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Novel NR/EPM Blends

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Vulcanisation of the NR phase of a NR/EPM blend during mixing is effected by using a very active accelerated-sulphur cure system. The crosslinking of the NR phase, albeit at a low level, results in a change in the blend rheology. A change in the blend morphology accompanies this process; the EPM is a disperse phase within a NR matrix in the control blend but is present as part of a co-continuous blend morphology in the dynamically vulcanised blend. The size of the domains of both polymers is also reduced in the dynamically vulcanised blend. When properly compounded with clay and oil, the dynamically vulcanised blends are readily processed, scoring 13+ in extrusion through a Garvey die. The properties of vulcanisates derived from these blends are generally good.

This work was carried out under a project funded by the Common Fund for Commodities, a United Nations funding body. The project was concerned with blends of natural rubber with speciality elastomers. One such elastomer is ethylene propylene rubber (EPM), a fully saturated polymer that has excellent ozone resistance. EPM is a relatively expensive class of elastomers. Blends of EPM and NR that retain the ozone resistance of the EPM should be cheaper than the single polymer EPM equivalents. Successful materials would have applications in the electrical cable industry as insulation sheathing and as seals and weather strips for the automotive and building industries.

MATERIALS AND METHODS

The rubbers used in this study were natural rubber, NR (SMR CV) and ethylene propylene rubber, EPM (Dutral Co 054, Enichem Elastomers). Rubber chemicals were standard commercial grade materials. Solvents were of AR grade.

Compounding of the NR masterbatch *(Table 1)* was performed by using a BR sized Banbury internal mixer with the curatives added on a cool two roll mill. The blend materials were mixed in a Brabender PL2000 mixer fitted with a 350S mixing head and Banbury style rotors, dynamic vulcanisation was performed with the circulating oil at 100°C, or in a BR sized Banbury mixer without cooling water. Cure times were determined by using Monsanto ODR or MDRE rheometers at 150°C. For samples with very short cure times the rheometry was repeated at 140°C. The extrusion performance of material prepared in the BR Banbury was assessed to *ASTM D2230* by using a Francis Shaw 30 mm extruder (L/D = 15) fitted with a Garvey die, and scored using Rating System A. The temperature controlled zones were heated to 95°C and 80°C–85°C (head and barrel).

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TABLE 1 NR MASTERBATCH FORMULATION

Ingredient	Loading
SMR CV	100
Zinc oxide	5 0
Stearic acid	2 0
Mix Cycle	
Time	Action
0	Start, add polymer
30 s	Add powders
90 s	Sweep
210 s	Dump

The efficacy of a second-stage peroxide vulcanisation was assessed as follows

A weighed sample of the unextracted NR vulcanisate (*ca* 25×25×1 mm) was painted with a liquid peroxide (2,5-dimethylhexane-2, 5-di-*t*-butyl peroxide (DHBP), a peroxide with a similar decomposition half-life to that of dicumyl peroxide *(Dicup)* The target peroxide loading was 1 p p h r After leaving the samples for 16 h to allow the peroxide to distribute homogeneously, each sample was reweighed to determine the exact peroxide loading within it The doped samples were returned to the press for an additional vulcanisation period of 1 h at 160°C

The crosslink densities of all of the samples, both original and peroxide doped, were interpolated from equilibrium volume swelling measurements in chloroform by reference to the crosslink density swelling ratio correlation shown in *Figure 1* This figure was generated from a series of NR vulcanisates, the swelling ratio was determined in chloroform and takes into account the level of zinc oxide in the formulation[1], the crosslink density was determined from stress-strain measurements[2] The efficacy of the secondary peroxide cure was then estimated by a comparison of the observed increase in crosslink density in the vulcanisate with that of a similarly treated *Dicup*-cured NR control sample, taking into account the exact loading of DHBP, and ranked as good, fair or poor

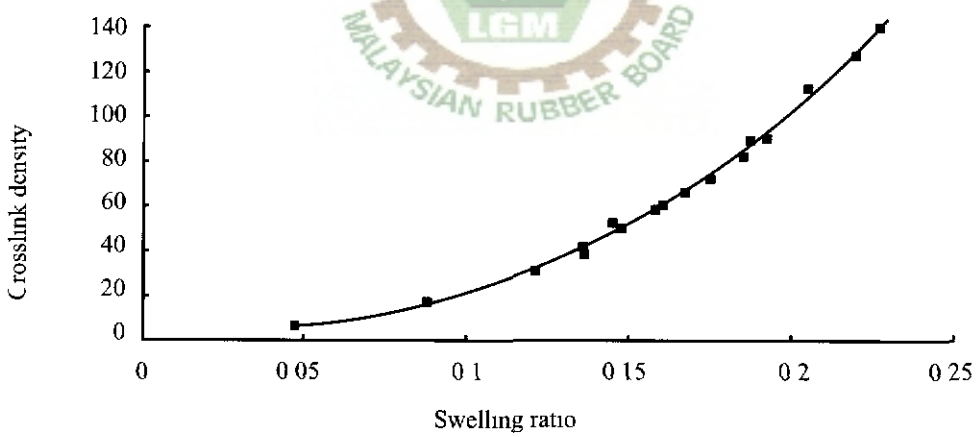

Figure 1 Crosslink density swelling ratio correlation for NR vulcanisates

The blend morphology was examined by phase contrast light microscopy on thin sections produced by using cryo-microtomy.

RESULTS AND DISCUSSION

For a blend of NR and EPM to show the excellent ozone resistance of the EPM component, the EPM should be a continuous phase. Gum mixes of these two polymers at polymer ratios varying from 1:3 through to 3:1 (by weight) were found to possess a disperse phase/matrix phase blend morphology. *Figure 2* shows a phase contrast light micrograph of a conventional 50:50 NR/ EPM blend at approximately 400 times magnification. Under these imaging conditions the NR phase appears darker than the EPM phase. Although there are difficulties in interpreting 3-D morphology from such 2-D images, due to uncertainties regarding continuity of phases out of the plane of sectioning, there is no evidence of substantial continuity of the lighter EPM phase. The EPM domains are elongated, roughly 20×5 μm in size, and separated by relatively narrow (2 μm – 10 μm) regions of NR. The inter-phase boundary appears to be smooth. The blends do not appear therefore, to naturally possess the desired morphology, rather the EPM is most probably dispersed in a NR matrix.

That NR is the matrix phase in the blend means that NR has the lower shear viscosity under the mixing conditions[3]. In order to change the morphology it is necessary to change the relative viscosities of the two polymers. This could be achieved either by increasing the viscosity of the NR phase, or by reducing the viscosity of the EPM phase.

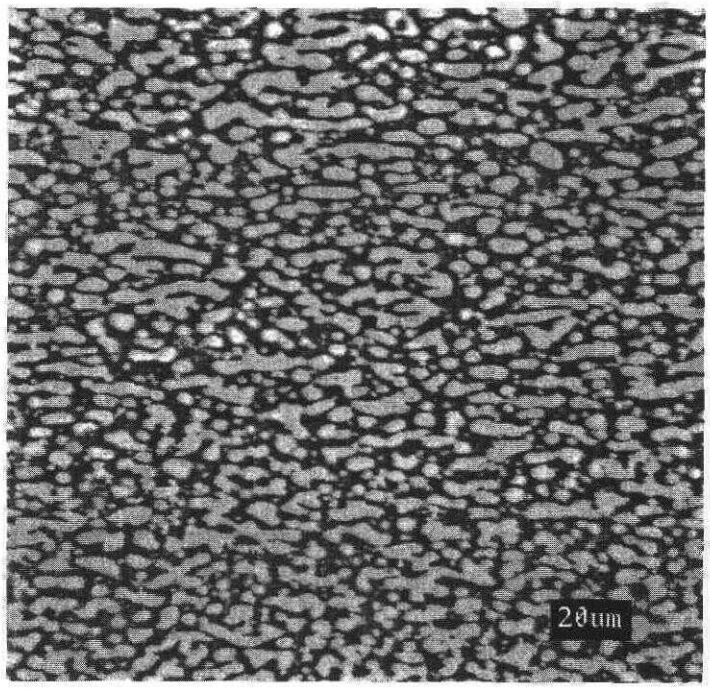

Figure 2. Phase contrast micrograph of a conventional NR/EPR blend.

TABLE 2. CURE SYSTEMS: SPEED AND SECONDARY CURE EFFICACY

Mix	Cure System[a]	Cure Time t_{max}, 150°C (140°C) min	Peroxide secondary cure
1	1.20 S, 0.35 CBS	19.5	Fair
2	0.20 S, 3.0 CBS	44	Poor
3	0.75 S, 0.75 CBS	20.5	Poor
4	0.75 S, 0.75 CBS, 0.10 ZBED	11.6	Good
5	0.75 S, 0.35 CBS, 0.35 ZBED	9.0	Good
6	0.75 S, 0.75 CBS, 0.10 TMTD	10.4	Good
7	0.75 S, 0.35 CBS, 0.35 ZDMC	4.0	Good
8	0.75 S, 0.50 ZDMC, 0.25 CBS	9.0	Good
9	0.75 S, 0.75 ZDMC, 0.10 CBS	8.0	Good
10	0.75 S, 0.75 ZDMC, 0.20 CBS	6.3	Good
11	0.75 S, 0.75 TBBS, 0.10 ZDMC	11.2	Good
12	0.75 S, 0.35 TBBS, 0.35 ZDMC	4.8	Good
13	0.75 S, 0.75 MBS, 0.20 ZDEC	15.5	Fair
14	0.30 S, 0.10 TMTM, 0.1 Robac γ[b]	10	Poor
15	0.50 S, 0.30 TMTD	7.2	Good
16	1.00 S, 0.40 CBS, 0.20 TMTD	9.4	Good
17	0.75 S, 0.35 ZMBT, 0.35 ZDMC	14	Good
18	0.75 S, 0.75 ZDMC, 0.10 DPG	2.5 (5.8)	Good
19	0.75 S, 0.75 ZDMC, 0.20 DPG	2.3 (6.0)	Good
20	0.75 S, 0.75 ZDMC, 0.30 DPG	2.0 (5.7)	Good

[a] Curative loadings in p.p.h.r., each mix based on a masterbatch comprising; SMR CV, 100; zinc oxide, 5.0 and stearic acid, 2.0 p.p.h.r.

[b] Mixed dithiocarbonate and dithiocarbamate derivatives, Robinson Brothers, West Bromwich, West Midlands, UK.

Dynamic vulcanisation has been used to improve the properties of thermoplastic elastomer blends[4], to control the dispersion and distribution of carbon black in polymer blends[5] and to alter blend morphology[6]. Dynamic vulcanisation is a procedure whereby one of the components of the blend is vulcanised, or partly vulcanised, during the mixing process, whilst the other component remains completely uncured. The introduction of crosslinks into one of the phases increases the viscosity of that phase, leading to a change in blend rheology, and hence in the morphology of the blend[3,6,7]. The uncrosslinked phase is unaltered by the vulcanisation in the other phase, permitting easy processing of the blend. The modified blend can then be additionally compounded (if required), formed to shape and a second cure system active in the uncrosslinked component can be used to 'fix' the finished article.

The fact that dynamic vulcanisation takes place during mixing, inside the mixer, there is an economic requirement for the mix cycle to

be as short as possible. There are, therefore, several constraints forced upon the dynamic cure system, it must:

- Be specific to one phase of the blend
- Be very active and fast
- Permit subsequent processing of the blend
- Not interfere with the second stage cure.

The feasibility of this using dynamic vulcanisation in this way was demonstrated in earlier work[8], but the subsequent peroxide vulcanisation was poor.

Selection of Dynamic Cure System

Achieving cure system specificity in favour of the NR component of a NR/EPM blend is relatively easy. EPM, being a co-polymer of two olefin monomers (ethylene and propylene), is a fully saturated elastomer; thus it is not crosslinked by the accelerated-sulphur cure systems commonly employed in the vulcanisation of NR. The subsequent vulcanisation of the blend using a radical crosslinking system (peroxide or high energy radiation) should occur in both phases. However, there is the possibility that residues from the dynamic cure system might interfere with the radical cure and significantly reduce its effectiveness, a problem encountered earlier[8].

A wide range of accelerated sulphur cure systems was studied using accelerator:sulphur ratios chosen to cover the whole spectrum of cure system efficiency *(Table 2)*. Data from the rheometers was used to assess the speed of vulcanisation and the duration of the initiation period. The more efficient cure systems, in a sulphur utilisation sense, and the conventional cures were far too slow for consideration (1 and 2, *Table 2*). A mixed accelerator system with a dithio-carbamate and a sulphenamide and thiuram accelerators gave faster cures with good peroxide second cures (8–13 and 15, *Table 2*), but these were still a little too slow for consideration. Addition of di-phenyl guanidine (DPG) to the carbamate system gave a considerable boost to the cure rate, cure times of the order of 2 min – 3 min at 150°C resulted from this modification, without affecting the subsequent peroxide cure. Three very fast systems based on sulphur, ZDMC and DPG, all with cure times below three minutes at 150°C, and a fourth, slightly slower, system using sulphur, ZDMC and CBS were found by this approach (mixes 7 and 18–20, *Table 2*).

Dynamic Vulcanisation of NR/EPM Blends

The dynamic vulcanisation in the NR phase of a NR/EPM blend could be monitored by its effect on the mix viscosity and hence the mixing torque. In normal mixing of NR, the mixing torque is usually observed to fall with mixing time as both the mix temperature rises and the molecular weight of the NR falls as a result of mastication. However, in the presence of the curatives for the NR phase, the fall in mixing torque was reversed when the mix temperature reached 125°C – 135°C. This temperature and the associated torque rise can be considered to mark the onset of the dynamic vulcanisation *(Figure 3)*. The mixing torque rises to a peak with the signal becoming somewhat noisier as the dynamic vulcanisation proceeds. The increase in mixing torque causes the mix temperature to continue to rise. It is this factor (mix temperature) that dictates events in the rest of the mix cycle, as the mix should be kept below 165°C to minimise polymer degradation.

Some curative levels used in the search for a suitable cure system (18, *Table 2*) were found to give poor processing behaviour, presumably as a consequence of too high a crosslink density in the NR phase. It was difficult to add the peroxide necessary for the second vulcanisation. Reducing the sulphur and ZDMC loadings to 0.13 p.p.h.r. and the DPG loading to

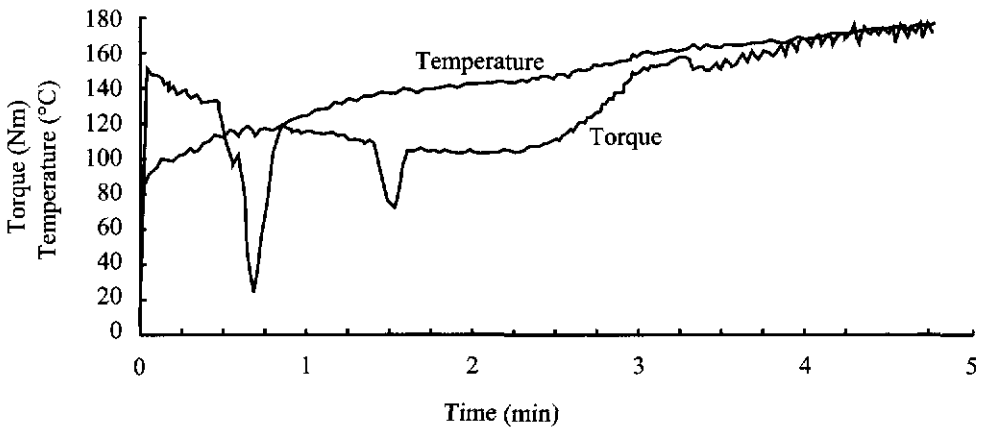

Figure 3. Mixer record of dynamic vulcanisation of a gum blend.

0.02 p.p.h.r. gave a dynamically vulcanised blend with improved processing. The increase in mixing torque was reduced, but still evident. These successful curative levels are considerably below those usually considered necessary to produce vulcanised articles. The crosslink density within the NR phase of the dynamically vulcanised blend must, therefore, be very low.

The morphology of the dynamically vulcanised blend was studied under identical conditions to those used for the conventional blend. A typical micrograph *(Figure 4)* shows a finer structure than found in the conventional blend. In addition, the phases appear to be co-continuous, there being substantial continuity in both phases in the plane of the section, and the phase boundaries appear to be much rougher than found in the conventional blend. It would seem that dynamic vulcanisation has produced the desired change in the blend morphology by creating a continuous EPM phase.

Clay Filled Dynamically Vulcanised Blends

In real applications the blends will contain filler and oils. The inclusion of these ingredients in the basic formulation *(Table 3)* caused some problems during mixing. Addition of the ingredients after a period of mixing, but before dynamic vulcanisation occurs, cools the mix and delays vulcanisation onset until nearly 5 min into the mix cycle *(Figure 5)*. If, however, the clay and oil are added after dynamic vulcanisation has occurred, the onset is again delayed. The mixer perforce operates at a low fill factor during the early stages of mixing, resulting in a slow temperature rise due to the reduced heat input. Thus the temperature necessary to initiate dynamic vulcanisation is not attained in a reasonable mixing time. The optimum mix cycle found was based on an upside-down mix cycle, but retaining a portion of the clay and all of the oil until after dynamic vulcanisation *(Table 4)*. Dynamic vulcanisation starts after 1 min – 1¼ min and the second portion of clay and the oil are added once the temperature reaches 150°C, after about 2 min. The addition of these materials cools the mix which allows additional mixing time for their incorporation. This mix cycle is quite short, taking 3 min – 3½ min to complete *(Figure 6)*.

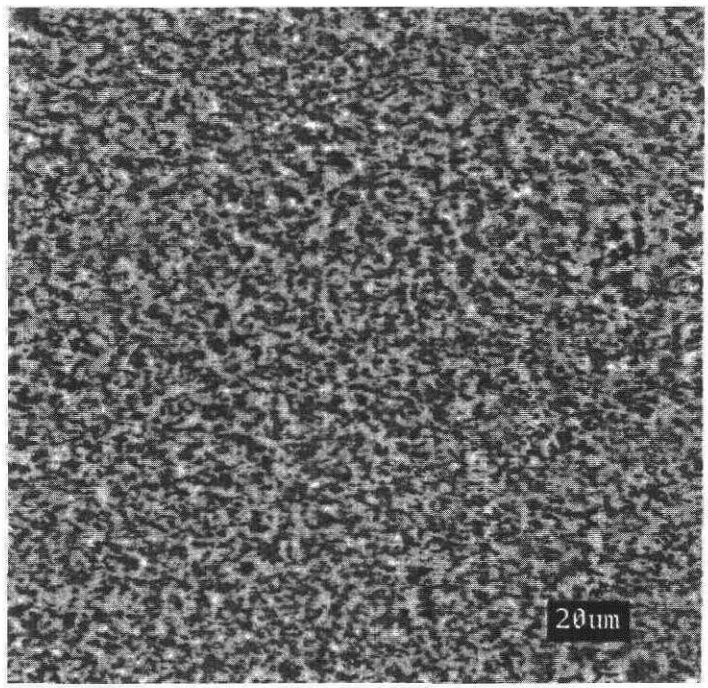

Figure 4. Phase contrast micrograph of a dynamically vulcanised NR/EPR blend.

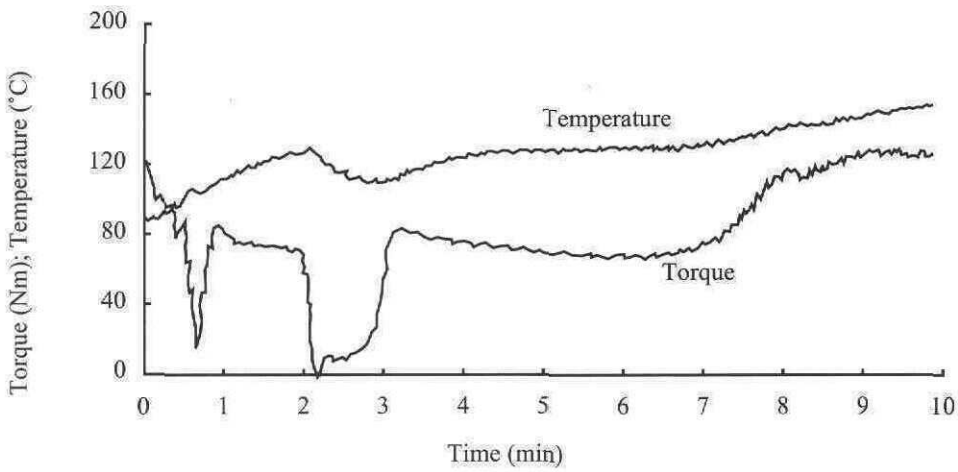

Figure 5. Mixer record of dynamic vulcanisation of a filled and plasticised blend, oil and clay added after 2 min (before dynamic vulcanisation).

TABLE 3 FILLED DV BLEND FORMULATION

Ingredient	Loading (p p h r)
SMR CV	50
Dutral Co 034	50
Zinc oxide	5 0
Stearic acid	2 0
Sulphur	0 13
ZDMC	0 13
DPG	0 02
Titanium dioxide (R)[a]	10 0
Polstar 300R Clay[b]	60
2280 oil	20
Lithene AH[c]	5 0
Silquest RC 1[d]	0 50
SR 350[e]	0 50

[a]Rutile structure titanium dioxide, Tioxide Group Ltd, London, UK

[b]Calcined clay, ECC International Europe, St Austel, Cornwall, UK

[c]Liquid, high 1,2 polybutadience, a process aid and radical cure co-agent, Revertex Chemicals Ltd, Harlow, Essex, UK

[d]Silane coupling agent to couple the polymers to the clay, OSi Specialities UK Ltd, Harefield, Middlex, UK

[e]Resin monomer to act as a radical cure co-agent, Chemox Ltd, Guildford, Surrey, UK

The resultant dynamically vulcanised blend has good extrusion properties When extruded through the Garvey die of *ASTM D2230*, a score of 13 – 14 5 was obtained The surface finish and profile replication were excellent, but the extrudate swell was less satisfactory, scoring 2 out of 4, although it was still acceptable This material was compounded with 2 p p h r of dicumyl peroxide and vulcanised for 1 h at 160°C The tensile properties of the resultant vulcanisate were reasonable, ozone resistance is good showing no cracking after 72 h at 40°C under an atmosphere of 50 p p m ozone and heat ageing at 100°C is also good *(Table 5)*

CONCLUSIONS

The use of a highly active, fast cure system to vulcanise the NR component of an NR/EPR blend during mixing (dynamic vulcanisation) effects a change in the natural phase morphology of the blend The control blend has the EPR present as a disperse phase within an NR matrix, the dynamically vulcanised blend has a co-continuous morphology with a finer phase size When compounded with clay and oil, the dynamically vulcanised mixes extrude well and can be readily compounded with a peroxide curative allowing vulcanisation in both phases

TABLE 4 FILLED BLEND MIXING UPSIDE DOWN MIX CYCLE

Time	Action	Fill factor
Start	Add polymers, powders, curatives and half clay	0 60
After DV cure	Add the oil, liquid BR, co-agents, coupling agents and the rest of the clay	0 80
3 5 min – 5 min	Dump, based on maximum mix temperature 165°C	

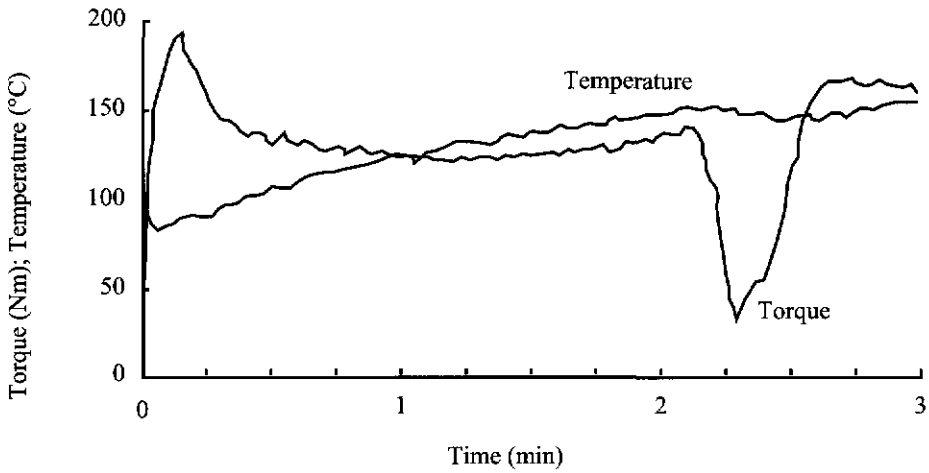

Figure 6. Mixer record of dynamic vulcanisation of a filled and plasticised blend mixed according to the modified 'Upside-down' cycle.

TABLE 5. PROPERTIES OF FILLED BLEND

Properties	Original value	Aged 7 days at 100°C	% Retention
Tensile strength (MPa)	11.2	10.2	91
Extension at break (%)	600	605	101
M300 (MPa)	2.88	2.88	100
Comp. set 1 day 100 (%)	21	24	114

of the blend. The blend vulcanisates have reasonable physical properties, are ozone resistant and show good resistance to heat ageing at 100°C.

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