Challenges in extrusions met with branched, high molecular weight Keltan 13561C EPDM

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Keltan 13561C was introduced as the premier EPDM grade for extruded seals. It has quickly become apparent that the unique combination of the grade’s characteristics makes this material one of the principal tools for other applications. The very high molecular weight and long chain controlled branching drive economical compounding and enhanced processing.

Hose formulations can benefit from these characteristics. Performance requirements of automotive hoses dictate high quality formulations. Such formulations are typically moderately filled, and often use blends of two or more EPDM grades. This article will show how costs can be reduced through the use of higher amounts of lower cost materials (carbon black, mineral fillers and process oil), while properties can be enhanced or maintained.

Very high molecular weight polymer is the key. It is well known that higher molecular weight EPDM enhances strength, hose collapse resistance, compression set and stress relaxation properties. High molecular weight EPDM grades are typically produced as solid dense bales with high levels of oil in the product. This new grade is different. The friable bale product form and low oil content of the very high molecular weight Keltan 13561C allow maximum flexibility for formulators, and fast mixing.

Controlled long chain branching (CLCB) is a technology Arlanxeo has perfected with more than a decade of production experience. Users of CLCB grades have benefited from the process improvements in mixing, as well as excellent extrusion surface and collapse resistance. Keltan 13561C is another of the dozens of Arlanxeo grades utilizing this branching.

This review concentrates on automotive hose specifications. In addition, typical extended formulations are shown, along with resulting properties. Compressive stress relaxation testing is covered, with key compounding techniques that are reviewed, along with processing enhancements.

Experimental

The rubber compounds were prepared in a Krupp GK 1.5E internal mixer (1.5 liter), followed by final dispersion on a 25.4 x 50.8 cm two-roll mill. Rubber, fillers, process oils and other compounding ingredients were used, as listed in the provided formulations. For mixing, unless otherwise specifically described, a filling degree of 68%, a ram pressure of 200 kPa and a rotor speed of 60 rpm were used. The mixer temperature was set to 30°C. An upside down mixing procedure was used, with compounds, carbon black, process oil and then polymer added at the start. At 110°C, the ram was lifted and swept, and at 130°C, the compound was discharged. The curatives were added on the mill tempered at 30°C. Finally, the compound was cut and rolled end-way six times, respectively. Details of the formulations will be provided in the examples presented.

The curing characteristics were obtained using an MDR 2000E rheometer (Alpha Technologies) at 180°C according to ASTM D5289. Test pieces were prepared by curing at 180°C using a curing time equivalent to twice Te(90) as determined by MDR rheology testing. Standard procedures and test conditions were used for hardness (ASTM D2240), tensile strength (ASTM D412), hot air aging (ASTM D573), compression set (ASTM D395), low temperature retraction (ASTM D1329), fluid resistance (ASTM D471), compressive stress relaxation (ASTM D6147), Garvey extrusion (ASTM D2230), and compound Mooney viscosity and scorch (ASTM D1646). Raw polymer characteristics were defined by a Mooney viscometer (ASTM D1646), ethylene content (C2) (ASTM D3900A), terpolymer type/content (ASTM D6047) and oil content (ASTM D5774).

Results and discussion

High molecular weight EPDM

Arlanxeo has been producing many high molecular weight grades of EPDM for decades. Advantages are realized in a variety of application spaces, and the various grades have been tailored to offer maximum advantages for each set of unique requirements:

- Keltan 5465, soft compounds, blend component
- Keltan 5469C, TPV, hose, soft compounds, branched
- Keltan 5467C, TPV, extruded profiles, branched
- Keltan 4577C, TPV, extruded profiles, soft compounds
- Keltan 4869C, soft extrusions and moldings, branched
- Keltan 8550, seals, mechanical goods, branched
- Keltan 9950, sponge extrusions, branched
- Keltan 13561C (new), automotive dynamic seals and hose, branched

The newest grade, Keltan 13561C, has been created to fit a space where no other grade in the market exists. Figure 1 shows a list of commercially available EPDM grades with low oil content. The 100 Mooney viscosity range was considered to be the maximum producible; but in recent years, that boundary was pushed to 130 MU. The Keltan 13561C grade has pushed that boundary even further to 150 MU measured at 125°C. The description of the experimental evaluations to arrive at the grade have been previously published (ref. 1).

The resulting polymer characteristics are outlined in table 1, where one can see only a very small amount of process oil is incorporated into the grade. The mid-level ENB, semi-crystalline polymer has a viscosity of 151 MU without oil, 130 MU with the oil; but reported as 92 MU as a higher 150°C temperature is used to move the measured value in the improved calibration range of the Mooney scale.

Automotive hose specifications

Automotive companies have a variety of specifications for radiator and heater hoses (figure 2). A survey of the specifications
was made, and no standard between the companies was found, but some trends emerged. Table 2 shows the results of parts of the survey, with American, European and Asian specifiers shown.

Requirements for compression set, fluid mixture percentages and fluid aging conditions varied from manufacturer to manufacturer. Additionally, some had requirements for swell in 903 oil, low temperature retraction measurements and compressive stress relaxation.

The trend has been for hardness ranges near 65 durometer A, tensile strength requirements near 10 MPa, and heat and fluid aging requirements eliminating sulfur cure formulations. Thus, subsequent work focused on these general requirements.

Generally, the overall requirements of automotive coolant and heater hoses call for an EPDM compound with moderate filling levels (210-260 phr). Crystalline EPDM is frequently used as a blend component (with amorphous EPDM) to lend improvements in surface smoothness, as well as increases in hose collapse resistance (green strength) (ref. 2). Zinc is avoided in any significant percentage to meet specification requirements intended to address coolant additive interactions, which can lead to deposits inside the radiator. To reduce electrochemical degradation of hoses, conductivity requirements dictate moderating carbon black use, and subsequently using some mineral filler (ref. 3).

Offering good green strength and surface appearance, due to the polymer branching, high molecular weight and semi-crystallinity, Keltan 13561C can be used as a single polymer and reduce factory SKUs or the need for handling a second material.
Economical compounding

Reducing costs by increasing levels of low cost ingredients (carbon black, mineral filler and process oil) typically comes with the compromise of strength, permanent set and force decay (refs. 1 and 4).

In a study comparing a standard high quality heat resistant hose formula with a series of formulas using Keltan 13561C at increased filling levels (table 3), hardness remains unchanged (figure 3), and one can see improvements in strength (figure 4) with direct substitution. But also, strength is maintained or values are well above targets as filler levels are increased. There is no compromise in heat age properties (figures 5 and 6), but improvements in compression set are apparent (figures 7 and 8). The strength and compression set gains are a result of high molecular weight (ref. 4). Swelling in radiator fluid mixtures remains excellent, likely improving slightly due to increases in

![Figure 3 - hardness unchanged](image1)

![Figure 4 - strength improved, maintained or above specification](image2)

![Figure 5 - excellent aging values](image3)

![Figure 6 - excellent aging values](image4)

![Figure 7 - Keltan 13561C improves compression set](image5)

![Figure 8 - Keltan 13561C improves compression set](image6)
chain entanglement density (figure 9). Low temperature properties are better as the overall crystallinity of the formula is decreased (figure 10).

**Compressive stress relaxation**

Polymers placed under stress see a decay of force with time or a change of shape in response to the stress. These effects are known as stress relaxation, or creep.

A common test measuring a form of stress relaxation is compression set, whereby a sample is placed under constant deformation. The stress actually decays as the sample undergoes permanent deformation as a result of polymer chain movements, as well as chemical reactions at high temperatures.

But compression set only measures the shape change, not the change in stress. Seal applications find this stress change particularly important, as stress must be maintained in order to ensure forces are in place to prevent fluid or gas traversing a boundary.

In hoses, seals are important to keep fluids inside the cooling or heating circuit. And many of the seals are simple clamps around the hose, utilizing the hose itself as a seal (figure 11).

Laboratory compressive stress relaxation (CSR) testing does measure the decay in force, and is becoming a commonly specified test for seal applications (refs. 5 and 6). Some requirements for hose are now specified.

CSR testing was conducted according to ASTM D6147, Method B. Samples were compressed (figure 12) for one hour, then sealing force was measured. For various time intervals, the sample compression was maintained at 150°C. After cooling for one hour at 23°C at each time interval, force measurements were taken under compression (figure 13).

Results of many formulations were made (figure 14), and conclusions drawn about best polymer types, as well as formulation adjustments. More polymer rich/low phr formulations (figure 15) with higher crosslink density via increased peroxide and coagent levels (figure 16) performed better.

Crystallinity in EPDM is detrimental (figure 17), while increased molecular weight is helpful (figure 18). It should be noted that testing was conducted according to specification, and
Figure 14 - many CSR tests were conducted examining the influence of polymer make-up and formulation design.

Figure 15 - polymer rich formulations perform better.

Figure 16 - increasing crosslink density improves CSR results.

Figure 17 - increasing crystallinity results in overall worse stress decay.

crystallinity effects could be more carefully studied examining annealing, time and thermal effects for crystallite formation in a method outside of the specification. Still, crystallinity is likely an unhelpful and random factor in an environment with non-constant thermal cycles.

Compounds with the very high molecular weight Keltan 13561C performed best (figure 19). Improvements could likely be found by also increasing the crosslink density (higher peroxide/coagent) levels, and is an area for further examination.

For performance equivalent to the standard 60/40 amor-
phous/crystalline EPDM formulation, Keltan 13561C can deliver this at higher filling levels of +50 phr, or at +100 phr and higher peroxide/coagent levels (figure 20).

**Processing**
The product form of Keltan 13561C is friable bale, which is well known and previously shown (ref. 4) to mix quickly compared to solid bales. The bale easily crumbles and breaks apart (figure 21) into small particles with a high surface area which quickly absorb oil and incorporate carbon black. Large lumps are eliminated.

Upside down mixing shows quick ingredient incorporation with fast mixing in the power curves (figure 22).

In extrusion performance, hose compounds need to process well, but are not the super fast, very smooth extruding compounds, like an automotive seal. They need to process, but also not collapse.

Garvey die curves of several compounds are shown in figure 23. The standard compound at 242 phr is shown at the top. A formula which switches to the very high molecular weight Keltan 13561C is rougher in appearance, as the Mooney viscosity increases. But higher extension levels (294, 344 and 416 phr) are smoother in appearance, and become better than standard as filling level increases.
Many hose formulations possible

Keltan 13561C can be used in automotive heater and coolant hose formulations, but also other automotive and industrial hoses. From soft compounds to high quality hoses to low cost types, table 4 shows some of the range of possibilities.

Conclusion

Keltan 13561C was originally targeted for seal formulations, where very highly extended formulas could successfully meet high compression set and tensile strength specifications.

Hose applications can take advantage of some of the same polymer attributes. The long Arlanxeo history of successful commercial branching technology has been applied to this very high molecular weight grade.

The molecular weight of this grade is greater than any other commercially produced, low oil content EPDM. Mooney viscosity of the polymer alone is in the 150 range.

Automotive specifications have been shown, as well as formulations targeting these, which can benefit productivity and lower compound costs.

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References