Methods to predict processing behaviour for cross linking polyolefin compounds by extrusion and Rheometer

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ABSTRACT
When extruding crosslinkable compounds the productivity of the process as determined by the length of run is largely dependent on low levels of scorch formation. Scorch is a deposit formed due to premature cross linking. It may be released as particles and lumps into the product and thereby jeopardize the quality. Mechanical properties will suffer unacceptably for high quality pipes and electrical properties for high voltage cables will become degraded. A method to use Rheometer measurements to simulate extrusion behavior, comparisons with a small scale extrusion and experience from full scale cable production will be presented. These results show that rheometer tests are indeed useful for determining critical rheological behaviour. Furthermore these test may be used to compliment full scale tests.

INTRODUCTION

Crosslinking of polyolefin's improves the use temperature range and gives excellent stress cracking resistance. Materials crosslinking by irradiation and condensation of copolymerised or grafted vinyl silanes are used for a variety of applications but in general not for thick sections. Peroxide crosslinking is the most common for cables used from 12 kV to 500 kV. It's also used for XLPE pipes and gaskets. Cables are made by coextruding an inner semiconductive XLPE on the conductor, the insulation on the inner semiconductor and an outer semiconductive shielding XLPE. Three extruders are used for this process. The cable is passing through a vulcanisation tube heated to up to 260°-300°C.

Fig. 1 150 kV cable with the layers from outside in. Outer PE-shielding for mechanical protection, Lead shield diffusion tight to water, outer semiconductor, XLPE-insulation, inner semiconductor, stranded copper conductor

In general the higher the voltage is the thicker the insulation and semiconductive sheeting's need to be and the slower the line speed has to be to allow sufficient heat transmission to cure the inner layer of the cable. Thus developments to get high speed resins[1,2] increase the productivity but also the risk for premature crosslinking and formation of deposits in the extruder. They may come off and give defects in the shielding or insulation layers. The semiconductive shielding is used to smoothen the electrical field gradient and to minimize the effects of defects on the conductor and in the insulation layer.

Fig.2 Cable line dismanteled showing stranded conductor for 20 kV and two of the three extruders used for three layer extrusion.

The surface smoothness and cleanliness[3] of the semiconductive material used has a great influence on the electrical properties of the cable. The smoothness of the interface between insulation and semiconductive layers is very critical. Protrusions from the semiconductive layer into the insulation will give locally enhanced electrical stress and a higher risk for tree growth. In this situation the concentration, shape and size of the defects all play a role in enhancing the local electrical stress; which leads to a higher probability of electrical failure. Thus materials that are less prone to scorch offer significant performance benefits.

A measuring technique has been developed to check the interface in extruded cables. With this instrument it is possible to detect, investigate and mark irregularities as pips, lumps, protrusions, voids etc. found in the insulation and inner semiconductive layer of a cable for further chemical analysis. The outer semiconductive layer of the cable is removed and the rest of the cable is immersed to hot paraffin oil. The crystalline part in the insulation is melted and it becomes totally amorphous and transparent, fig.3.

Figure 3. Hot oil test, example of lump in inner semiconductive layer, width 0.5 mm, height 0.05-0.1 mm.

HOW TO SECURE HIGH QUALITY

The high voltage cable needs only one defect to have an electrical break through. Such a failure scraps the whole cable length. However productivity demands that there are only few stops for cleaning and that long length of cable can be made. The insulations and semicons have therefore been developed to allow long runs. Methods for development and control of scorch properties are needed. The cable works needs a week and several tonnes of material to find out in production if a material is good. The cure properties and the scorch properties are both important.

Scorch testing

Tedious empirical work with laboratory extrusion could be used to correlate with full scale cable production.

This test is designed to quantify the degree of scorch, which occurs during extrusion. It accelerates scorching; producing in a few hours a degree of scorch which in normal operation would take several days to build up. A laboratory extruder is used with a special designed die for evaluation of scorch in the die (figure 4). A die with a relative long channel (constant diameter) and a long residence time is used.

The test can be carried out at a range of selected temperatures with a constant output. The material is run continuously for at least 5 hours. After the test the hot sample in the die is taken out and its content, the carrot, is analysed to give the scorch percentage (figure 4, 5). Complete analyses may take a week.

The amount of scorch is measured in the sample, by examining 0.2-0.3 mm cross-sections taken from six different positions. The volume of scorch in the six cross sections is measured by the use of a microscope. The mean value of the six cross sections is reported. This test is often referred to as "The Carrot Scorch Test" as a result of the shape of the sample from the die[4].

Figure 4. Die used in "The Carrot Scorch Test".

Figure 5. A typical "Carrot".

The testing shows a linear relation between temperature and scorch over a big enough range to allow single point testing for control of standard materials with well known characteristics.

A single point analyses needs one working day and about 10 kg's of material

RHEOMETRIC METHOD TO EVALUATE CURE AND PROCESSING PROPERTIES

Methods to evaluate the cure behaviour have previously not given information on the scorch behaviour. The peroxide crosslinking takes the material from liquid to solid stage during the processing by formation of a three dimensional network. The test equipments therefore have oscillating plates or cones with controlled temperature. The geometry is made to give good torque transfer also to the solid.

Fig. 6 Monsanto Moving Die Rheometer, MDR, die with pellets and compression moulded specimen.

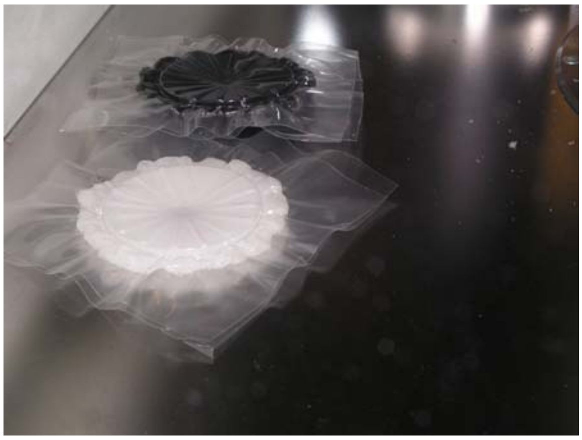

Fig.7 Specimens used in the Göttfert with imprinted pattern from the instrument.

Fig. 8 Instruments to measure cure behaviour; Göttfert, Monsanto MDR and Monsanto ODR

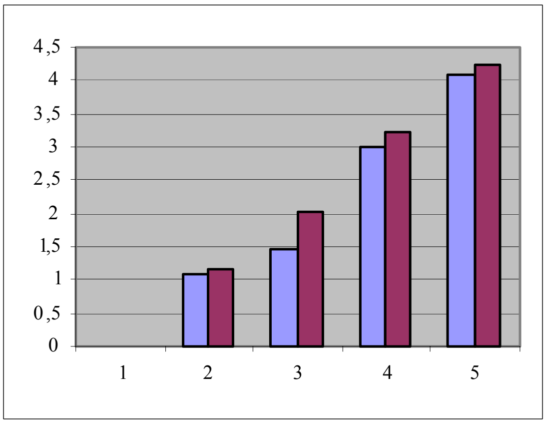

Fig. 10 Time, min., to reach curing stage 2, 20% of maximum; 3 50%; 4 80% and 5 90% of maximum for A and B at 180° C

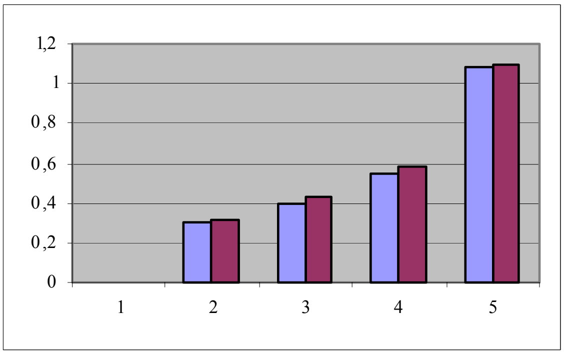

Fig.11 Time, min., to reach curing stage 2, 20% of maximum; 3 50%; 4 80% and 5 90% of maximum for A and B at 200° C

Insulation materials.

XLPE insulations are made unfilled and with extremely high purity to have optimum dielectrical properties. Vulcanisation is evaluated by testing with a Göttfert rheometer at 180° C and Monsanto Moving Die Rheometer, MDR at 200° C, fig 9.The development of viscosity/torque over time gives good correlation with how high degree of crosslinking that will be achieved with proper processing conditions Both insulation A and B, development for high performance, have sufficient curing properties to be used continuously at elevated temperatures typically 60 to 90°C but short time up to 120°C.Increasing the test temperature to 200°C does not change the similarity in behaviour, fig.9 to 11

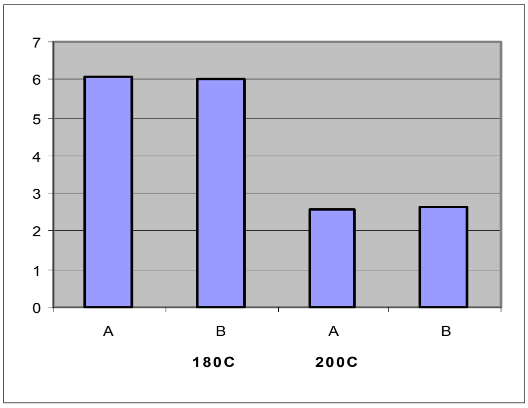

Fig. 9 Max. torque Nm at 180° C by Göttfert Rheometer and at 200° C by Monsanto MDR.

The cure development for the insulations are fairly similar and offers no clear judgment on which one to select to minimise scorch. The carrot method shows that B is less scorchy than A, fig. 12, which is also confirmed in full scale cable production

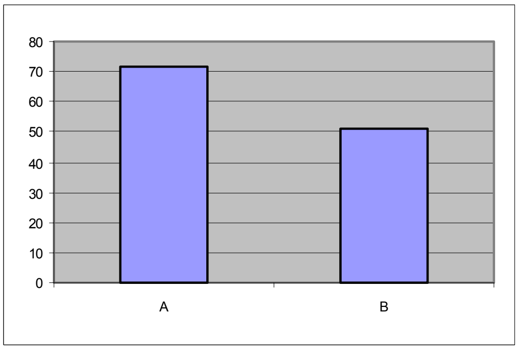

Fig.12 Volume % of carrot scorch after 1 day extrusion trial Insulation B has less scorch than A

Testing for longer times at lower temperature has previously not been considered because it takes much longer time to full cure and could give irrelevant information on the cure characteristics. However it could be interesting to look at the differences between materials, fig. 13.

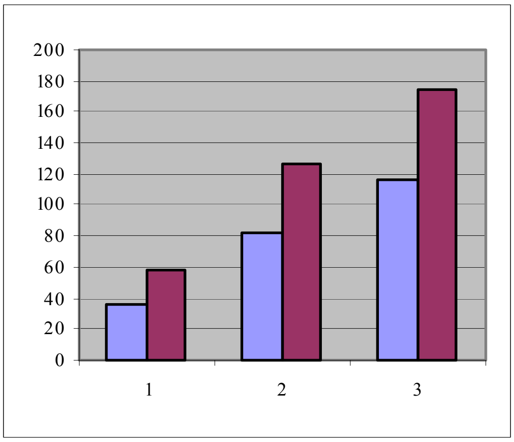

Fig.13 Time, min., to give torque 1, 2, and 2, 5 dNm at 140°C. Monsanto MDR

Already after 2 hours insulation B differentiate from A showing 50% longer time to torque 2 dNm, 126 min. vs. 82, but having about the same time to cure to 90 % of maximum. Maximum was approx 6 Nm for both formulation at 180C and 1.1 at 200° C, The improvement in time to torque 2 dNm and decreased volume % of scorch measured by the carrot scorch method corresponds well with the experience from cable works where B is the preferred material for long production campaigns.
With B time to shut down for cleaning can be doubled

Semiconductors
Semiconductors are made by using high filling loads of conductive carbon black .The behaviour for semiconductors should be more difficult to interpret than that of insulation materials because of the added complexity by particle-particle, particle-resin and coupling interactions. A series of commercial and developmental standard and high performance grades have been tested from rheometric to full scale fig.14, 15.

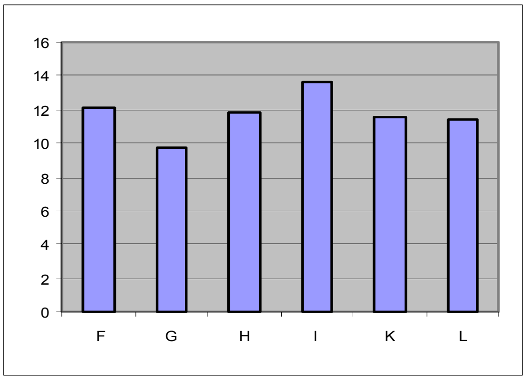

Fig.14 Max torque Nm at 200° C for semiconductors. Monsanto MDR

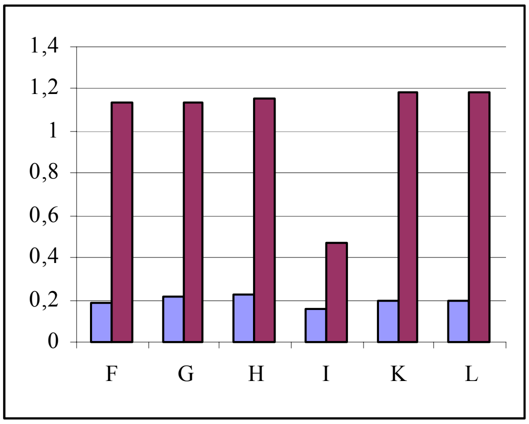

Fig.15 Time, min., to 10 % and 90 %) of max torque at 200°C

The crosslinking is highest for material I and lowest for semiconductor G although they all give crosslinking enough for the application. The time to 90% of maximum torque is about the same, 1 min. for all the formulations except I which is significantly faster, 0.5 min. Fig 15. How will the scorch behaviour be?

Testing at 140° C with the moving die rheometer was used to predict the scorch formation, fig.16. I is by far the fastest to all torques. G and H comes out about the same at torque 6 but G takes much longer time to torque 9 because it’s close to the maximum torque for G. Thus torque 9 is to close to the span of maximum torques to be useful.

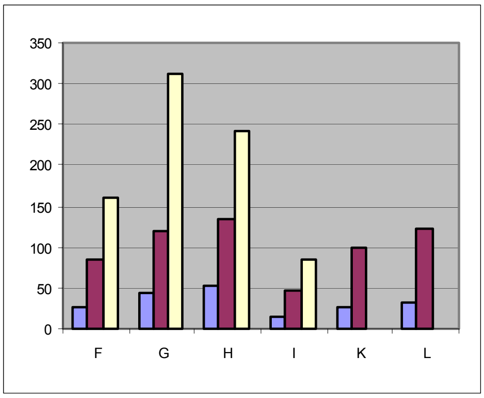

Fig.16 Time, min., to torque 3, 6, and 9 Nm for semiconductive materials MDR at 140°C

Looking at time to torque 3 Nm H and G should be best with 54 and 45 minutes L with 33 minutes. should be better than F with 26, minutes K with 25 minutes and I worst with less than 14 minutes. fig 16.Time to torque 6 ranks H as best with 135 minutes followed by L 124 minutes., G 120 minutes., K 100 minutes., F 86 minutes. and I 46 minutes.

The carrot scorch test was done with target 134°C melt temperature for comparison with the rheological testing

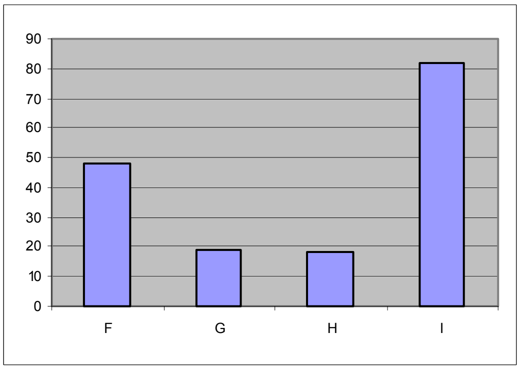

Fig.17 Carrot scorch % by volume at 134° C for semiconductors F; G; H and I

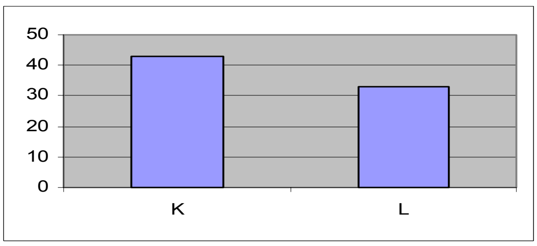

Fig.18 Carrot scorch % by volume at 135° C for semiconductors K and L

The carrot method ranks the materials from best G, H, L, K, and F to I being worst. Fig.17 shows that G and H performs approximately the same in scorch at 134° C with a little less than 20 volume %, F, 48%, is worse and I with more than 80% worst. K,43%, is worse than L,33%, at 135° C., fig.18 and both are less scorchy than F. Both by the rheometer method and by the carrot extrusion the low scorch materials are identified as G and H, L as better than K and F and I as the worst, tab. 1.

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Formulation	Vol % scorch	Formulation	Minutes to 3 Nm
G/H	18	H	53,9
H/G	19	G	44,9
L	33	L	33,2
K	43	F	26,3
F	48	K	25,1
I	82	I	14

Tab. 1 Volume % carrot scorch and minutes to torque 3 Nm. Ranking from best to worst.

The full scale production with the materials confirms the ranking by the carrot and rheometer methods.

CONCLUSION

Testing at 140° C and using time to reach specific torques from 3 to 6 Nm gives results that correlate well to full scale cable production and laboratory scale extrusion test method. The rheometer testing secures high quality and is accurate enough for a more speedy development of XLPE for the future materials with the improved scorch performance required for high quality materials.

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