

**The High Shear Mixer –  
The Application of Mechanochemistry to the Recycling of  
Vulcanized Rubber**

by

**David Brown  
William Watson  
Christopher Brown**

**Watson Brown (HSM) Ltd.,  
Glossop,  
England**

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# **The High Shear Mixer – The Application of Mechanochemistry to the Recycling of Vulcanized Rubber.**

**By D.A. Brown, W.F. Watson and C.J. Brown  
Watson Brown (HSM) Ltd., Glossop, England**

## **Abstract**

*The ability to efficiently incorporate previously vulcanised material back into fresh recipes without degrading the chemical and mechanical properties must be the ultimate goal for the recycling Industry. The engineered application of the principles of mechanochemistry, as demonstrated by the High Shear Mixer, promises to reach this goal.*

*In this paper, the High Shear mixer is described, together with an overview of its background and the results of recent trials on NR, SBR, EPDM and Nitriles.*

## **1 Introduction**

At present, vulcanised rubber is not recycled – it is either disposed of or destroyed. In the Oxford English Dictionary, the word “recycle” is defined as “return (material) to a previous stage of a cyclic process, esp. convert (waste) to reusable material”. Typical examples of this can be found in the glass and aluminium industries.

In dealing with the vulcanised rubber waste generated both from industrial scrap and used products, the main focus to date has been on methods of disposal and destruction. In considering disposal methods we include the traditional approaches of burying, both in landfill sites and in the sea, as well as the inclusion of reduced waste as bulk filler in various materials. Material destruction has typically centred on incineration. None of these approaches make full use of the material properties of rubber nor do they solve the environmental problem of tire dumps.

In this paper the term recycling is used to refer to the re-inclusion of waste rubber in a process so that a significant portion of the material properties of that rubber are utilised. As such, we are looking for a technique whereby the vulcanised material can be SOLUBILISED and so reincorporated into stock with limited reduction in material properties.

## **2 Scientific Overview**

For more than fifty years, organisations supported by governments and rubber suppliers have endeavoured to dispose of a substantial amount of used tire rubber by including it in new tires and road surfaces – with limited success.

Polymer science studies have long shown that this is expected. Recycling is not feasible while the used rubber waste remains in an INSOLUBLE network. The cured waste is preserved as a separate phase in the uncured stock, which is carried through into the vulcanisate. Processing is more difficult and the material properties are unacceptably degraded. Vulcanised crumb in asphalt likewise confers only disadvantage to properties relevant to its handling and performance.

Work has long been carried out to solubilise waste vulcanisate. “Reclaim”, made by cooking vulcanisate in acid or alkali solution or by heating with an oxidative reagent such as MBT, is a soluble product but has virtually no strength left. Acting only as a plasticiser, it significantly reduces the strength of the parent material. This makes it unacceptable for performance related applications, such as for modern tires. These effects have also long been well known via polymer science; rubber segments between crosslinks as well as some of the crosslinks have been split by this process to give a jumble of small molecule fragments with little elastic strength.

What is needed is for the cured rubber network to be cleaved only at the crosslinks, thereby reproducing the original rubber chains with only occasional side groups where previously there were crosslinks. This would provide both solubility and elasticity in the resultant material.

Academically, some thermal chemical reactions can so convert a vulcanisate. Warner [1] has summarised such chemicals, which have been found to be chemical probes capable of splitting various sulphur bonds. Unfortunately, none has led to a commercial process.

In a previous paper [2], we envisioned a commercial process via Mechanochemistry and reported it taken to the scale of around 2g to 10g charges of material. We concentrated there on factory waste of the main types of rubbers. This paper demonstrates the process extended to the 2kg charge scale where both scalability and economic feasibility are being verified for this as a pilot scale recycling process. We concentrate here on used-tire waste.

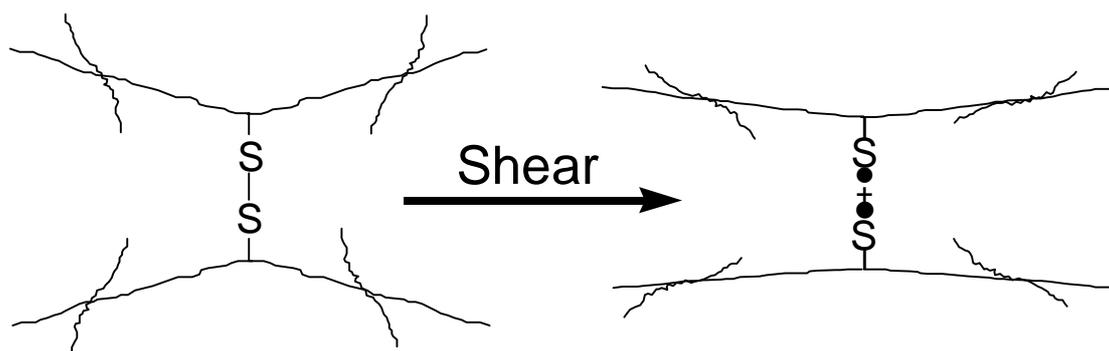
### 3 The Mechanochemistry Mechanism

Watson and co-workers in the 1950's showed [3] that the softening of rubber by cold mastication was due to the rubber chains being so extended in their central sections that a main-chain bond there was ruptured. The ruptured ends were free radicals. Normally these free ends were terminated by combining with oxygen. They could be arranged to react otherwise, combining in pairs in absence of oxygen, reacting with an added small-molecule radical acceptor, adding to the surface of a reinforcing filler and initiating free-radical chain reactions.

We predicted [2] that a rubber network sufficiently extended would rupture preferentially at crosslinks. These were likely to be regions of stress concentration and the sulphur bonds at the crosslinks were of less bond strength than the carbon-carbon bonds of the chain segments between crosslinks.

It was further expected that bonds within the crosslink rather than adjoining bonds in the chain segments would split.

These two predictions are represented in the equation represented in Figure 1.



**Figure 1: Effect of selective shear on vulcanised bonds**

It was further expected that this devulcanisation process would apply to all vulcanised rubbers.

Another issue is the identification of the mechanism for directing shear to the network so as to put regions near the crosslink under sufficient extensional shear to rupture the crosslink. It is found that incorporating crumb within a matrix of stock and mixing in an internal mixer only

moves the particles within the matrix. If it did rupture crosslinks, this would have been discovered empirically years ago.

We concluded that a more effective form of mixer capable of applying higher shear was required. We therefore designed and constructed a High Shear Mixer with the productivity of an internal mixer and yet with the capability of imposing shear comparable to that by the tight nip of a two-roll mill. Such a machine on the laboratory scale was described in the previous paper [2]. We outline in the following section a scale-up of this 50ml capacity machine to a machine of 5 litres capacity.

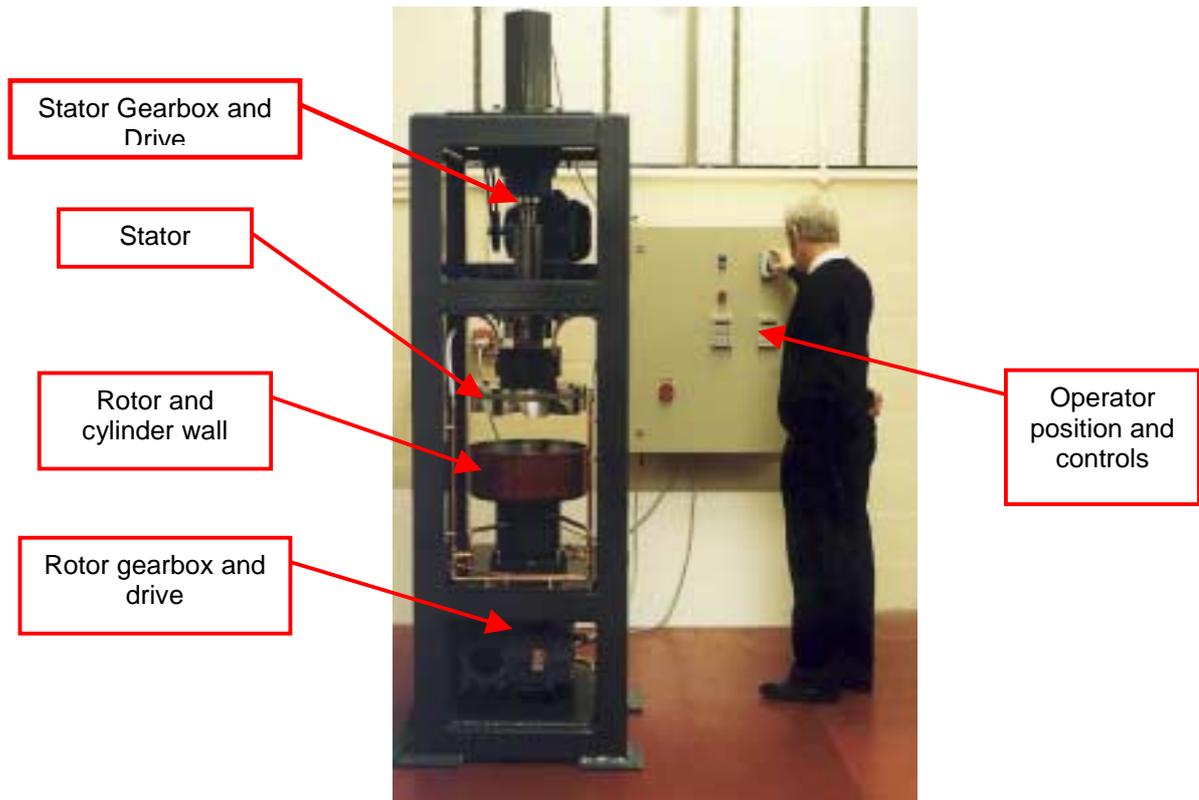
## **4 The new 5 litre High Shear Mixer**

The High Shear Mixer subjects a viscoelastic material of over 3000 poise to very high levels of stress at a controlled, typically low, temperature.

The primary aim of building a machine capable of handling 2 kg loads with a free volume of 5 litres was to verify that the effects obtained using the laboratory machine are indeed scalable. It was therefore important to ensure the correct scaling of the forces achieved by the laboratory machine in designing a small-scale production mixer to meet the process requirements. Both batch and continuous mixing variants were considered during the design process although it was decided that the batch version would enable closer modelling of the laboratory machine. A range of sizes was considered, to include sizes of up to 200 kg. batch and 5000 kg/hr continuous output.

### **4.1 Machine Design**

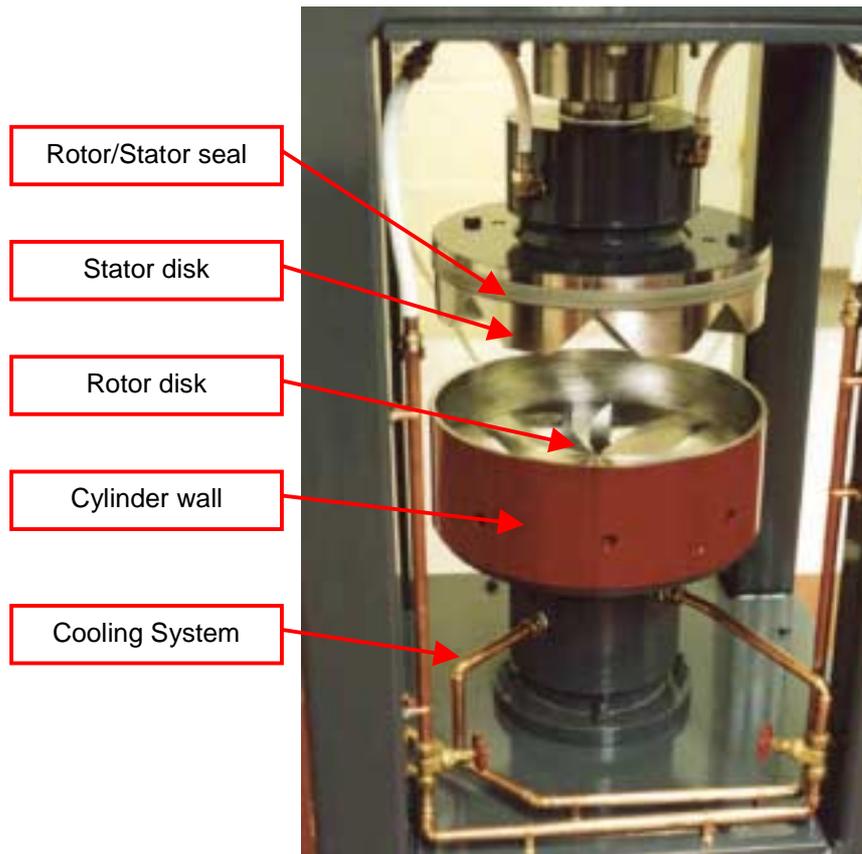
The HSM<sub>B</sub> is a batch vessel driven about the cylindrical axis. The vessel comprises of a cylinder with one end permanently closed. The permanently closed end of the vessel comprises of a disk with a set of grooves machined on its inner surface – the rotor disk (See Figure 2 and Figure 3).



**Figure 2: Full view of HSM showing operating position**

**Note: Some guarding has been removed for clarity. The machine will include these safety measures when it is supplied.**

A correspondingly machined disk that is not permitted to rotate – the stator disk – temporarily closes the other end of the cylinder during mixing. This is done by moving the stator along the cylindrical axis of the vessel, withdrawing it for loading and unloading and inserting it into the vessel during operation. Material is thus compressed within the chamber formed between the stator and rotor disks. Compression loading of up to 20 tonnes can be applied on the stator. A motor operating between limit switches drives the raising and lowering of the stator.



**Figure 3: Detailed view of the Stator-Rotor assembly**

The rotor is driven by a 5kW 3 phase asynchronous motor via a gearbox to provide a maximum speed of about 19 rpm and a maximum torque in the order of 3.2 kNm. Speed is variable via a programmable controller and in the test model, a computer constantly monitors the motor current to provide an indication of the power consumed.

The rotor and stator assemblies are mounted within a sturdy machine frame. All machine movements are precisely controlled so that during operation, gaps of less than 1mm can be obtained between stator and rotor.

When the vessel is closed the gap between the internal cylinder and the stator is sealed to ensure containment of the material. The atmosphere within the closed vessel can be controlled during mixing. Inert gas, typically nitrogen, can be piped into the mixing chamber for use when required.

Circulating water that is piped to extensive flowpaths within the rotor and stator disks controls the temperature during mixing. Typically open loop flushing with tap water is sufficient to maintain material temperatures below 70° C for most cases, with the surfaces of the machine being cold to the touch after mixing. Closed loop cooling or heating can be added.

The combination of the specifically designed rotor-stator geometry, the intense cooling and the precision of manufacture all contribute to the uniqueness of the HSM<sub>B</sub>.

#### **4.2 Operational features**

In operation, the geometries and low temperature of the rotor and stator disks provide a sequence of intensive:

- Shear stressing to fragment and soften the material;
- Shear and extensional stressing to align the molecular structure
- Extensional stressing to rupture aligned bonds;

- Shear and extensional stressing to rupture transverse and/or crosslink bonds
- Circulatory flows to ensure distributive mixing and to avoid the formation of hotspots and deadspots

Precise control of the process is obtained through:

- the accuracy of the axial movement, which manipulates the compressive stress fields
- the high surface area to volume ratio, which optimises the machine-material interface for maximum process efficiency and heat transfer rates
- the low thermal inertia, which maximises the heat transfer rates
- the mechanical accuracy and power of the rotational movement

The advanced and unique processing system of the HSM<sub>B</sub> is designed to:

- restructure crosslinked materials into uncrosslinked forms under controlled conditions, particularly to convert vulcanised rubber into devulcanised and hence soluble rubber
- increase the effectiveness of dispersive and distributive mixing of viscoelastic materials by intensifying and controlling stresses
- increase the efficiency of dispersive and distributive mixing of viscoelastic materials by intensifying and controlling the transfer rates of mechanical and thermal energies
- provide a controlled reaction environment, e.g. for processing under an inert gas to mechanochemically manipulate molecular weights.

The aggressive initial action of the machine allows material to be loaded with little or no pre-treatment. The final form of material, a disk-like sheet, is readily unloaded from the machine.

### 4.3 Operating Performance

During the commissioning and initial testing of the machine, general operating performance figures have been obtained, as shown in Table 1.

Materials	NR, SBR, BR, EPR, EPDM, CR, NBR, etc.
elastomer state	Cured, uncured or any % mix
fill factor	0.25 to 0.75
batch time	Typically 5 to 10 minutes
typical temperature range	50° C to 160° C
specific power range	0.4 to 4.0 kW/kg
specific energy range	400 to 1600 kJ/kg

**Table 1: Some operating values for the 2kg batch HSM**

The machine is relatively insensitive to fill factor, which makes it suited to situations where variable amounts of materials need to be processed. The sealed nature of the cylinder cuts down on noise and spews while providing an ideal container for buffings and finer ground particles. Given that the operation of the HSM<sub>B</sub> is similar in many ways to open-mill mixing on cold rolls, the machine also has many applications in the conventional compounding of viscoelastic materials; masticating, masterbatching, blending and finals.

## 5 Results of recent Trials

During the setting up and commissioning of the High Shear Mixer, numerous runs were carried out with various materials ranging from Natural Rubbers and EPDMs through to Nitriles and SBRs. Material was typically presented in sheet form although fine mesh crumb and buffings were also tested. In a number of cases the exact composition and history of the material was not disclosed to us.

For the purposes of this conference a trial was set up with known, specified materials designed for use as typical car and truck tire tread. These experiments and their results are described here.

In addition, some preliminary results are provided from a series of tests that are being carried out together with Flow Polymers Inc in which their Ground Rubber Additive is being added to 40 mesh tire crumb in the High Shear Mixer [4].

### 5.1 Treatment of Tire Tread Rubber

In preference to solubilising tire-tread rubber from a commercial source of unknown formulation, we mixed and cured as sheets a car-tread and a truck-tread recipe so that we had complete knowledge of materials. A summary of the formulations is presented in Table 2.

Material 01 - Car tread		Material 02 - Truck tread	
Composition	phr	Composition	phr
SBR	75	SMR20	70
BR	25	BR	30
N234	60	N220	55
Process oil	15	Process oil	8
Sulphur	1.5	Sulphur	2

**Table 2: Composition of Reference Car and Truck tread material**

Curing time for both materials was 15 minutes at 160° C. The uncured stocks for these were used as our solubilising agent.

The procedure we adopted for each solubilising treatment was to place pieces circa 100 cm<sup>2</sup> by 0.5 cm thick in the rotor basin of our HSM and to grind it to circa 1 cm<sup>3</sup> particles with the rotor and stator 1 mm apart. Pieces of the uncured stock were added on top and the mixer was closed on rotation to a 1 mm gap for 5, 15 and 30 minute cycles.

We chose 50% tread to stock as the standard test. Additional runs were carried out at 75% and 90% to establish sensitivity of mix. Nine runs were carried out as shown in Table 3.

Material	Tread to Stock Ratio	5 minutes	15 minutes	30 minutes
01	50/50	✓	✓	✓
	75/25		✓	
	90/10			✓
02	50/50	✓	✓	✓
	75/25			
	90/10			✓

**Table 3: Overview of runs carried out for trials on 30<sup>th</sup> September and 1<sup>st</sup> October 1998**

The total charge was kept constant at 1.4 kg. Cold water was run continuously to keep the vulcanisate from ambient temperature circa 17° C to less than 80° C by the end of the solubilising treatment.

In all cases, a softened mass was obtained. Lumps were seen, decreasing to less than 1mm in size and 10% amount with time to 30 minutes.

To recycle these mixings in uncured stock, two letdown approaches were examined. In the first method, the same ratio's used in the mixing were used to let down the uncured stock. For example, taking a 50/50 mix, 200 g of solubilised material was blended in with a further 200 g of uncured stock on a cold mill. The sample material was banded and removed after approximately 30 seconds. Next the uncured stock was banded and removed after 30 seconds. Finally banded sheets in an uncured stock sandwich were blended for 4 minutes at 1/6 friction speed with a nip of approximately 3 mm before sheeting out.

In the second method, a letdown of a fixed ratio was used for the processed material from the mixer to the uncured stock. This was fixed at a chosen 25% level, so that 100g of material from selected trial runs was blended on a cold mill with 300g of stock and sheeted at 3 mm.

The blends and controls of 100% stock were then cured as a 2mm sheet at 160° C for 15 minutes. Lumps were observed in the blended materials after curing, their size and quantity being consistent with the condition of the material from the trial runs.

## 5.2 Results of physical and chemical testing of recycled material

Standard dumb-bell test pieces were cut out for stress-strain measurement and the results are shown in Figures 4 and 5.

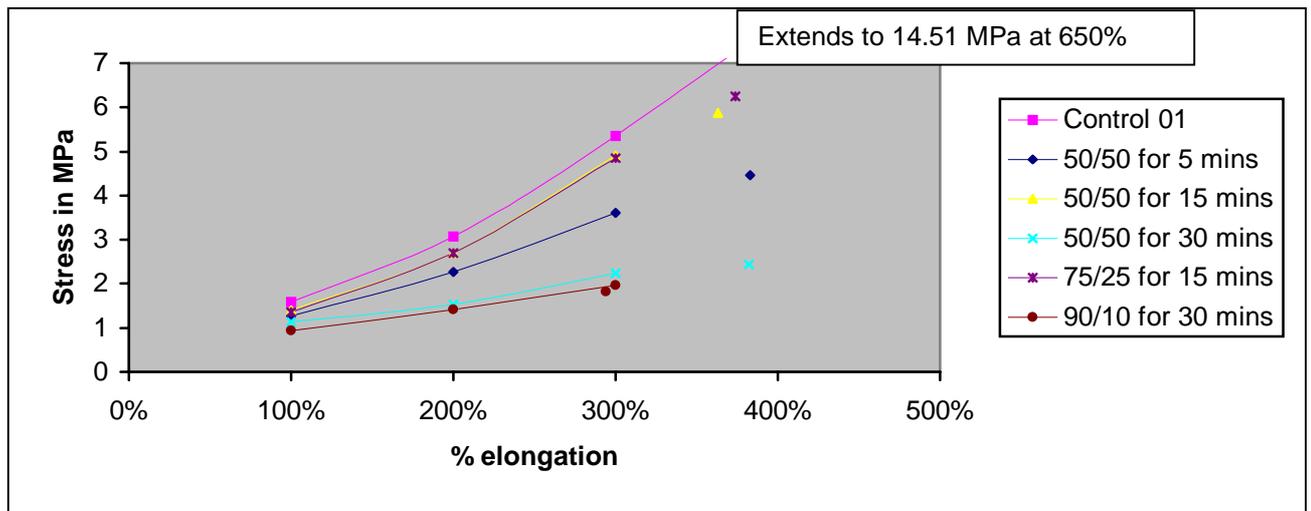
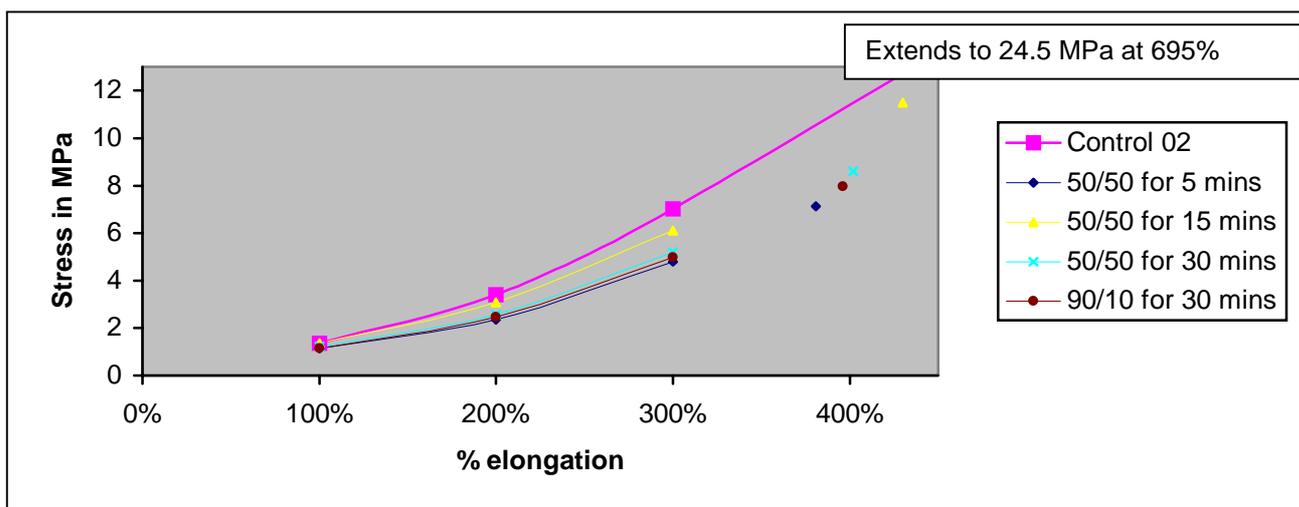


Figure 4: Stress/Strain results for the car tire recipe



**Figure 5: Stress/Strain results for the truck tire recipe**

The dumbbells with recycled material all broke before 500% extension. During the test, localised rupturing around lumps in the material was clearly visible.

Samples were placed in a Monsanto rheometer and the scorch time and time to 90% cure was measured. Volume tests were carried out by placing samples in n-decane for 24 hours to ISO 1817, 1975. Hardness tests were completed using the IRHD method using a 2.5 mm indenter with a 20 mm foot to ISO 48. The results of these tests are shown in Table 4.

Material	Treatment	Monsanto Rheometer (% of original)		Swelling (% of original)	Surface hardness IRHD
		T90	Scorch		
01	Control, pure tread mix	100.00 %	100.00 %	100.00 %	64.0
	50/50 for 5 mins	97.22 %	88.00 %	109.10 %	59.5
	50/50 for 15 mins	97.22 %	88.00 %	106.54 %	61.5
	50/50 for 30 mins	104.17 %	80.00 %	125.10 %	53.0
	75/25 for 15 mins	97.22 %	80.00 %	97.47 %	70.0
	90/10 for 30 mins	97.22 %	72.00 %	104.45 %	56.5
02	Control, pure tread mix	100.00 %	100.00 %	100.00 %	60.0
	50/50 for 5 mins	84.34 %	89.47 %	100.24 %	56.0
	50/50 for 15 mins	84.34 %	73.66 %	103.02 %	63.0
	50/50 for 30 mins	78.02 %	78.95 %	105.36 %	61.0
	90/10 for 30 mins	100.00 %	94.74 %	105.91 %	59.0

**Table 4: Swelling, Hardness and Monsanto Rheometer results**

### 5.3 Mixing of 40 Mesh tire crumb and Ground Rubber Additive from Flow Polymers Inc.

An additional series of tests have been carried out together with Flow Polymers Inc., using 40 mesh tire crumb, their patented GRA (Ground Rubber Additive) and a compounded uncured NR. In one of these trials, 0.5 kg of tire crumb, 0.1 kg of GRA and 0.5 kg of uncured NR were mixed for 5 minutes in the HSM<sub>B</sub>. This was then blended with uncured stock at 26 phr and evaluated against non-treated 40 mesh crumb and a control batch in a basic tire tread formulation. Physical properties, i.e. moduli and tensile values, were within 8% of the control batch whilst the non-treated crumb yielded a reduction in physical properties of more than 20%. The processing characteristics of the treated material were also significantly better than

the non-treated crumb, with mold flow and crumb incorporating properties also being significantly improved. The Mooney viscosity of the treated material was within 7% of the control whilst the non-treated batch deviated by more than a 20% viscosity increase.

These joint trials are continuing and the results will be published at a later stage.

## 6 Conclusion

Although the process has been subjected to only a limited amount of evaluation on the 2 kg machine, these early results appear to be promising. Results such as those reported in this paper indicate that, while we appear to be on track to developing a true recycling process for rubber, work still needs to be done in terms of optimising the process.

The inclusion of insoluble lumps is the unsatisfactory feature of this set of trials. They appear to be the cause of low Elongation at Break and correspondingly low UTS values. We see three routes to eliminating this problem:-

1. Starting with a 40 mesh or finer crumb
2. Altering the variables of the mechanochemical process
3. Straining out unwanted lumps.

The engineering approach to the scaling up of the batch machine has proven successful. The results obtained using the 2 kg HSM are comparable with those obtained from the 2g machine, 1000 times smaller. Initial calculations indicate that the batch machine should be scalable up to 200 kg beyond which the powers required to drive the machine form a major limitation. The initial design work on a continuous version of the mixer indicates that this approach is feasible for mixers with volumes of up to 5000 kg/hr. The designed optimum process time of between 5 and 15 minutes appears to be validated by the test results. These cycle times contribute to an economically feasible approach.

Through these trials using the HSM technology, there is a strong indication that the application of the principles of Mechanochemistry may well be a route to the true recycling of vulcanized rubbers. We are now entering the phase where specific applications are being identified to which this technology may be applied to exploit new market opportunities. These opportunities flow from the potential ability of this unique technology to upgrade and hence add value to waste rubber materials previously disposed of or destroyed.

## 7 Acknowledgements

The authors would like to acknowledge the support of James Hoover at Flow Polymers Inc. for information on the GRA technology and Dr Simon Read and Dr Mark Clemens of the Manchester Metropolitan University for the testing of the materials.

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## 9 How to contact us

Watson Brown HSM Ltd.  
First Floor Offices  
59-61 High Street West  
Glossop  
SK13 8AZ  
England

Phone: +44 1457 858800

Fax: +44 1457 862207

Email: [Sales@wb-hsm.com](mailto:Sales@wb-hsm.com)

Website: [www.wb-hsm.com](http://www.wb-hsm.com)