analysis to monitor power output on mills and mixers. The collected data was used by a Process Engineer to develop a Standard Operating Instruction that was applied to each experimental formulation.

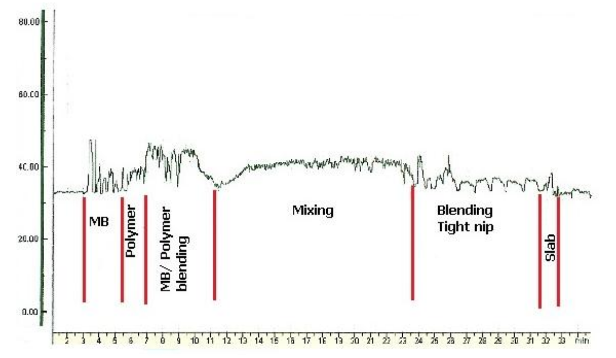

Fig. 4: Monitoring of power output on open mill produces a mix profile for each batch

Initial evaluations

Good results were seen in moulding trials for Formulation X, but it failed to meet the physical testing specification (Table 3). Substitution of some carbon black with surface-treated silica to produce Formulation Y improved physical properties. Moulding trials of Formulation Y showed good results for the diaphragm, but the bladder showed moulding issues, including warping and mould adhesion.

Property	Spec	X	Y
Hardness (IRHD)	50 – 60	52	55
T.S. (psi)	≥2000	1639	2350
E@B (%)	≥ 600	519	681

Tab. 3: Properties of Formulations X and Y

Optimization of formulation using Design Of Experiments (DOE)

Process aids improve compound processing by reducing viscosity, prevent sticking to process equipment, act as dispersing agents for highly-active white fillers and improve mould release. Various packages based on three process aids A,B and C (A= blend of fatty acid alcohol and ester, B= low molecular-weight polyethylene, C= high molecular weight fatty acid esters) were added to aliquots of masterbatch based on Formulation X and tested. Experimental design software was used to evaluate the relationship between process aids, peroxide and physical properties (Figure 5). Peroxide strengthened the rubber but reduced ultimate elongation. Process aid A improved elongation but reduced tensile strength. Process aid B also reduced rubber strength. Process aid C did not cause a statistically significant effect on strength or elongation. Interestingly, a synergistic effect of Process aid A and peroxide improved strength.

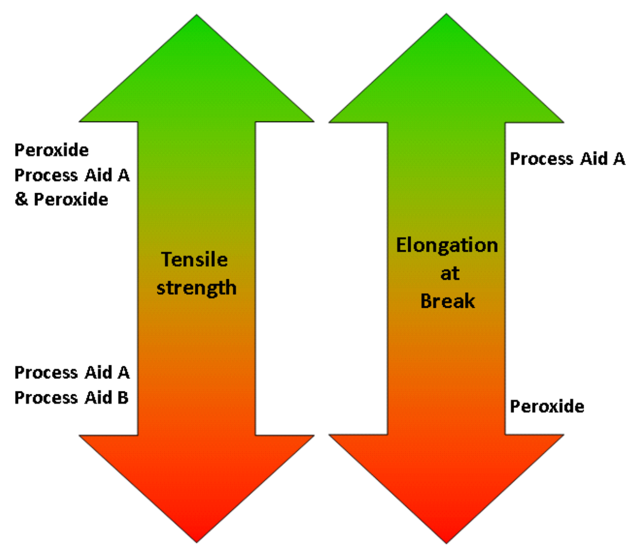

Fig. 5: Peroxide and process aids affect physical properties

In order to meet the user specification, there must be a balance between process aids and peroxide levels. The end result was Formulation Z, which had a medium peroxide level and a combination of two process aids at a low level. Use of multiple process aids gives a synergistic effect on mould release; yet minimizes the decrease in tensile strength (Table 4).

Property	Spec	Z
Hardness (IRHD)	50 – 60 IRHD	50
T.S. (psi)	≥2000 PSI	2059
E@B (%)	≥ 600	621

Tab. 4: Properties of Formulation Z

Conclusions

Formulation Z balanced the addition of process aids to increase elongation and facilitate demoulding, with increased peroxide in order to obtain satisfactory tensile strength. Moulding trials using Formulation Z were successful for the bladder and diaphragm.

Study 3 – Evaluation of technical fibres in high-modulus rubber compounds

In recent years, the use of technical fibres in rubber compounds has become more prevalent as compounders aim to produce high hardness compounds which also have high tensile strength at low extension modulus. Kevlar$^{®}$ (para-aramid) can be added to various rubber types to increase stiffness and tensile strength at low extension. Alternative technical fibres for use in rubber compounding include Nomex$^{®}$ (meta-aramid), which can be added directly to rubber without pre-blending with the polymer, and carbon fibres (CF), now commercially available in a range of sizes.

Compounds containing fibres are frequently used in applications where the part must be able to withstand extrusion at high differential pressure; for example, anti-extrusion seals. Such compounds generally have high viscosity, which can cause processing issues. Although moulding methods that take into account the high minimum viscosity of technical fibre-containing compounds have been developed in order to produce defect-free parts, they still cause processing issues for the compounder. These include excessive strain on mixing equipment, poor dispersion; high risk of premature cure (scorch) and high production costs; caused by high use of electricity, mixing time and manpower.

We investigated the effects of various combinations of Kevlar$^{®}$, Nomex$^{®}$ and carbon fibres on the rheology and physical properties of HNBR compounds, with the aim of producing high-modulus compounds with improved processability.

Rheology

Samples were tested on a MDR at 165°C. Similar t_{05}, t_{50} and t_{90} values were obtained for all formulations, but minimum and maximum torque values differed significantly, depending on fibre type and loading level. Nomex$^{®}$ and carbon fibres caused a smaller increase in minimum viscosity (ML) than Kevlar$^{®}$/EVA (Figure 6).

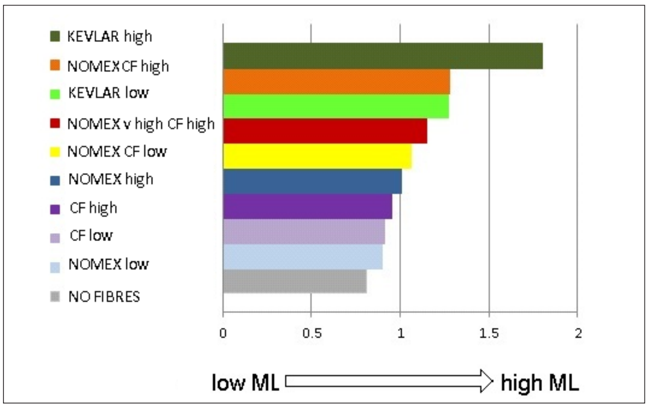

Fig. 6: ML of selected formulations

Physical properties

Stress-strain curves were obtained with (Fig. 7) and against (Fig. 8) the grain. The area of interest in anti-extrusion applications is stress at <10% strain, since above this level, a seal would already extrude from its groove.

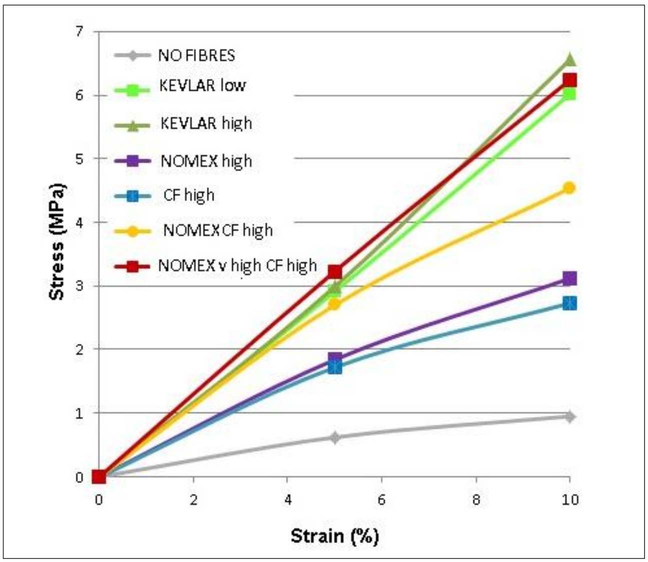

Fig. 7: Stress-strain curve with grain (up to 10 % extension)

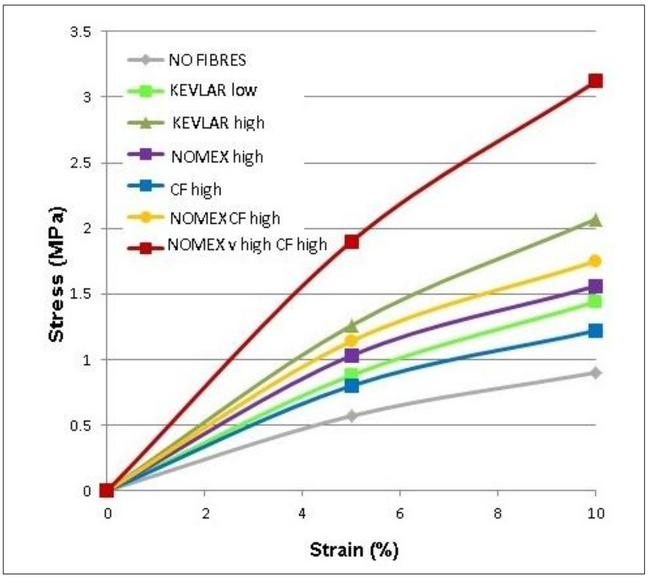

Fig. 8: Stress-strain curve against grain (up to 10 % extension)

Conclusions

HNBR formulations containing technical fibres show increased viscosity, hardness and tensile strength at low strain (up to 10% extension). Physical properties are dependent on fibre type and loading Compounds containing Nomex® or carbon fibres alone can't reach the high tensile strength at low extension of Kevlar®-containing compounds. However, a blend of very high-load Nomex® and high-load carbon fibre offers reduced compound viscosity, but comparable hardness and strength at low extension to a compound with high Kevlar® loading. This result suggests that a combination of Nomex® and carbon fibres may be considered for use in high-modulus compounds designed for conditions of high differential pressure.

The additional heat stability of Nomex® and carbon fibres may offer an advantage over Kevlar® in high-temperature applications. With appropriate compounding, HNBR can be used at temperatures of up to 175°C but the maximum recommended service temperature of Kevlar®/EVA masterbatch is 165°C.

Acknowledgements

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