

The Influence of the Polymers' Quality Parameter Long Chain Branching to the Mixing Process Being Controlled by the MixCont System

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1. Abstract

The purpose of the study presented in this paper was to investigate an advanced mixing control system called MixCont. The system was investigated concerning its possibilities to adjust the mixing cycle to perform constant mixing quality although polymers were used having varying parameter specifications. The parameter varied in this investigation was the long chain branching level of EPDM polymers, which is characterised by the $\Delta\delta$ parameter.

The recipe used in this investigation is an EPDM based two step mixed compound for a brake membrane application for the automotive industry. The systems actions to adjust the different polymer performance properties were controlled by testing the compound properties and by analysing the mixing curves. The tests were the standard tests done in the rubber industry and additional two advanced test methods, which were the RPA and the RELMA method.

Due to earlier findings of the existing influence of the long chain branching level to the mixing process it can be stated that the system managed to even out differences in the compound quality. The system calculated different mixing schedules according to the type of long chain branching of the polymers.

As a general conclusion of this study it can be established that the polymer having the highest long chain branching has the best processing behaviour in comparison to the more linear polymers used.

The high-branched polymer has advantages concerning the consumed mixing energy to reach good mixing quality characterised with the traditional test methods in the rubber industry in the used mixer type.

A trend for the mixing behaviour in the terms of mixing time and energy consumption could be detected. In the beginning the more linear polymers have better and easier mixing performance. The mixing behaviour of the total mixing cycle showed the opposite picture of what we get by looking at the crumbling phase. The higher branched polymers have shorter total mixing times and less total energy consumption during the mixing cycle. It can be stated that with increasing mixing time the dispersion level and mixing behaviour of the more branched polymers turned out to have better values.

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2. Introduction

The mixing process for the production of technical rubber compounds is a complex process and is depending on several influences. Due to the huge influence of the raw material quality parameters in combination with the mixing process to the compound and end article quality a sophisticated mixing control is a major request for the rubber industry. An advanced mixing control system enables the possibility for the production of constant batch-to-batch quality, which is very important for a good processability in the next process chain stages.

One solution for an advanced process control system controlling the mixing process is the MixCont system. This system will be tested in the following study in combination with varying the long chain branching level of the polymers.

Since the polymers are the basic ingredients in every rubber compound they have large influence to the whole process chain. For this reason, parameter variations of polymers can be expected to have a big impact on compounding, further processing as well as on end article properties.

In this investigation the focus was put on three EPDM polymers with varying $\Delta\delta$ values. The $\Delta\delta$ value characterises the polymers long chain branching level. High $\Delta\delta$ accompanies a low degree of long chain branching, which indicates linear polymer structure, and vice versa.

Often the characterisation of EPDM polymers is given more roughly by showing the Mooney viscosity, ethylene and propylene content, diene monomer type and content and oil type and content. The molecular weight distribution is divided into the three major groups broad, medium, and narrow. [1]

The influence to the mixing process is depending how the structure of the polymers looks like. Molecular weight and weight distribution, composition, crystallinity, distribution of monomer units within a chain, and the extent of long chain branching are the most interesting characteristics. Broad molecular weight distribution or high branching level is known for high dispersion levels after longer mixing times with lower cure rate and crosslink density but higher compression sets at increased branching levels [3].

This mixing behaviour can be explained by analysing different stages in the mixing process inside the mixer chamber. The process starts with the crumbling of the polymers. In this phase less energy needed to lower the viscosity of the more linear polymers and to enlarge their surface for the next process step when compared to the more branched polymers. The surface enlargement is necessary for the wetting of the filler. In the next process phase, the start of the carbon black incorporation, a multi phase system can be found in the mixer. This system consists of the polymer the carbon black and some chemicals. The mixing during this phase is characterised by wall slippage effects due to the different adhesion behaviour between the fillers, the chemicals, the polymer, and the system to itself or to the chamber wall. The adhesion within this system is higher than the adhesion to the chamber wall, which leads to wall slippage. This slippage prevents laminar mixing for which the dispersive mixing cannot proceed during this phase, since this type of mixing needs high shear and strain stress.

The dispersion starts not until the incorporation is finished which is the so-called black incorporation time (BIT). After the BIT the dispersive mixing with the laminar mixing effects starts.

The study described in this paper handles the possibility of the MixCont system to react to the variations of the quality parameter long chain branching of EPDM polymers with respect to its processing behaviour. The mixing performance and compound properties are taken into account to compare the polymers. The chosen two step mixed EPDM recipe for the investigation is used for brake membranes in the automotive industry. Mixing trials on a 315 litres intermeshing mixer equipped with the MixCont system were performed to analyse the controlling of the process and with this the compound quality by the system MixCont.

3. Experimental

3.1. Ingredients

For the selection of the polymers for this investigation the Mooney viscosity was the decisive parameter. The Mooney Viscosity was defined by the viscosity of the original polymer used in this recipe to enable the mixing of compounds having almost the same quality as the standard compounds to get a good and broad comparison by calling in the production results to compare the study results with. All polymers chosen for this investigation are as constant as possible concerning all specification parameters except the $\Delta\delta$ value.

In the following table the specifications for the polymers are shown. The three chosen polymers are KELTAN 4703 Z with the highest degree of long chain branching, the Buna EP G 6850 with the medium degree of long chain branching and Buna EP T 6850 with the lowest degree. The remaining parameters as the ENB content is about 8 wt% for the polymers and the Ethylene content is in a range from 48 to 51 where KELTAN has the lowest value.

Table 1: *Polymer specification.*

Polymer	Mooney ML(1+4)125°C	ENB [wt%]	Ethylene- Content [wt%]	Morphology	$\Delta\delta$ [°]
Buna EP T 6850	60	8	51	Amorph	43
Buna EP G 6850	60	8	51	Amorph	31
KELTAN 4703 Z	65	9	48	Amorph	25

To define the degree of long chain branching the company DSM established a new parameter called $\Delta\delta$ (delta delta). The derivation of the parameter is based on the dynamic mechanical testing. The difference of two-phase angles at two different frequencies is taken to characterise the compound or polymer. In the following Figure a frequency sweep for an EPDM polymer is shown.

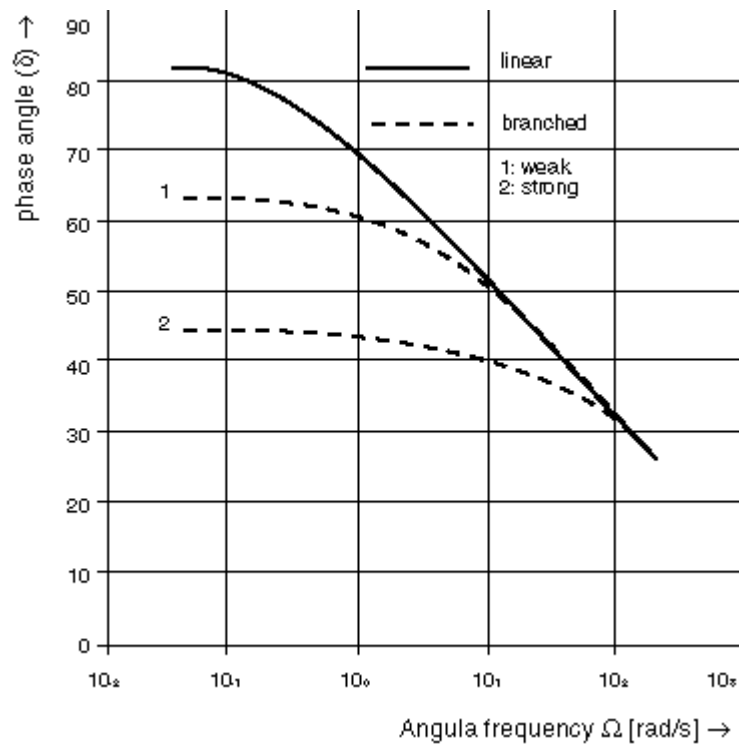


Figure 1: Frequency sweep of an EPDM-Polymer [DSM 99].

The parameter $\Delta\delta$ is defined as the difference of the loss angle at low frequencies and the loss angle at high frequencies measured with a rubber process analyser (RPA) at 125°C, 0,5 deg amplitude and a frequency sweep from 0,1 to 180 rad/s and presented in a frequency sweep

$$\Delta\delta = \delta [10^{-1}\text{rad/s}] - \delta [10^2\text{rad/s}]$$

With increasing degree of long chain branching the parameter $\Delta\delta$ decreases due to the more elastic behaviour at low frequencies and the parameter increases with decreasing degree of long chain branching.

In the next table the used recipe for this investigation is shown. The recipe is an application for the automotive industry with EPDM as base polymer, carbon black as filler and peroxide as crosslinking agent.

As no further adjustments or changes were done with the recipe than varying the type of EPDM polymer there will not be any more detailed discussion about the used recipe.

Table 2: *EPDM recipe.*

Ingredients	Parts / phr
Polymer: EPDM, Butyl	87, 13
Fillers: Carbon black	45,7
Plasticizers: Oil	1,74
Chemicals:	1,74
Total:	149,18
Finalbatch	
Masterbatch	149,18
Crosslinking system:	7,67
Small chemicals	6,75
Total	163,6

3.2. Mixing Equipment

The mixer used in this investigation is a Francis Shaw K7 315-litre production mixer equipped with the process control system MixCont. The mixer is an intermeshing mixer with a hydraulic ram and a mill as next down stream equipment. The mixer is equipped with automatic carbon black feeding as well as automatic oil feeding. In the next table the specifications of the mixer are shown. The mixer is water cooled in several separate cooling circles like the rotors and the chamber.

Table 3: *Mixer characterisation K7.*

	K7
Chamber volume	315
Rotor geometry	NR5
Max Ram pressure	5,4
Var. Rotor speed	Yes
Cooling control	Yes
Process control	Yes

The computer controlled mixing control system MixCont was developed to enable a more efficient and steady quality in the rubber production. The system was developed for the technical rubber industry having high demands to the produced quality. It is an additional tool, which can be installed at top of a conventional process control system. The system is a self-teaching mixing program, which works with real time simulation and calculation. Changes during the process are recognised and adapted to fulfil the quality requests, like viscosity, dispersion or curing properties, which is very important for the following process steps.

The system does not follow the standard way of process control system like performing a constant temperature increase or energy consumption it adjusts the process by calculating special control demands with mathematical algorithm. The adjustment calculations are based on the system experiences made during the

before mixed compound of the same recipe. The changes are made smoothly and not directly in the next batch. Therefore it is necessary to mix several compounds to give the system the possibility to carry out all the calculated changes between the different polymers.

These requests are even fulfilled at varying ingredient parameters (like polymer LCB) or varying start conditions.

The parameters MixCont is working with to control the mixing process are the

- Mixing time
- Rotor speed
- Ram pressure
- Number of ram lifts
- Material feeding

Additional to the computer controlling the compounder still has the possibility to influence the process manually. Some information are a must input for the system as dump temperature or the order of material adding. But the determination of when what should happen could be fully is controlled by the system itself. The compounder has also the possibility to partly control the process. Like it was done in these trials, where the compounder controlled the with his data input the first 90 seconds of the mixing process by determining the speed and ram lift time.

3.3. Mixing Procedure

The process procedure is divided into two parts a passive controlled MixCont part and the active controlled MixCont part.

The base-mixing schedule used for this recipe is shown in the table 4. The recipe is mixed in a two step process. The first step starts with the polymer crumbling where only the polymers are feeded to crumble them before the carbon black and the chemicals are feeded. During the further masterbatch mixing step the carbon black and chemicals are added. The next ram lifts during the mixing cycle are done both for the adding of chemicals and to enable the moving of the compound inside the mixer chamber to get increased laminar mixing for good mixing qualities.

In the second stage only the crosslinking agents are added to the masterbatch compound.

The process is at first time and then temperature controlled. The dumping temperature for the masterbatch is 135°C and 105°C for the finalbatch.

The fill factor for the masterbatches was 67% and for the finalbatches the fill factor was 65%.

Altogether 14 masterbatches and 14 finalbatches were mixed. The trials started with mixing 6 batches with the most linear polymer EP T, continued with mixing of 4 batches with the medium branched polymer EP G and finished with mixing of 4 batches with the most branched polymer KELTAN to keep a certain order of the mixing behaviour due to the different degrees of branching.

Table 4: *Mixing schedule for the masterbatch and finalbatch.*

Step	Rotor Speed / rpm	Cumulated Mixing Time / s	Temperature / °C
Masterbatch			
1 Feeding Polymer + Chemicals	70	-	-
2. Polymer Crumbling	70	-	-
Feeding Carbon Black	25	30	-
4.Mixing	25-50	90	100
5.Feeding chemicals	25-50	-	100
6.Cleaning	25-50	-	120
7.Dumping	25-50	-	135
Finalbatch			
1.Feeding Masterbatch + chemicals	18-35	-	-
2.Mixing	18-35	30	-
3.Ram lift	18-35	60	-
4.Ram lift	18-35		90
5.Dumping	18-35	-	105

All batches were afterwards milled as short as possible with a mill gap of 10mm just to enable the storing and the finalbatch feeding so the influence of the milling was kept as small as possible. Of every mixed compound both of the masterbatch and the finalbatch a sample was taken and tested. At the masterbatches only the Mooney Viscosity was tested where as at the finalbatches the standard production quality tests and additionally the RELMA and RPA tests were performed.

During the first four minutes cumulated mixing time the process was controlled by the data input of the compounder by demanding a certain speed level and certain time for the ram lifts and material feeding. First after 3 minutes total mixing time MixCont took over the total process control. Within the first 90 seconds of the active mixing time the system could only read the different behaviours of the three EPDM compounds to react on these in the rest of the mixing cycle for performing an equal a constant batch to batch quality. This passive MixCont time was in this case demanded by the compounders but is not absolute necessary for the system to get good mixing process control.

3.4. Characterization

For the characterization of the compound quality the standard test method in the rubber industry were used. The tests were done at the laboratories at Trelleborg. The methods used for the characterisation of the masterbatch and finalbatch quality are the Mooney Viscosity tested with a Monsanto MV 2000E at 125°C for 4 minutes. The rheological tests were done with a Monsanto Rheometer 2000E at 175°C and 10 minutes test time. The hardness in Shore A was tested with Fritsch equipment. The density tests were done with a Monsanto Densitron 2000. At last the tensile strength and elongation at break tests were done with a Monsanto Tensometer 2000.

The Standard methods are:

- Mooney @ 100 °C ML (1+6), ML (1+8): ISO 289
- Rheometer MDR 2000, strain: 0,5°, 175 °C: ISO 6502: 1991
- Hardness Shore A: DIN 53505
- Density: ISO 2781: 1988
- Tensile Strength: ISO 37: 1994
- Elongation at Break, Break Resistance: ISO 37 Dumbbell spec. type 3
- Modulus M 100/200
- Tear Resistance, Tear Strength: ISO 34
- Compression Set 100 °C, 24h, 25%: ISO 815: 1991

Additional to these standard methods also the new test methods RPA and RELMA were performed at the batches to compare the mixing quality. The RPA tests were done at the University Pierre et Marie Curie at Paris and the RELMA tests were done at the University of Paderborn.

The RELMA unit is a pulsed laser beam, which produces plasma on the surface of a sample. The material ablates from the surface and enters a plasma cloud. The electrons of the outer orbits are brought to a higher energy level with an unstable condition. Going back to a lower energy level specific radiation is emitted. This radiation can be detected by spectroscopic methods. As the measuring time is quite short, the system can work with a frequency of 25 Hz. By scanning the surface, the content of chemical elements at each measured spot can be indicated. By statistical methods, the distribution of the elements in the surface can be determined [10].

The tests made at the batches are the mean value of intensity between sulphur and carbon black and between zinc and carbon black as well as the variation coefficient for both values.

The RPA tests, which were done with the RPA advice at Paris, are a method to characterise the viscous and elastic properties of compounds and polymers. A frequency sweep at a constant strain to carry out the viscous and elastic moduli G' , G'' and the $\tan\delta$ values. The tests are carried out at a temperature of 100°C and a strain of 0,5 degrees.

Finally, besides the characterization of the compound properties even the final product properties were analysed. Therefore brake membranes were produced at the laboratory at Trelleborg Ind AB and then tested at VW in Wolfsburg with the standard test methods for this type of product.

- Hardness / Shore A before and after aging
- Tensile strength / Mpa before and after aging
- Elongation at break / %
- Modulus (100 % elongation) / Mpa
- Tear resistance / N/mm (DIN 53507 A)
- Compression set / % against PV 3307
- Deformation 50 %, 22 h/140 °C

All tests were performed before and after two aging processes at 140°C at 46h and 500h.

3.5. Results and Discussion

3.5.1. Analysis of the Mixing Process

The mixing curves presented in the following are always the last mixed batches in the series with each of the three polymers. This procedure was chosen because the system needs some batches to adjust the mixing process to the changed raw polymer parameters. The adjustments were not done direct in the first mixed batch but step by step during the next mixed batches to avoid making changes for just short-term property variations. And in the series by mixing at least 4 batches with the same polymer the changes due to the different mixing behaviour were carried out more or less completely at the last mixed batch. By taking only the last mixed batch into the evaluation the differences between the three different polymers come best visible.

The first Figures show the mixing curves of the masterbatches.

The mixing curves, which are shown, represent all actions at the mixer during the mixing trials. As there is the time between the single mixing cycles and the mixing itself. The time scale on the x-axis is the total mixing time.

The first curves are the masterbatch mixing curves, showing the power and temperature curves.

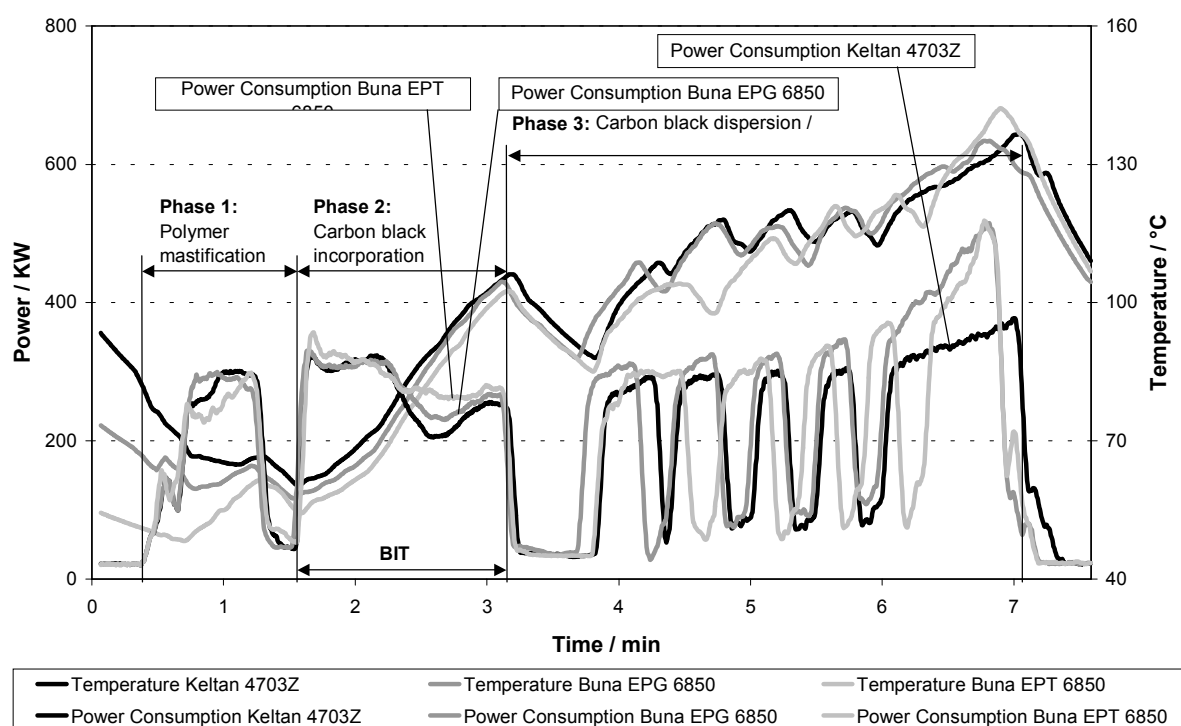


Figure 2: Power and temperature curves of the three last mixed masterbatches

The first 50 seconds are the phase between the mixing of two batches and do not belong to the actual mixing cycle of the compound. The mixing process starts with the start signal given after 50 seconds of the operation person at the mixer. Then the first 30 seconds belong to the crumbling phase and after the first ram lift the carbon black is added and the carbon black incorporation starts.

There are two characteristic parts for the different used polymers in these mixing curves. At first the behaviour of the different polymers during the crumbling phase which is performed during the first 30 seconds of the mixing cycle. Then the next interesting part is the direct following sequence of the carbon black incorporation.

During the crumbling phase the polymers having the highest degree of long chain branching consume most energy and the more linear polymer EP T consumes less energy during this phase.

Then in the next mixing phase during the carbon black incorporation the more branched polymer KELTAN consumes less energy than the linear polymer EP T. The difference between the EP G and the KELTAN is in general not that big due to the smaller difference in the degree of long chain branching.

The curve of the KELTAN shows pronounced concave curve behaviour in comparison to the two other more linear polymers. The more concave the curves run the better is the degree of carbon black incorporation. The better the carbon black is incorporated the faster decreases the power consumption due to the more decreasing viscosity than with free carbon black in the mixer.

The increasing power at the end of the mixing cycle appears due to the fact a dumping temperature of 135°C should be reached and with the calculated power respectively speed level this was not possible in a reasonable mixing time. Therefore the speed was increased to reach the demanded temperature faster. It is also a sign for the mixing behaviour of the three polymers that the more linear polymers need higher speed levels than the more branched polymers. This points at the known theory that the more branched polymers are more difficult in their processing behaviour in the start phase but proceed better mixing behaviour and though better dispersion levels at the end of the mixing cycle. [1] [2] [7] This more difficult processing behaviour in the beginning of the mixing process was attempted to minimise by the company DSM by adding some amounts of zinc stearate to the polymers. Zinc stearate acts as processing aid in form of relieving the brake down of the polymer chains during the crumbling phase. [11] This higher amount of zinc stearate in the Keltan polymers in comparison to the Buna polymers is shown in the RELMA results in picture 12.

In the next Figure the energy consumption during the crumbling phase, the carbon black dispersion phase and during the total masterbatch mixing cycle is shown.

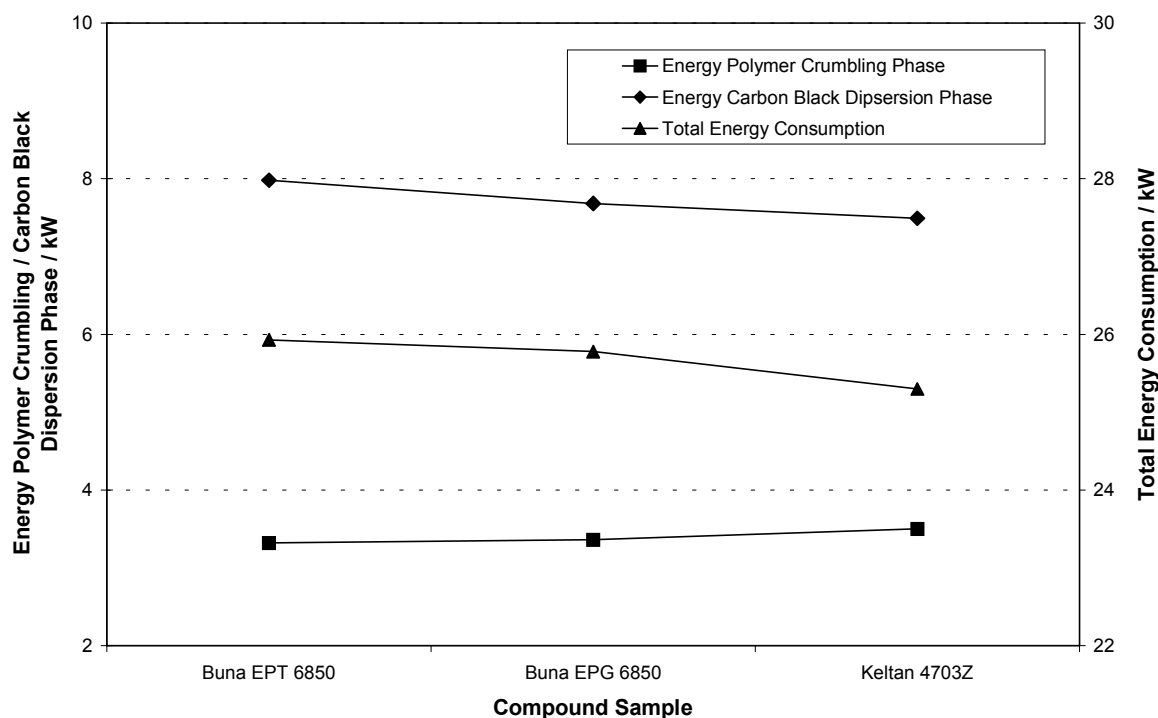


Figure 3: *Energy consumption during the masterbatch mixing.*

The Figure supports the above mentioned mixing behaviour of the different degrees of long chain branching levels of the three polymers.

The KELTAN with the highest degree of branching consumes most energy during the crumbling phase but in total less energy in comparison to the two other polymers. And the EP T the most linear polymer behaves exact the opposite way around with less energy consumption during the crumbling phase but the highest energy consumption in total.

With increasing degree of long chain branching increases the energy consumption in the crumbling phase but decreases the total energy consumption. This is as it was written in the literature that more branched polymers have more difficult mixing behaviour in the beginning of the mixing cycle but reach better dispersion levels in total than the more linear polymers. [1][4]

The mixing behaviour can be made visible by the idea of a layer structure of the polymers. If the polymers have low $\Delta\delta$ this means they are more linear and in this case the single layers slip by another at low shear rates because the connection in between them is not that big. If the polymers are more branched the single chains have higher adhesion to another and though it is more energy necessary to entangle them, which ends in higher energy consumption. With ongoing mixing they offer higher surfaces are for the carbon black wetting which ends in better dispersion levels and then in better compound qualities.

The following Figure includes the ram position and the speed level of the masterbatch compounds.

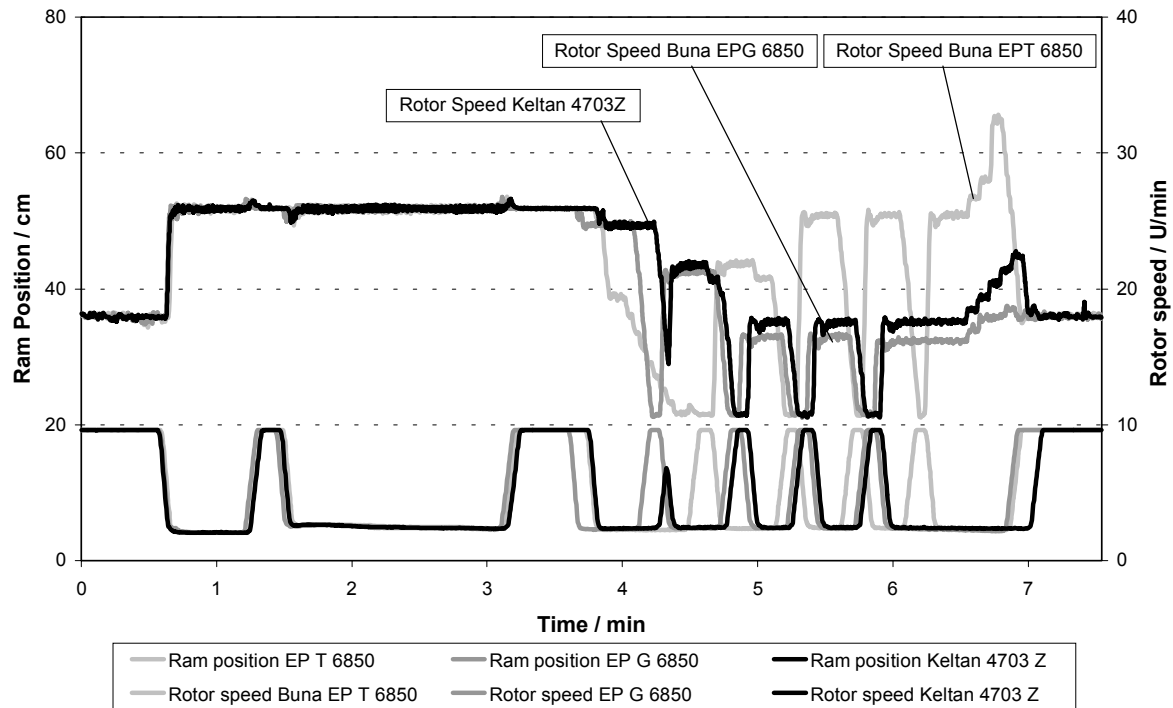


Figure 4: Rotor speed and ram position curves of three masterbatches.

At this Figure the passive control phase of the MixCont system can be observed. The compounder controls the first 3 minutes or the first two ram lifts with his certain data input for the system and after this point the system takes over the active control of the mixing cycle. In the beginning the speed level is kept constant before MixCont adjusts the speed and the ram lifts to its calculations.

This Figure shows the different behaviour concerning the speed level of the three polymers in the active MixCont control phase. The more linear polymer has lower speed in the beginning of the active MixCont mixing cycle but higher speed levels to the end of the cycle. Where as the more branched polymer KETLAN behaves the opposite way.

This can be again explained with the mixing behaviour mentioned in the literature about the easier process behaviour during the polymer crumbling but the poorer reachable dispersion level of the more linear polymers. [1] [3] Therefore the system calculated higher speed level to increase the energy input to the end of the mixing cycle to get good mixing quality and to reach the demanded dump temperature within an acceptable time.

The following Figure shows the power and temperature curves of the finalbatches belonging to the before shown masterbatch curves.

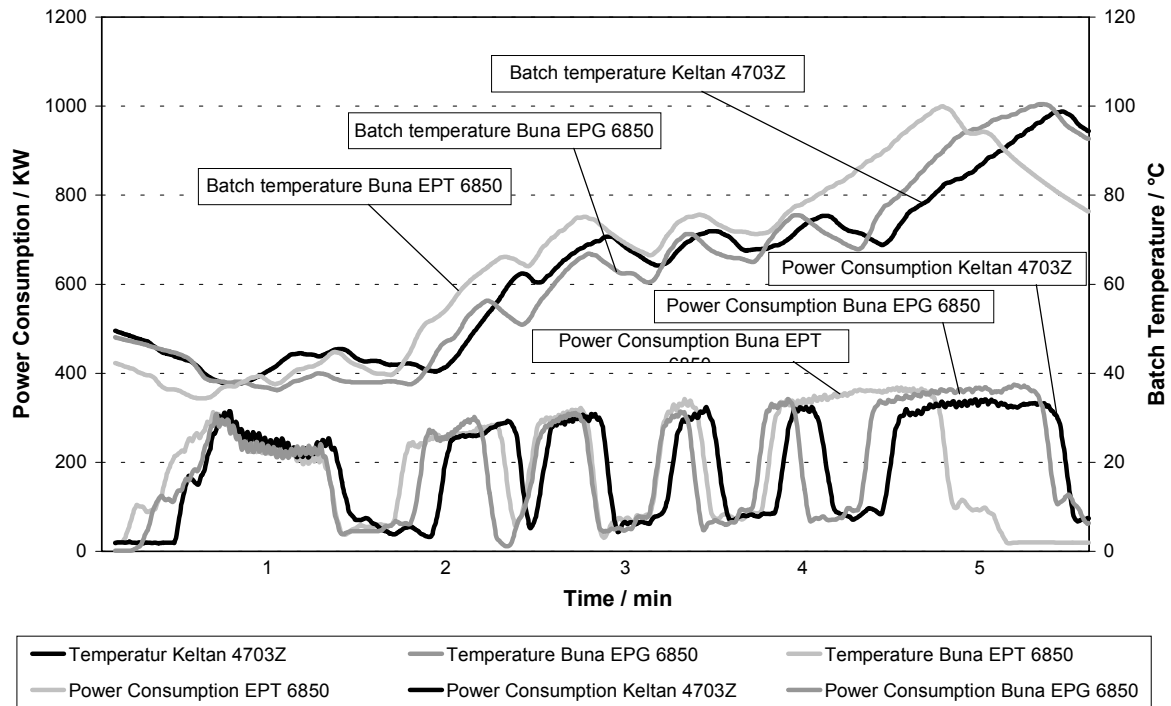


Figure 5: *Power and temperature curves of the Finalbatches.*

This Figure illustrates how the MixCont managed it during the masterbatch mixing to adjust the polymers influence to the mixing process so that no more differences are detectable in the finalbatch mixing. The power curves look almost the same and deviate only in between a very small range. The differences in the mixing time can be attributed to the varying start times, which means when the system received the start order from the machine personal.

The large differences in the polymers mixing behaviour appearing during the masterbatch mixing could be reduced almost completely by adjustments calculated by the MixCont system. Therefore more or less identical mixing curves can be observed during the finalbatch mixing.

3.5.2. Analysis of the Compound Properties

In the following the test results of the tests made at the laboratories concerning the compound properties are presented.

The tests were preceded both at the master and finalbatches before and after milling. But due to the fact that the milling had no bigger influence on the interesting compound properties, they are not shown in detail in this report. Even the test results, which had not efficient importance for the understanding, are not shown in detail.

For most of the test all batches are taken into the evaluation to show up the trend during the changes of the MixCont system with mixing the four batches. With every new mixed batch the system adjusted the mixing cycle a little bit to fit better for the used polymer. How good these changes made bit by bit fulfil the demand of the quality can be observed by looking at the trend of the test values.

At first the Mooney Viscosity of the masterbatch compounds is shown.

Here still some differences between the three used polymers can be seen. The EPT has the lowest Mooney Viscosities over all mixed batches. The two other polymers are very close together due to the smaller difference in the degree of long chain branching. This Figure supports the before mentioned mixing behaviour of the three polymers. Due to the more linear structure decreases the viscosity faster, which makes further carbon black incorporation more difficult and leads to poorer dispersion levels.

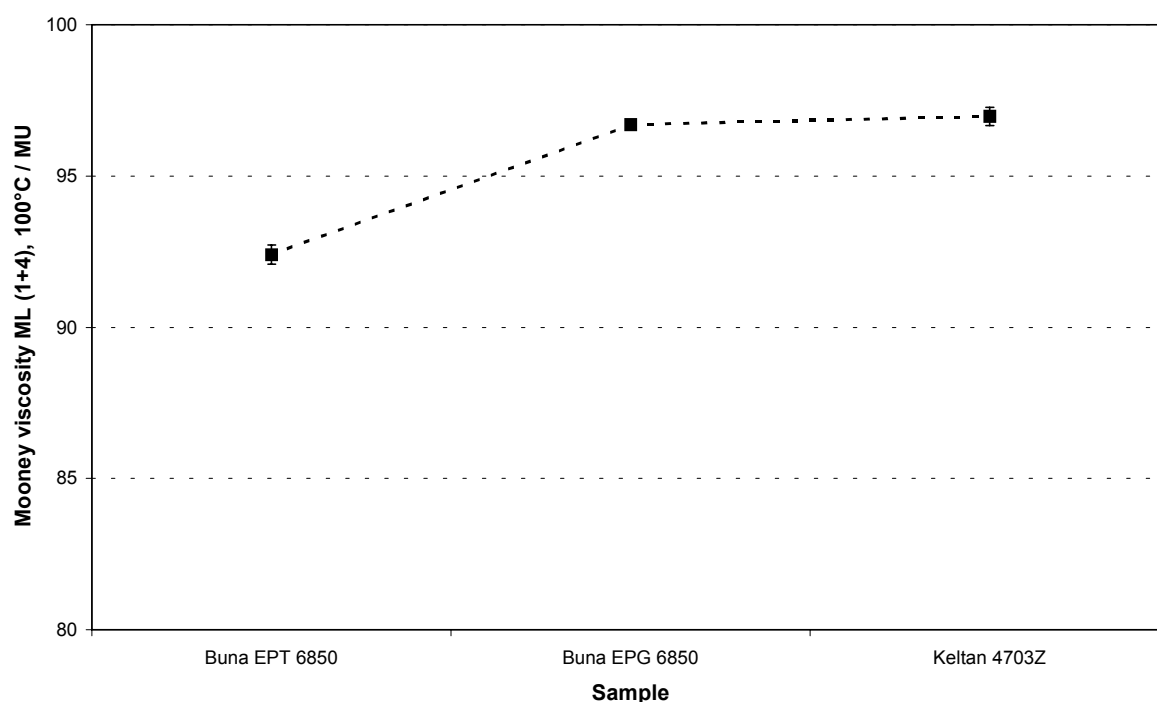


Figure 6: *Mooney Viscosity of the three last mixed masterbatch compounds.*

The differences in the Mooney Viscosities of the masterbatches between the three polymer mixing series could be minimised during the finalbatch mixing as it is shown in the Figure. The viscosity is varying in a range from +/-5 points over the whole finalbatch mixing series.

The different mixing behaviour, still observable in the masterbatches, is decreased to almost zero during the finalbatch mixing.

Summarising the results of the Mooney Viscosity it is shown that a very constant quality level was reached despite of the different start conditions concerning the polymer parameters.

The mean level of the Mooney Viscosity of the finalbatches is about 71,88 and a standard deviation of 1,56. The KELTAN has a mean value, which is slightly higher than the two other with a mean value of 73,45.

During the adjustment process under the 4 mixed batches it can be observed by looking at the Mooney Viscosities that the calculated mixing procedure for the before mixed polymer does not fit for the next one. This can be seen by looking at the lower Viscosity levels for the earlier mixed batches of each series. But than at the last mixed batch of each series the differences are adjusted.

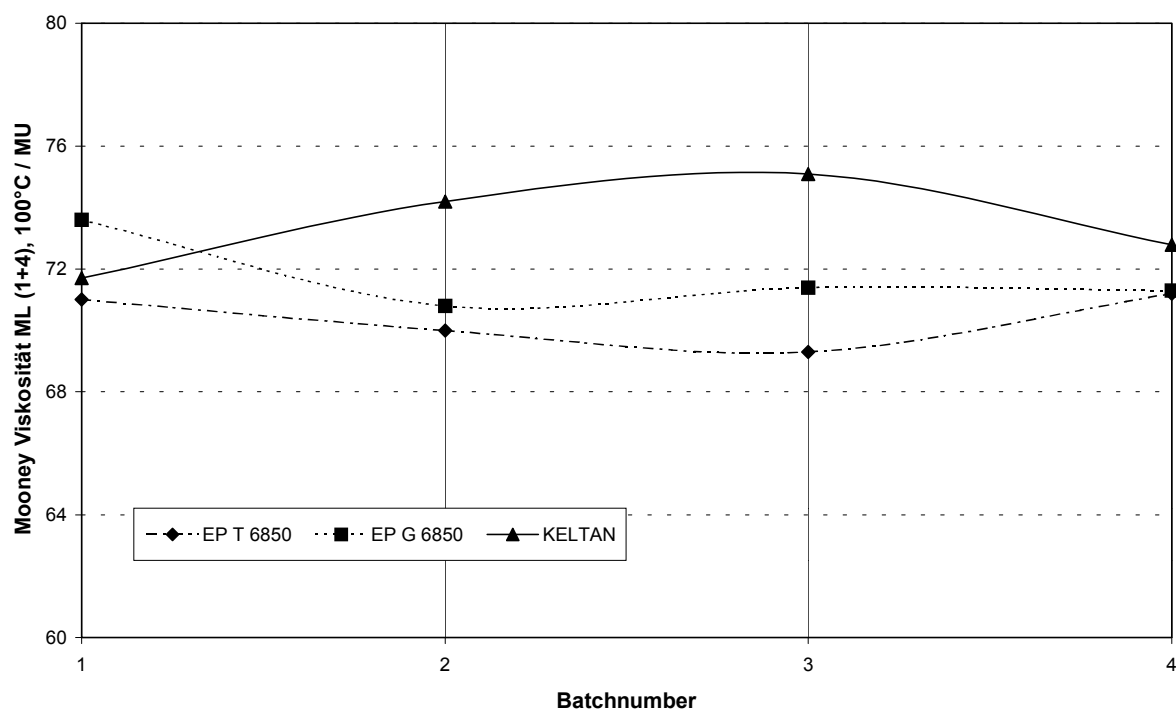


Figure 7: *Mooney viscosity of the finalbatches.*

The tests concerning the compression set just supports the constant batch quality of the finalbatches.

All results are within a range of +/- 2 %points, which is a very narrow range for this type of technical compound.

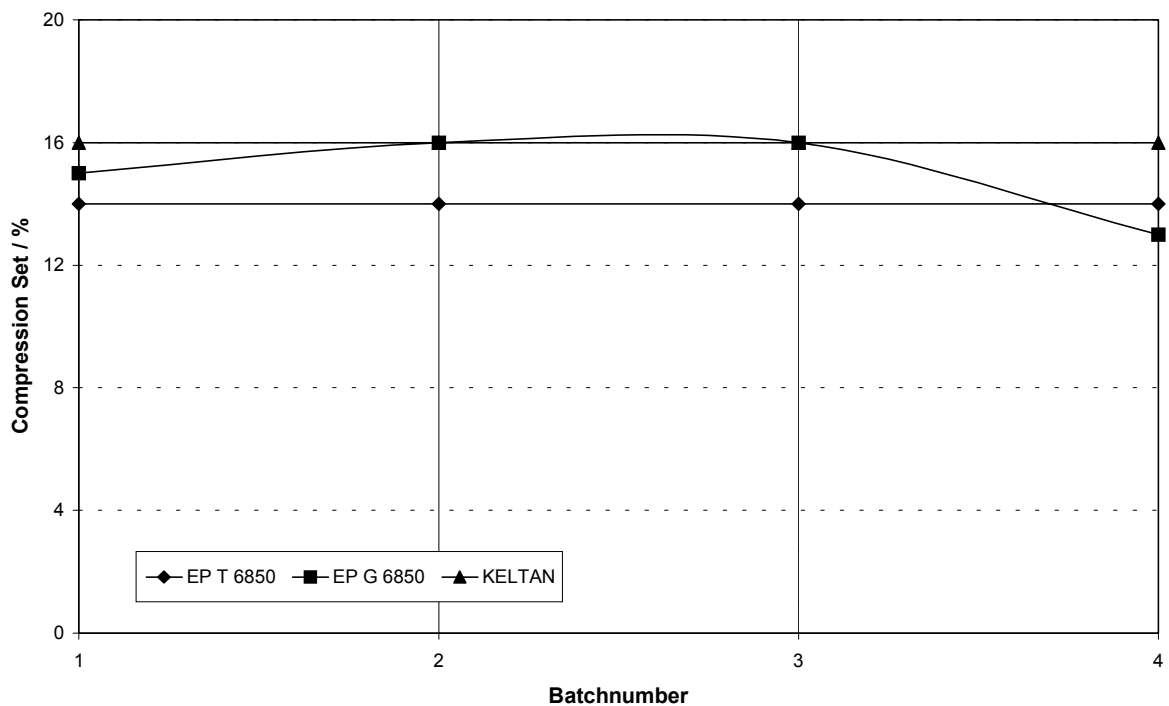


Figure 8: *Compression set of the finalbatches.*

The rheometer test shown in the Figure showed no bigger variations either in comparison to the standard production variations.

The next two Figures summarise the tests concerning the MH and ML tests and in the Figure the t_{s2} and t_{90} values are shown.

The Figure 9 shows the MH and ML values.

The batches based on the KELTAN polymer have always the lowest MH and ML values, which is a known fact from the literature. [2] [4] But the deviations are all in between a very small range so they can be more or less been taken out of account for bigger influences for the following process steps.

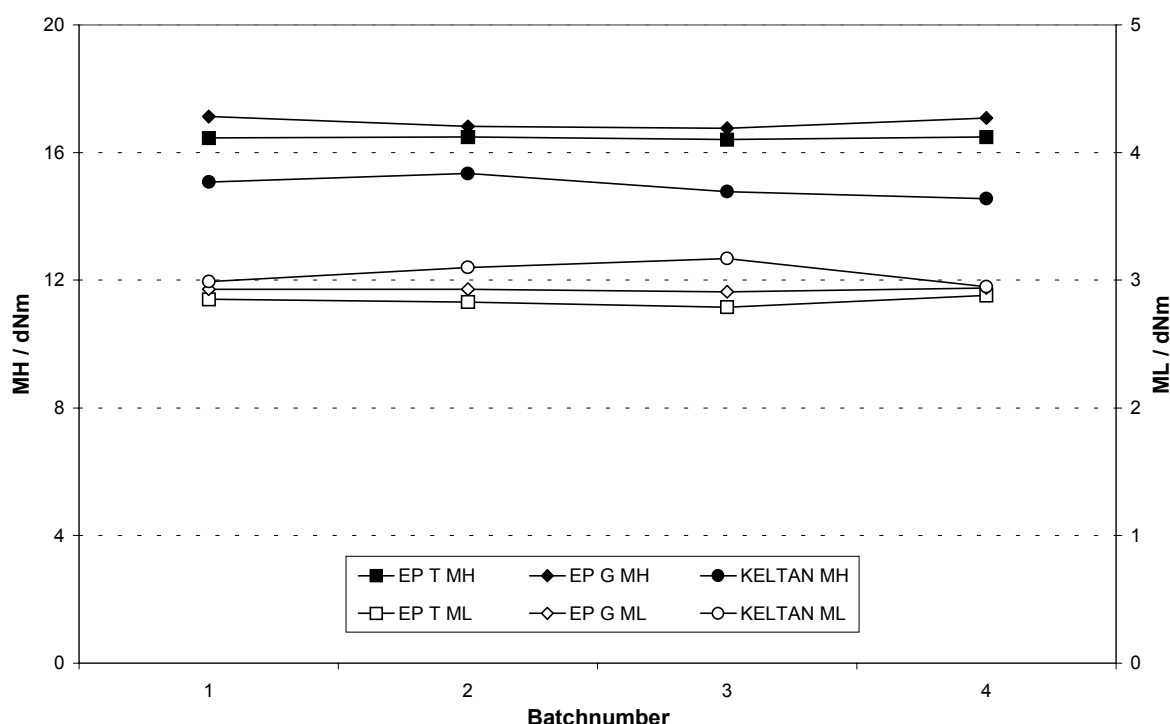


Figure 9: *MH and ML values of the finalbatches.*

The same Figure can be observed by looking at the t_{s2} and t_{90} values. Where as here the behaviour is exact the opposite way around where the KELTAN polymer with the highest degree of branching have the highest values. But even here the deviations are in between a very small range. This behaviour was explained with the following in the literature. The “dangling ends” from the highly branched KELTAN polymer is mentioned as being responsible for these higher value respectively lower values. These dangling ends have no meaning for the crosslinking but influence the mixing process in the way that the crosslinking is negative influenced.

All the values are in between the normal production range and only the trend can be observed with KELTAN having lower values than the two other polymers.

The differences, which can be observed here, are not due to the mixing cycle but due to the different structure of the raw polymers used for this investigation. Some influences of the polymers structure could be adjusted by the MixCont system but the

remaining differences are due to the general differences between polymers for which different types are used.

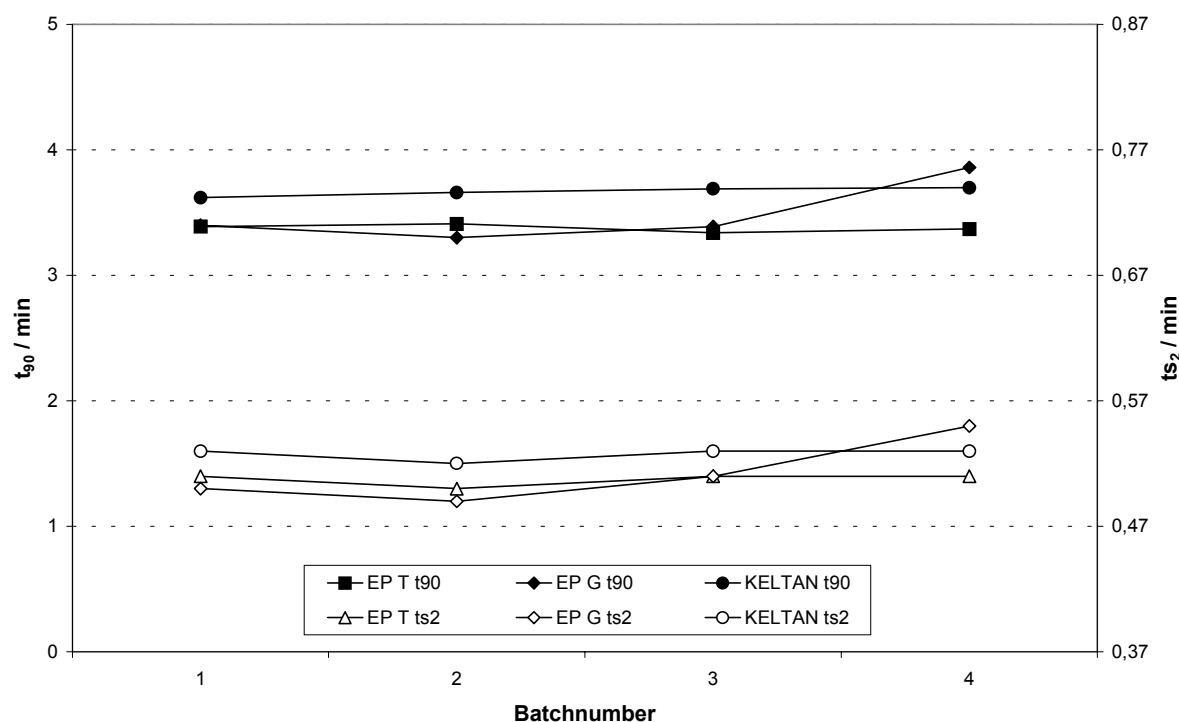


Figure 10: t_{s2} and t_{90} of the finalbatches.

The elongation at break and the tensile strength are shown by calculating the mean values in each polymer series to exclude accidentally deviations in between one series as it was already done for other tests. Otherwise the standard deviation within this test procedure is that large that single test results only would have a confusing and falsifying character for the interpretation.

The tensile strength and thus also the elongation at break are increasing with increasing degree of long chain branching. This behaviour is due to the structure of the polymer where more entangled chains prevent the slippage of the chain along each other which gives an increased viscosity during the crumbling phase and the carbon black incorporation phase which leads to an increased dispersion level. This better dispersion level leads in its way to the higher tensile strength and elongation at break.

The test about the density and the hardness showed no new aspects and were both very constant and are therefore not shown in detail in this report.

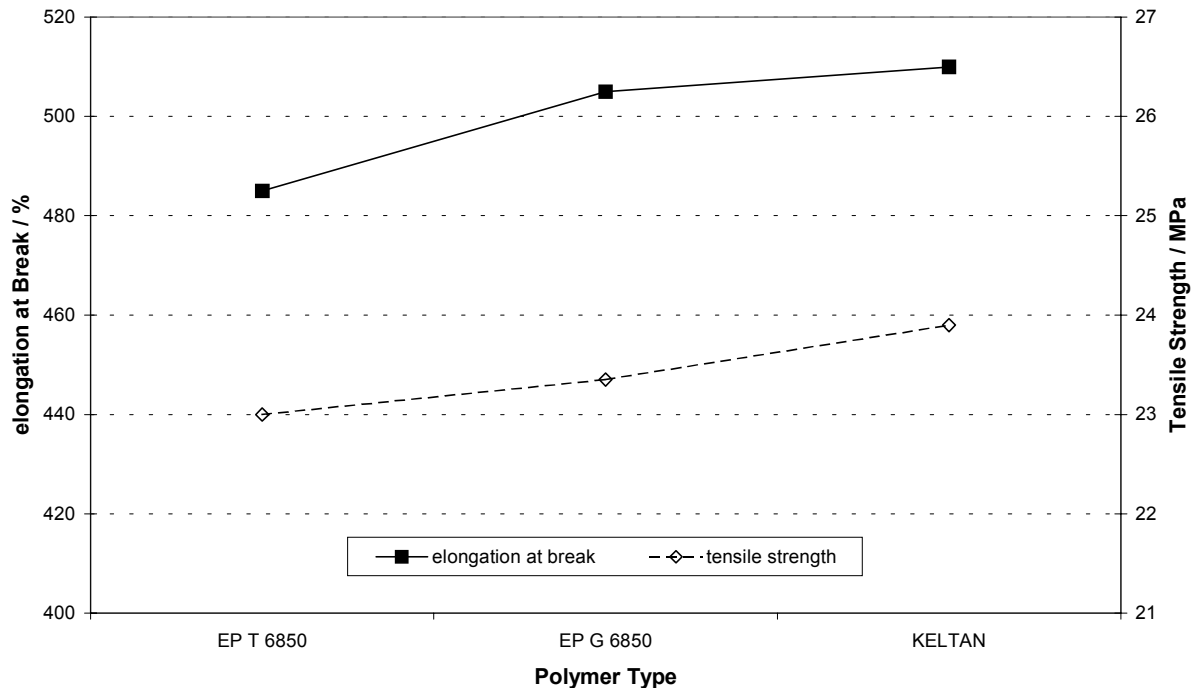


Figure 11: *Elongation at break and tensile strength of the final batches.*

The RELMA test shown in the next two Figures deliver an impression about the dispersion of chemicals in the compound. In this case the sulphur and zinc content was measured. The two test values, which are shown, are the mean value of intensity and the variation coefficient of the measurements. Experiences showed, that variation coefficients, which are smaller than 5% are corresponding with very good measurement results. As the shown values are slightly higher is due to the fact that during the test procedure there occurred some problems concerning the sample preparation. The sample surface was not smooth enough to enable reliable measurements; this was especially the case at the batches mixed with the EP T and the EP G where as the KELTAN delivered the best surface quality. This behaviour could also already be observed at the behaviour on the mills. But by leaving out the absolute values some trends can be observed by taking the results into account. Another problem was the very low sulphur content in the compound, which made it difficult for the RELMA unit to deliver constant test results, and there for the variation coefficient for sulphur is higher than for the peroxide.

In general the batch-to-batch quality is quite equal even between the different mixed polymers, which indicates good mixing quality by the process control system to adjust the different mixing behaviour of the polymers.

The RELMA tests were preceded at the master and at the final batches both before and after the milling process. The first shown value is before the milling and the second value of each polymer is after the milling process.

It can be observed that for the master batches the milling had larger influence for the RELMA values than for the final batch properties tested by RELMA.

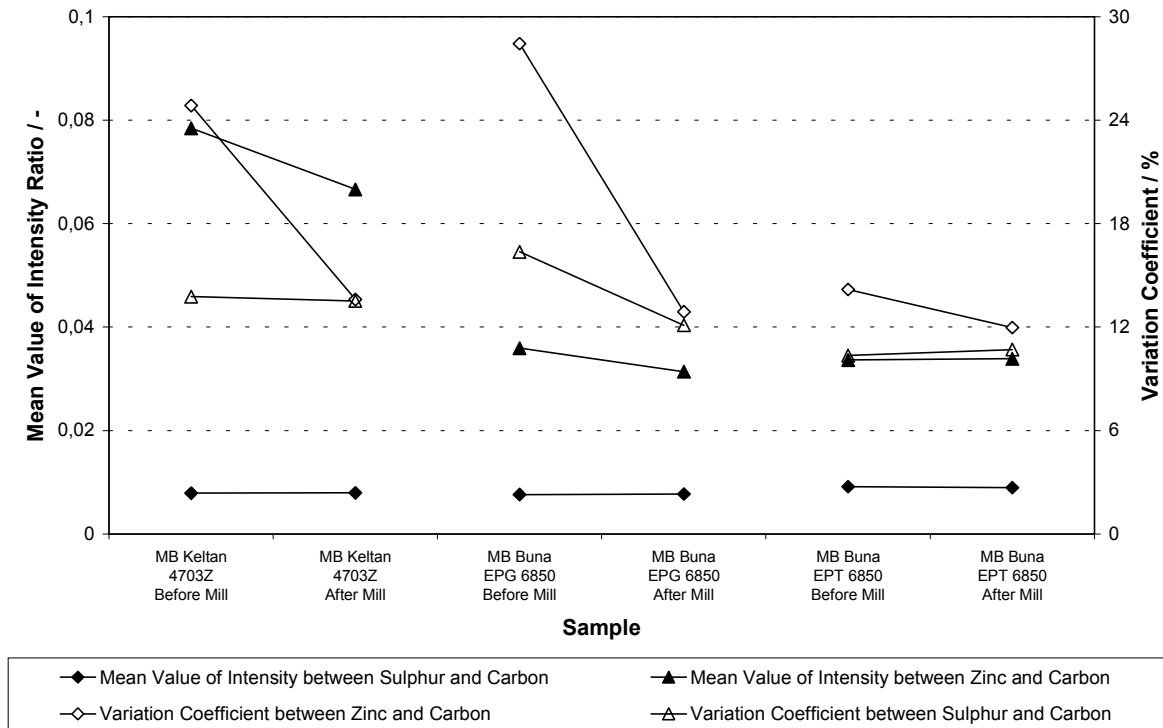


Figure 12: *RELMA results of the masterbatch compounds.*

An interesting point in the masterbatch test results is the higher amount of zinc in the KELTAN polymer based batches. This uncovers the fact that zinc stearate is already been added to the raw polymers to get better processing in the polymer crumbling phase [11].

The RELMA results of the finalbatch compounds show no considerable variations between the three different used polymers. The batch to batch deviations are in between a very small range, which indicates good mixing quality. Even the differences before and after milling were smoothed out, which means that the mixing quality was that good after the internal mixer that the quality could not be improved by the milling process.

The still very high variation coefficients are due to the problems mentioned before with the test surface of the samples.

Summarising the RELMA results there are no differences detectable, which point to higher variations in the batch quality. Some influences destined by the mill process could be detected with decreasing variation coefficients of the samples taken after the mill process.

The finalbatch results of the RELMA showed the same trend, which could be observed by looking at the mixing behaviour and at the other test methods that the batches mixed with the KELTAN delivered slightly better compound quality than the other with more linear chain structure. They tend to lower values for the variation coefficient, which indicates the mixing quality

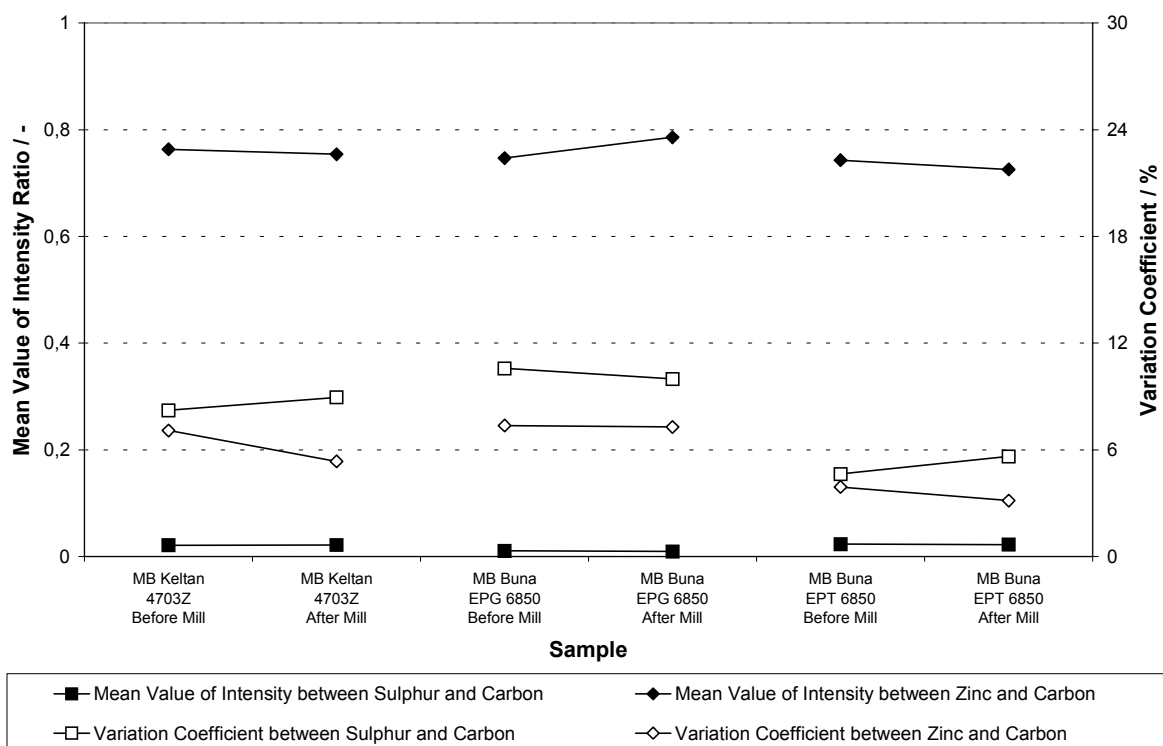


Figure 13: RELMA results of the final batch compounds.

In the following Figure the results of the RPA test at Paris are shown. The values are the G' , the G'' and the $\tan \delta$ of the masterbatch compounds. The test concerning the viscous and elastic moduli G' and G'' on which the $\tan \delta$ value is based are made at 100°C with a frequency sweep up to 180 rad/s and a degree of 0,5°.

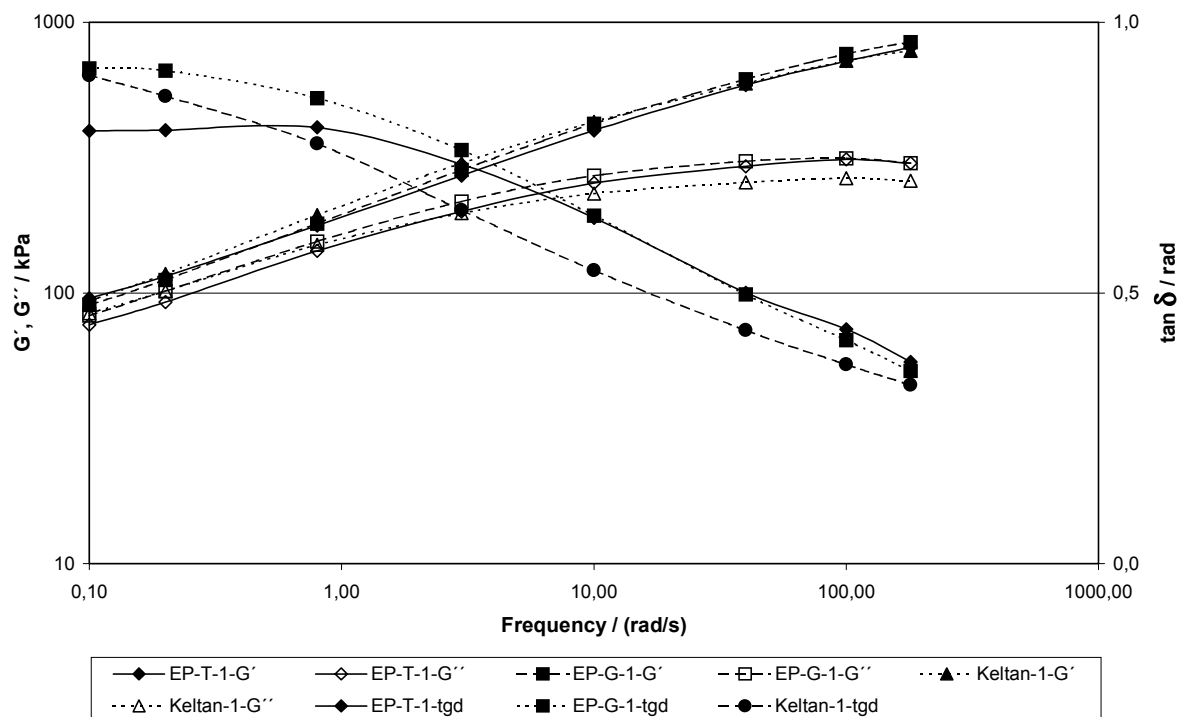


Figure 14: RPA test results G' , G'' and $\tan \delta$ of the masterbatches.

The results, which are presented in this Figure, are based on the three finally mixed batches of each series. All test results are in between a small variation range and can be seen as sufficient equal to precede good end product quality in the next process steps.

There are still some deviations in the values due to the different degree of long chain branching and the varying behaviour during the mixing cycle. But the differences could be minimised within the common mixing cycle.

To finish the analysis of the properties, the test results of the final products are presented. The brake membranes were produced in the laboratory at Trelleborg and the product tests were performed at the laboratory at VW in Wolfsburg.

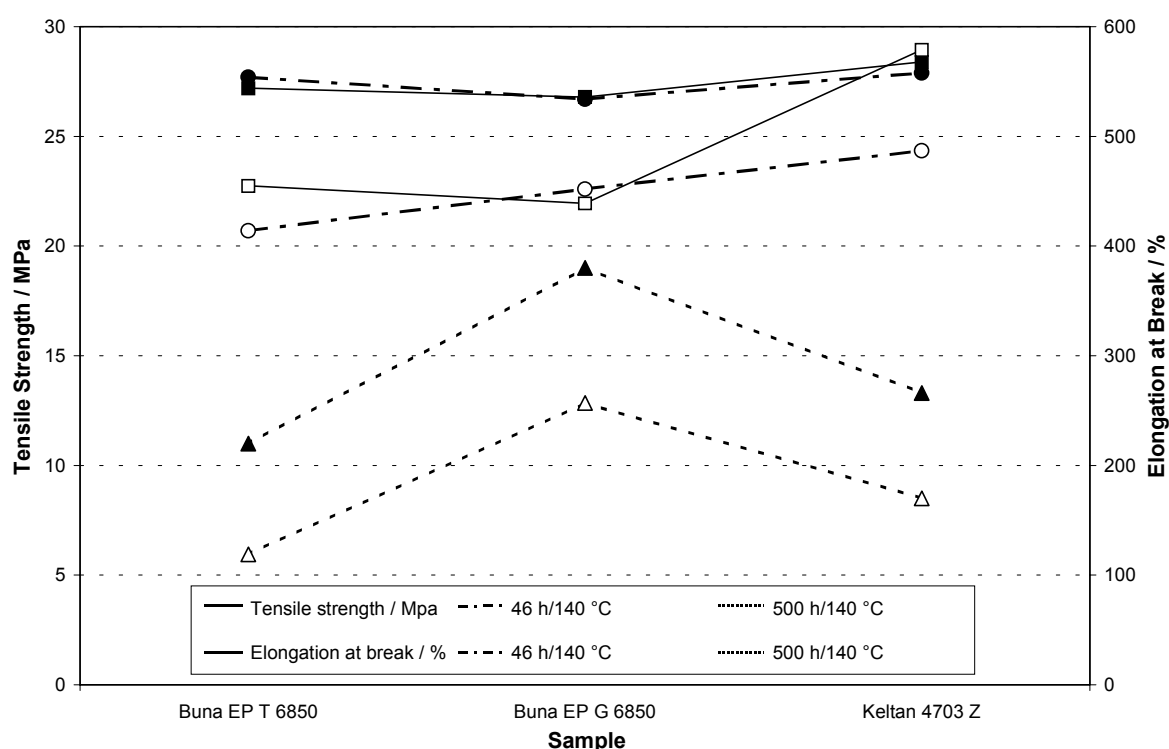


Figure 15: *final product properties.*

The tests of the final product properties which were carried out are not all presented in detail in this report only the most characteristic ones, the tensile strength and the elongation at break test results before and after aging are presented.

The tensile strength did not show bigger variations between the three different polymer types for the non-aging test. But after aging the EP T 6850 and the KELTAN decreased more than the EP G 6850. The EP G decreased only about 30% whereas the two others had a drop of about 60% after 500h aging at 140°C.

For the elongation at break the appearance is almost the same as for the tensile strength. Here the Keltan had a little bit higher values before aging than the two other polymers. But after aging the same behaviour as before appeared. Again the EPG has the best aging behaviour of these three polymers.

As this behaviour was the same for both the high and the low branched EP T and Keltan it seems nothing to do with the degree of long chain branching and the mixing process itself. This behaviour can be explained with the chemical interaction based on the polymer type EP G in contrast to the other EPDM types.

So first by looking at the aging properties can differences be detected between the three different types of polymers.

4. Conclusions

The study presented in this paper investigated the influence of the degree of long chain branching of EPDM polymers to the mixing process. Simultaneously the possibility to adjust these differences for constant batch-to-batch quality by an advanced mixing control system called MixCont was investigated.

To summarise the results of this study it was shown that the degree of long chain branching of the EPDM polymers influences the mixing process. And at the same time the advanced mixing control system MixCont managed to adjust these differences in the mixing behaviour in order to achieve equal compound properties.

The different mixing behaviour could be detected by analysing the energy consumption and the speed levels during the masterbatch mixing. The mixing curves of the masterbatches are also the most significant aspects to point out the differences between the polymers different mixing behaviour and the control action of the MixCont system to adjust these differences. During the finalbatch mixing most actions concerning the adjustments of the difference in the mixing cycle due to the different polymers long chain branching levels were already done. So curves for the finalbatch mixing showed no bigger variations. Not even the final product tests showed any major differences. Only by looking at the ageing behaviour differences could be detected. But these differences in the ageing behaviour of the final products could not only be explained with the long chain branching levels of the three different polymers. Instead are other reasons more likely to be responsible for the general appearance of the polymers.

The process behaviour of the different polymers can be divided in to two major parts during the masterbatch mixing which were defined by the energy consumption. The first part is the crumbling phase where the more branched polymers shows higher energy consumption than the more linear polymers due to their more difficult mixing behaviour.

In the next part mainly determined by the carbon black incorporation the energy consumption show the opposite behaviour. With increasing long chain branching the energy consumption decreases.

For the whole mixing cycle this means that the more branched polymers behave more difficult in the beginning of the process but tend to improve mixing behaviour in comparison to the linear polymers gives in the end better dispersion levels than the more linear polymers.

This behaviour was detected by the MixCont system, which then adjusted the mixing schedules for every single polymer. The more branched polymers having higher speed levels to the begin of the active mixing control phase and the more linear ones higher speed levels to the end of the mixing cycle to perform the same mixing quality as the more branched polymers.

The adjustments of the mixing control system MixCont resulted in more or less constant batch-to-batch uniformity, which could be observed in the homogeneous test values.

The disadvantages by using polymers having different degrees of long chain branching could be adjusted satisfactory by the MixCont system to get even start parameters in the meaning of homogenous batch quality for the following process steps.

The general summary of this investigation is that with a good process control system it is possible to perform good and constant mixing quality even if there are process influencing start parameter variations.

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