A new development in melting the Tyre Mountain

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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 HSM Technology, promises to overcome the economic and technical barriers to reaching this goal.

In this paper, HSM Technology is described in the context of the need for the true recycling of rubber materials. The description includes an overview of its background and the results of recent trials on SBR and tyre compounds in which high values of UTS have been obtained.

Acknowledgements

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1 Introduction

Rubber is not regarded as an environmentally friendly material. Once valuable resources (raw materials and energy) have been invested in a rubber product they are effectively locked-in by the vulcanisation process. The inability of current technologies to provide environmentally friendly and economic processes to effectively unlock these invested resources, has resulted in waste rubber being viewed as a costly problem rather than as a valued asset.

Tyres account for nearly half of the rubber consumed. An estimated 270 million tyres reach their end of life in the US each year, over a billion throughout the world [1]. Each tyre constitutes a particularly difficult problem environmentally: its rubber does not break down to be recyclable as do, for example, glass, paper and metals, its shape harbours insects, its volume encloses much air and it is dangerously combustible.

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"*. In dealing with the vulcanised rubber waste generated both from industrial scrap and end-of-life products, the main focus to date has been on rubber waste as "the problem" rather than as "the asset".

Current approaches to waste rubber may have the potential to deal effectively with the volume of waste generated, but are not effective in truly recovering the investment made in the rubber material or products. They typically yield low-cost fuels or low-specification materials at fractions of a percent of the original product value [14]. As considerable further investments in energy and resources are often required to further process these materials a point is quickly reached where all the previous investments must be written off if any financial margin is to be retained.

Legislation and social pressures, driven by environmental concerns and practical issues such as landfills reaching capacity, are forcing the rubber industry to address the problem of waste materials more acutely. Without a technical solution and a sustainable economic model, these pressures will only serve to increase industry costs and further reduce margins throughout the supply chain.

To reverse this downward spiral, more of the value of the rubber material must be unlocked to provide higher value materials. Ideally, if vulcanised rubber could be returned to an unvulcanized state, it could be recycled into products of the same or similar economic value and technical performance.

In this paper, a new technology based on the principles of mechanochemistry is presented. Recent results show that this approach yields relatively high specification recycled materials from both end-of-life products and in-house scrap. At the heart of the technology is a radical mixing process which appears to be scalable and which operates within industry recognised energy and process limits for mixing . As such, HSM technology promises to be the key to unlocking the value of waste rubber in the future.

1.1 The problem

Since Goodyear's discovery that, by subjecting a combination of sulphur, carbon and rubber gum to heat and pressure, a strong durable engineering material can be produced, the global application of vulcanised rubber has grown to a yearly production level of 17.02 million tonnes in 1999 [2].

Approximately 40% of this, 6.84 million tonnes was natural rubber, whilst the remaining 10.18 million tonnes consisted mainly of oil-based synthetic rubbers. In the same year, around 1 billion tyres were manufactured, requiring approximately 10 million tonnes of rubber material, including most of the 6.84 million tonnes of natural rubber produced.

Once vulcanised rubber has reached the end of its working life it must be recycled or disposed of. In 1998 it was estimated that between 750 million and 1 billion tyres were scrapped globally, weighing 6 to 10 million tonnes. Approximately 550 million tyres weighing about 5.7 million tonnes were recorded as being

scrapped in Europe and the US alone. Although most of the published figures report scrap tyres, it may also be assumed that other rubber products are reaching their end-of life and that the total rubber waste stream may therefore tend towards the production totals of 16 to 17 million tonnes p.a. A simple life cycle model shows that the majority of end-of-life material is either landfilled or incinerated (see **Figure 2**). Note that estimates have been used in the absence of recognised reporting. Additional rough estimates have been included of energy inputs into the life cycle, based on information drawn from a variety of sources [1,2,4,5,7,8,9,13,14]
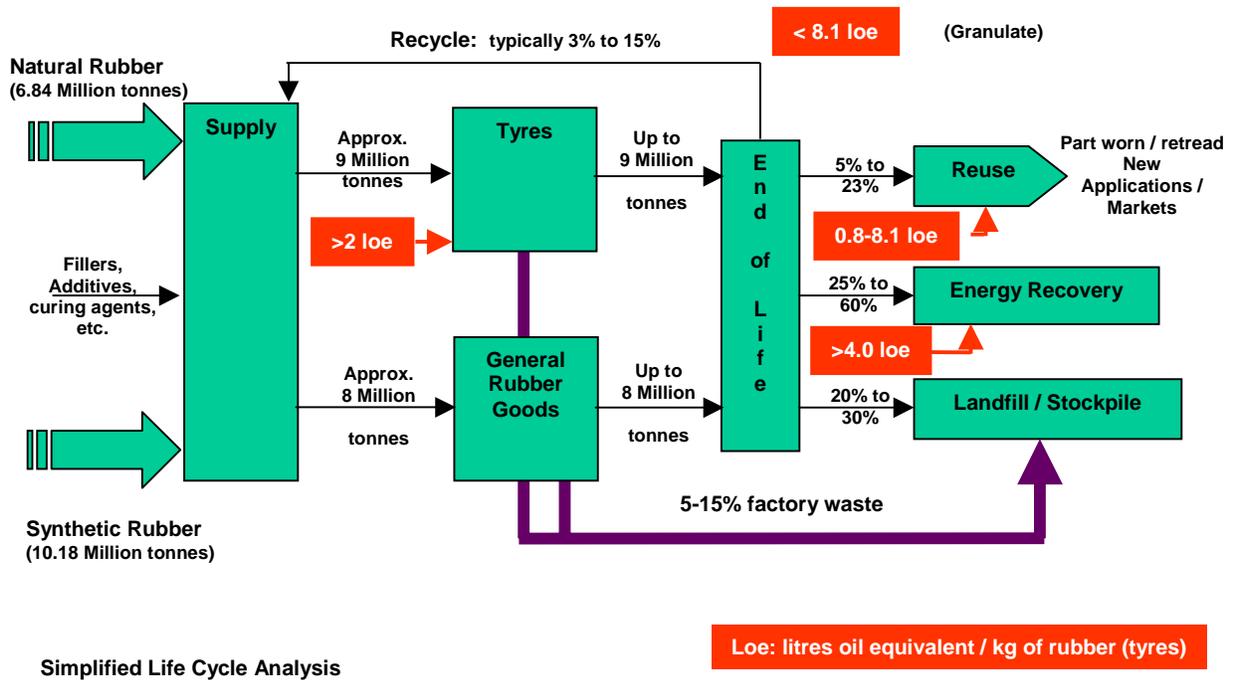

Figure 2: Simplified Lifecycle for rubber products

In reviewing the status of the waste rubber problem, the following observations have been made [14]:

- rubber waste is viewed as a problem, not as an asset
- low levels of invested resource are recovered at end of life
- there is a high environmental cost of disposal
- no economic / technical alternatives to rubber exist for major applications
- there is a steady increase in the number of products such as tyres in use every year

The resistance to change the way that waste rubber is treated has a number of origins, which include:
- The lack of technologies capable of economically unlocking the investment in rubber materials and returning them into valuable feedstock
- The market perception that products containing high levels of recycled materials are of lower quality or value than those made from virgin materials
- The low prices of raw materials

However, the economics of the situation are changing as rising material prices, particularly oil-based materials, force up manufacturing costs. In addition, processing costs, which are sensitive to both energy and taxes, are increasing, waste disposal opportunities are decreasing and waste disposal costs are

increasing. Concerns such as the long-term environmental impact of waste rubber in regard to pollution, environmental loading and energy consumption can be added to a number of practical issues such as the landfill sites reaching their capacity.

Landfilling and stockpiling tyres are now regarded as not being environmentally sustainable solutions. For example, the UK Environment Agency has reported a number of problems associated with the landfilling of tyres [4]. Tyres buried in landfill sites are a fire hazard and ignition can cause serious air pollution as well as the pollution of underground water supplies(a fire that started in 1989 in a dump with 10 million tyres in Powys in Wales is still burning). Buried tyres also tend to rise to the surface, affecting long-term settlement and possibly causing problems for future land use and reclamation. The Environment Agency report [4] has also indicated that the effects of the long term leaching of organic chemicals are not known.

As a direct response to this problem, a number of countries are legislating against the landfilling of rubber materials, while the European Landfill Directive will ban the burying of whole tyres in landfill sites by 2003 and shredded rubber by 2006. A number of landfill site operators have already responded by dramatically increasing the disposal cost of tyres or by simply refusing to accept tyres or rubber waste.

Increasing use is being made of legislation to force industry to tackle the long-term problems of pollution. In 1993 the European Commission set pan-European targets for the year 2000 of 65% recovery (including energy recovery) and 25% retreading, with 10% undefined. Although these targets have yet to be achieved they do form the basis of the EC Landfill Directive.

The increase in environmental concern, legislation and financial penalties will continue to act as primary drivers in this field. Economic alternative approaches are, therefore, urgently required if the Rubber Industry is to meet this challenge effectively.

1.2   Current approaches to recycling tyres

The generally accepted hierarchy of measures for the management of waste materials [9] as depicted in Figure 3 shows that the most favourable measures ensure the maximum usage of the resources already invested in the waste product, whilst the least favourable require considerable further investment of resource for very little, or no return.
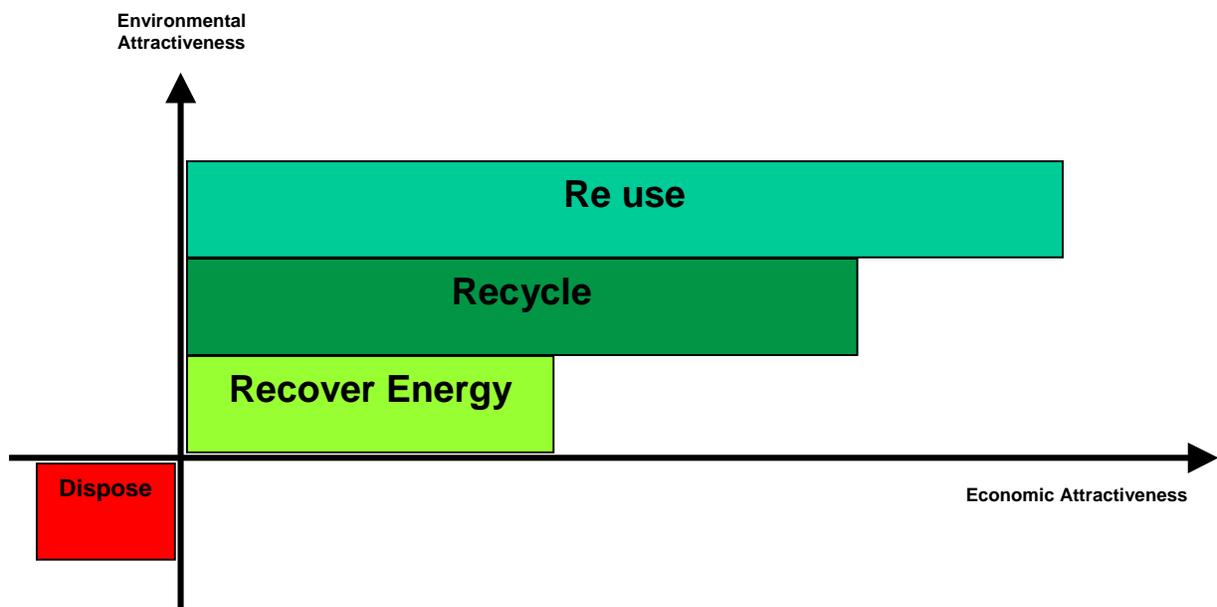

Figure 3: Waste Management Hierarchy

When positioning waste rubber products on this hierarchy, the following observations can be made:

- **Disposal**, which mainly consists of landfill / stockpile and incineration, currently handles a significant portion of the waste stream, although this is set to change as legislation comes into force
- **Energy Recovery** is particularly favoured in the US, handling more than 60% of the tyre waste stream. It is noted that although some countries, such as Finland, are taking steps to legislate against rubber incineration as a protection against global warming, this is currently the main technology applied to rubber waste.
- **Recycling** currently accounts for 5% to 15% of the waste stream.
- **Reuse** ranges from the extension of product life (notably the use of part worn tyres for less demanding operating conditions and retreading), through to the use of the product in new application areas, such as in the construction industry.

Although recent efforts in Europe and the US have focussed on managing the disposal of scrapped tyres, a difference in the current implementation can be observed. The reliance on energy recovery in the US is much higher than in Europe. It should be noted however that the Scrap Tire Management Council in the USA reported in 2000 that a 20% decrease in its usage occurred over the previous two years, partly as a result of furnace efficiency requirements.

Although Europe appears set to follow the USA path of energy recovery, concerns associated with the environmental impact of the incineration process, particularly in cement kilns, have also been expressed. These concerns range from the emissions and by-products generated, through to the environmental impact of burning synthetic rubbers which represent high hydrocarbon investments. During the oil crises in the 1970's it was estimated that it required 3.5 tonnes of oil to produce 1 tonne of SBR. Whilst current manufacturing efficiencies have been improved, a high level of hydrocarbons is still involved, up to 10 times that of natural rubbers. A carbon black filler content of circa 30-40% further increases the hydrocarbon value. It has also been observed that the continuing increases in targets embedded within environmental control legislation tend to reduce the economic feasibility of the total process of incineration.

Given the concern generated by the topic of global warming, it would be prudent to evaluate current and future rubber recycling strategies in terms of the total energy balance throughout their lifecycle in order to determine their "environmental friendliness".

2 HSM in context

The lack of an economical recycling technology that can unlock the true economic value of waste rubber by providing a recycled material with properties approaching those of virgin feedstock, is the major barrier to the implementation of models based on rubber as a recyclable material. The ideal form of recycling is through devulcanisation, in which the vulcanisation process is reversed to provide a soluble material for re-use. In basic terms, a technology that can break existing crosslinks whilst causing minimum damage to the polymer backbone and can produce a stable material that can readily take part in further crosslinking processes is all that is required.

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 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 waste rubber 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 probably because the main polymer chains as well as some crosslinks have been broken by this process to give a jumble of small molecule fragments with little elastic strength. This makes it unacceptable for performance related applications, such as for modern tyres.

What is needed is for the cured rubber network to be cleaved only at the crosslinks, thereby re-forming 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 [20] 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 papers [15] and [16], we envisioned a commercial process via Mechanochemistry and reported initial results obtained from 2g, 20g and 2kg machines. Both in-house factory waste and end of life waste were treated. In paper [16], particular attention was paid to the scalability and feasibility of the approach for waste tyre materials.

2.1   Mechanochemistry

Mechanochemistry is the term given to describe mechanically induced chemical reactions. Initially this branch of chemistry was used to increase the understanding of the effects of mastication on uncured rubber. Watson and co-workers in the 1950's showed [6] that the softening of rubber by cold mastication is due to the rubber chains being so extended in their central sections that a main-chain bond there is ruptured. The ruptured ends are free radicals which are normally terminated by combining with oxygen. However, they can also be arranged to react otherwise, such as by 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.

For cured materials, it has been predicted [2] that a rubber network sufficiently extended will rupture preferentially at crosslinks. These are likely to be regions of stress concentration and where the sulphur bonds at the crosslinks are of lower bond strength than the carbon-carbon bonds of the main polymer chain. It is further expected that bonds within the crosslink will break rather than adjoining bonds in the chain segments .

These two predictions are contained in the equation represented in Figure 4.
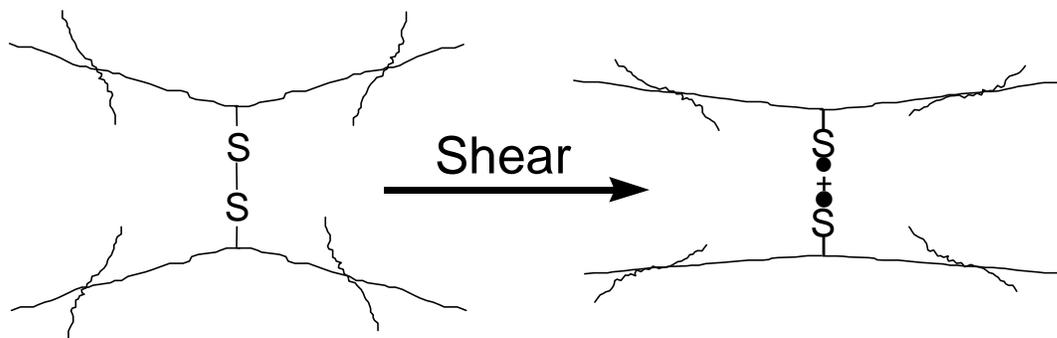

Figure 4: Effects of selective shear on vulcanised bonds

It has further been anticipated that this devulcanisation process will 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 known that incorporating crumb within a matrix of stock and mixing in an internal mixer only moves the particles within the matrix. Any rupture of crosslinks would have been discovered empirically years ago if this was not the case.

W.F. Watson concluded that a more effective form of mixer capable of applying higher shear was required and in the 1990's conducted a series of laboratory scale experiments (2g sample size) using a novel processing machine to show that a rubber network, sufficiently extended, would rupture preferentially at crosslinks. This work has been patented (PCT/GB96/00956) and the machine, which has the productivity of an internal mixer but with the capability of imposing shear comparable to that by the tight nip of a two-roll mill, termed a High Stress Mixer (HSM).

This early work has been extended to include a wide range of viscoelastic polymers, including NR, SBR, BR, EPR, EPDM, CR, and NBR and an initial 1000 times scale-up to a 2kg batch size in 1998.

Whilst work on SBR and NR tyre compounds reported in 1998 [16] indicated the potential of the technology, recent work has revealed very promising results. Already capable of providing a useful material for a number of applications, further optimisation of the process should result in an economical and energy efficient technology capable of fulfilling a major recycling role.

2.2   HSM technology

The High Stress Mixer repeatedly subjects a viscoelastic material of typically above 3000 poise to very high levels of stress in a controlled and consistent manner. Analysis of existing internal mixer technologies, such as the tangential rotor (Banbury) and the interlocking rotor (Intermix)), indicates that their geometries are not suited to this form of mixing. They are neither capable of imparting the levels of energy required for bond breakage, nor of controlling the temperature with sufficient accuracy.

HSM represents a fresh look at internal mixing. Material is moved through zones of very high stress in a controlled manner, after which it is allowed to relax in zones of low stress (see Figure 5). The flowpath through the mixer is designed to ensure good distributive mixing whilst the infinitely variable gap enables levels of stress to be adjusted to suit specific mixing requirements. The repeated stressing and relaxing of the material reduces the risk of over-mixing and enables chain alignment, whilst a highly effective cooling system ensures tight control of the material bulk temperature.
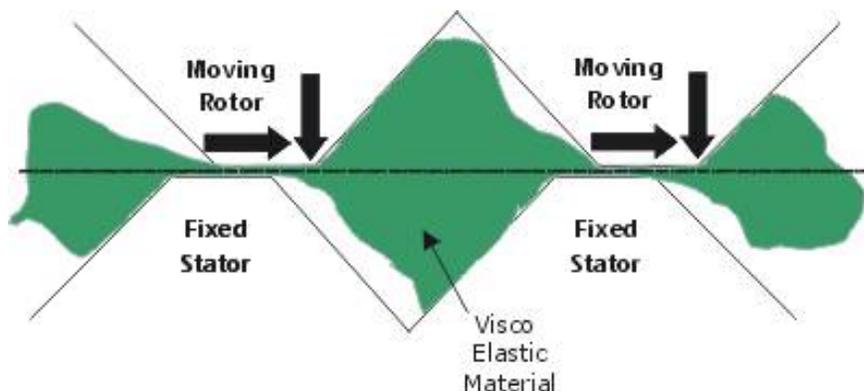

Figure 5: Schematic representation of a HSM geometry showing areas of high and low stress

These principles have been used to develop rotor geometries for a range of HSM machines, from 2g and 20g batch sized laboratory bench top machines (see **Figure 6**) to larger 2kg (see section 2.4) and 20kg

machines. It is envisaged that 200kg (1 tonne/hr) and 500kg (2.5 tonne/hr) machines will be required for larger processes and operations.
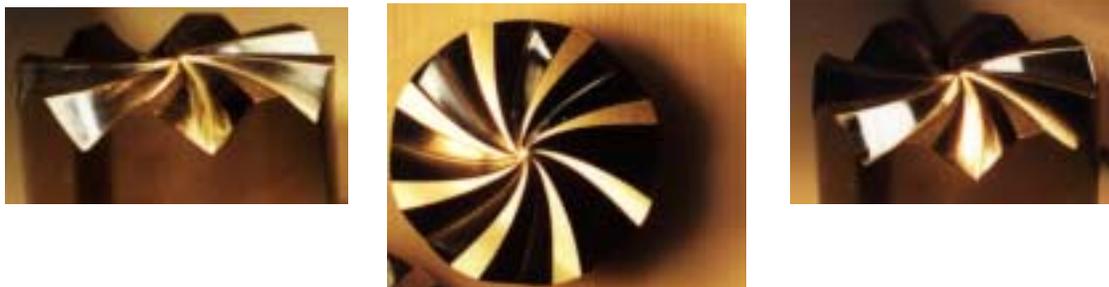

Figure 6: Views of a rotor geometry based on HSM principles (20g machine)

Although a continuous variant is envisaged, current work is based on batch machines to enable tight control of process parameters to be maintained during low-volume runs.

2.3   Operational features of the HSM

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 determines 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_B 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 is readily unloaded from the machine.

2.4   Design of the 2kg Machine

Work on scaling HSM geometries has resulted in a range of small-scale machines from 2g to 2kg batch capacities. Development work on a 20kg machine is currently under way with the first deliveries scheduled for Q4 2001 (see chapter 4.1 - CRAFT project). Regarded as a small sized production machine, the 20kg HSMb will be capable of processing approximately 0.1 tonnes/hour.

For the 2kg machine, the design incorporates a rotating chamber (the rotor) and a stator that can be lowered into the rotor to form a sealed mixing chamber. These are illustrated in Figure 7 and Figure 8.
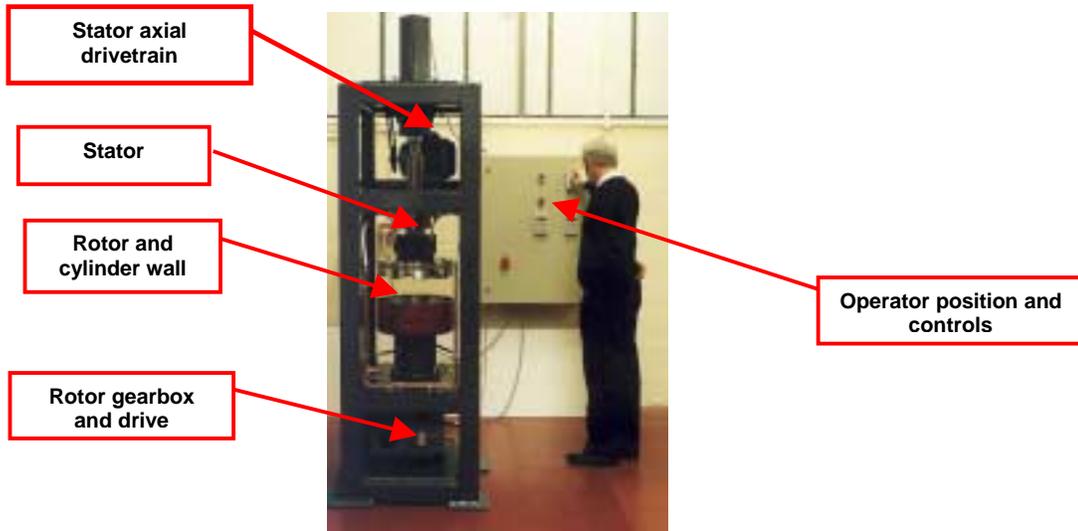

Figure 7: Full view of 2kg HSM showing operating position

Note: Some guarding has been removed for clarity. The machine includes these safety measures when supplied.
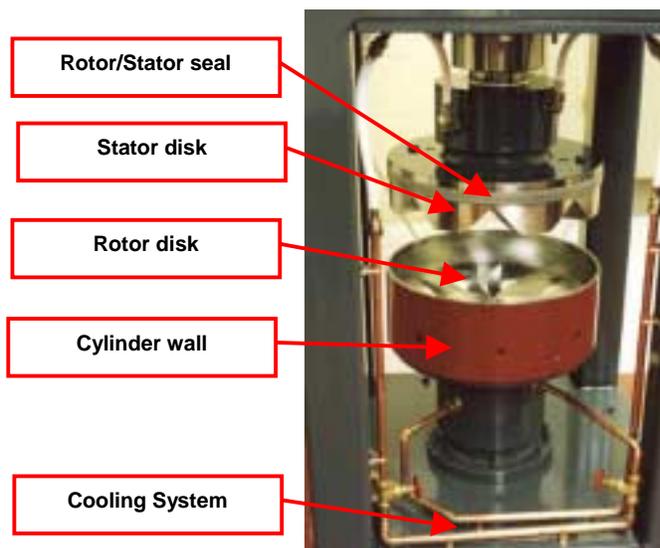

Figure 8: Detailed view of the 2kg HSM Stator-Rotor assembly

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, axial separation gaps of less than 1mm can be obtained between stator and rotor. When the vessel is closed, the gap between the internal cylinder wall and the stator is sealed to ensure containment of the material. The atmosphere within this 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 mains water at less than 20°C 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_B.

2.5   Operating Performance of the 2kg Machine

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 15 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 sprews while providing an ideal container for buffings and finer ground particles. Given that the operation of the HSM_B 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, and blending. HSM promises to offer a number of advantages over conventional mixing when compounding silica filled materials, such as:
- tight temperature control
- high wear resistance as seals are not part of the mixing chamber
- controlled atmosphere which includes mixing under vacuums

2.6   The economics of the approach

Whilst it is not intended to provide a detailed analysis of the economics of the HSM approach in this paper, the following points can be made:
- the HSM operated as a mixer and can be placed in a mixing line along with other processing equipment. It requires energy to run (of the same order as similar sized internal mixers), but no additional chemicals. The resultant process material can be regarded as a compound that includes fillers but not the curing system.

- Payback times vary depending on the value of the materials being recovered and the local waste disposal costs, levies and fees. For high cost materials, payback can be within 6 months.

Economic models need to include the total process and not just the HSM element. For this reason, detailed analysis is carried out on a case-by-case basis.

3   Proving the Concept

The ultimate aim for HSM technology is to facilitate true recycling of rubber materials. The success of this must be judged by the recycled material retaining or regaining close to it's original properties, both as an uncured raw material and as a crosslinked product. The material should be capable of being re-used in it's original application, either wholly or as a high proportion of the compound. From an economic and environmental standpoint, this aim could be restated as "unlocking the value of waste".

In order to prove the concept, a number of experimental trials have been undertaken using machines from 2g to 2kg in capacity. A wide range of materials have been investigated and the resulting HSM processed materials evaluated by both chemical and physical testing procedures. These are described below.

3.1   Initial trials

During the setting up and commissioning of the 2kg 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 processed 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 were not disclosed to us.

In order to establish a more controlled approach to the evaluation of the performance of the machine, a trial was set up in 1998 with specific model compounds designed to be typical of those used as car and truck tyre tread. The two formulations are shown in Table 2. The results of these experiments were originally reported at the Rubber Recycling '98 conference in Toronto and the results are summarised below.

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

The curing time for both materials was 15 minutes at 160°C. The uncured compounds of these were used as the solubilising matrix material. The procedure adopted for each solubilising treatment was to place pieces of around $100cm^{2}$ by 0.5cm thick in the rotor basin of the 2kg HSM and to grind it to approximately $1cm^{3}$ particles with the rotor and stator 1mm apart. Pieces of the uncured compound were added on top and the mixer was closed on rotation to a 1mm gap for 5, 15 and 30 minute cycles. A mixture ratio of 50% tread to stock was chosen for the standard test and additional runs were carried out at 75% and 90% to establish the effect this had on the process. Nine runs were carried out as shown in Table 3. The total charge was kept constant at 1.4kg. Cold water was run continuously to keep the material below 80°C by the end of the process.

Material	Tread to Stock Ratio	Mix Time (minutes)		
		5	15	30
01	50/50	✔	✔	✔
	75/25		✔	
	90/10			✔
02	50/50	✔	✔	✔
	75/25			
	90/10			✔

Table 3: Summary of initial trials

In all cases, a softened mass was obtained. Lumps were seen, decreasing to less than 1mm in size and about 10% of the overall material after 30 minutes. The initial mixtures were let down with additional uncured material in two ways. In the first method, the same ratios used in the initial HSM process were used to let-down the uncured stock. For example, taking a 50/50 mix, 200g of solubilised material was blended in with a further 200g 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 3mm before sheeting out. In the second method, a let-down 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 3mm. 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.

Standard dumbbell test pieces were cut out for stress-strain measurement and the results are shown in Table 4 & Table 5

Material	Tensile strength (MPa)	Elongation at break (%)
01 Control	14.5	650
50/50 5 minutes mix time	4.5	383
50/50 15 minutes mix time	5.9	363
50/50 30 minutes mix time	2.4	382
75/25 15 minutes mix time	6.3	374
90/10 30 minutes mix time	1.8	294

Table 4: Results for trials using material 01 (SBR based tread material)

Material	Tensile strength (MPa)	Elongation at break (%)
02 Control	24.5	695
50/50 5 minutes mix time	7.1	381
50/50 15 minutes mix time	11.5	430
50/50 30 minutes mix time	8.6	402
90/10 30 minutes mix time	8.0	396

Table 5: Results for trials using material 01 (SBR based tread material)

The dumbbells with recycled material all broke before 500% extension and the tensile strength values obtained were relatively low. During the test, localised rupturing around lumps in the material was clearly visible. In addition to tensile testing, the samples produced were evaluated by Monsanto rheometry, and the swelling behaviour and hardness determined, although the results were somewhat inconclusive.

These limited trials using the 2kg machine produced promising results and indicated that the HSM approach to rubber recycling was worth pursuing. But it was clear that further work needed to be carried out in order to fully optimise the process. The engineering approach to the scaling up of the batch machine had proven successful. Initial calculations indicate that the batch machine should be scalable up to at least 200kg. The initial design work on a continuous version of the mixer indicates that this approach is feasible for mixers with volumes of up to 5000kg/hr. The designed optimum process time of between 5 and 15 minutes appears to be validated by the test results and contributes to an economically feasible approach.

3.2   Recent Trials

Whilst the results from the initial work on the 2kg HSM were promising, it was clear that more detailed experimentation was required to prove the HSM concept more conclusively. It was therefore decided to undertake a series of experiments using a 20g machine in an attempt to map the process more fully. The 20g HSM is a bench-top version of the 2kg machine, ideal for carrying out mixing trials on a small scale. The basic mode of operation and mixing head geometry (see Figure 5) are very similar to the larger machine, except that the gap between rotor and stator is changed manually by adjustment of a helical thread. Cooling is limited to the chamber in which the stator is located, but is very efficient at maintaining material temperatures to below 80°C.

3.2.1   Material Choice

The material selected was one of those used in the initial work, namely, the model passenger tyre tread compound 01, based primarily on SBR. This material was chosen to enable comparison with the work carried out on the 2kg machine and because passenger tyres make up a large proportion of the scrap rubber being produced. SBR is also interesting to consider from an environmental and economic point of view because of the large amount of energy invested in it's production, compared to natural rubber, for example.

3.2.2   Experimental approach

As with any compounding technology there are numerous variables that have to be considered. In order to map the process effectively, it is necessary to look at several key variables simultaneously. This can be achieved using statistical experimental design techniques, which allow sufficient data to be collected from a reasonable number of trials. In the experiment to map the mixing process in the 20g machine using material 01, the following key variables were selected, based on the results of preliminary trials:

> Mix time (5 to 25 minutes)
> Operating gap between rotor and stator (0.8 to 1.6mm)
> Ratio of cured to uncured material 01 (80 to 100% cured material)

All other parameters were fixed as follows:

> Water cooling: on (8 to 16°C)
> Batch size: 18g
> Mix cycle: fixed for each rotor gap
> Material form: the same thickness (ca. 6mm) of cured and uncured slabs used throughout

The quadratic response surface experiment consisted of 21 trials of which 5 were replicated. Each of the trials was repeated 5 times to provide sufficient material for testing. After HSM processing the materials were lightly milled, at which point sulphur was added according to the proportion of cured material present in the sample, such that the sulphur available for curing was the same as for the original compound. None of the samples were let down further. The cure characteristics were determined by Monsanto rheometry and all samples were cured at 150°C for 24 minutes. Dumbbell samples from the resulting cured sheet were subjected to tensile and hardness testing. In addition to measuring the physical properties of the resulting materials, the HSM process itself was carefully controlled and monitored throughout each experiment. Both material and cooling water temperatures were measured before and after each run and the motor current was logged throughout.

3.2.3   Results

The test results obtained, along with data collected during the experiments were analysed using ECHIP experimental design software. The results of this analysis not only identified the significant variables, but also generated response surface maps showing the effect of the variables on each response. The main significant effects are summarised in Table 6 below:

Response	Effect on Response of Increasing Variable		
	Gap	Mix Time	% Cured Material
Tensile strength	Small decrease	Small increase	Large increase
Elongation at break	Small decrease	Small increase	Large increase
IRHD Hardness	Not significant	Not significant	Not significant
Monsanto cure Minimum torque (T_{min})	Small increase	Large decrease	Quite large increase
Monsanto cure Maximum torque (T_{max})	Not significant	Quite large decrease	Quite large increase
Monsanto cure T_{max} - T_{min}	Not significant	Quite large increase	Not significant

Table 6: Significant effects and responses

All of the other responses were not significantly, or only slightly, affected by the chosen variables. The generated response surface plots illustrate graphically the effect of the significant variables on the chosen responses. Figure 9 to 10 show how the percentage of cured material in the mixture impacts upon the cure characteristics as revealed by the Monsanto rheometer cure curves. Figures 8 & 9 both show the same trend, in that both the minimum torque (T_{min}) and the maximum torque (T_{max}) values decrease as mix time increases. This was no surprise and would indeed be expected for a cold mastication process that leads to a breakdown of molecular weight and hence material viscosity. What was more interesting was the effect of the percentage of cured material in the mix. After a mix time of 5 minutes, the observed torque was much lower when there was the greatest proportion of uncured material in the mix. As the mix time increased, the torque observed fell regardless of the amount of cured material present, but most sharply when the mix consisted of 100% cured material. After 25 minutes, there was an almost insignificant difference between mixes containing 80, 90, or 100% cured material. The clear implication of this observation is that the cured material is being broken down during the mixing process, resulting in a lower overall viscosity and subsequent cured stiffness. What could be concluded from these results alone is the precise nature of this breakdown of the cured material. The question at this stage was whether this torque / viscosity reduction is due to the breaking of crosslinks, or simply the breakdown of cured fragments into smaller particles.

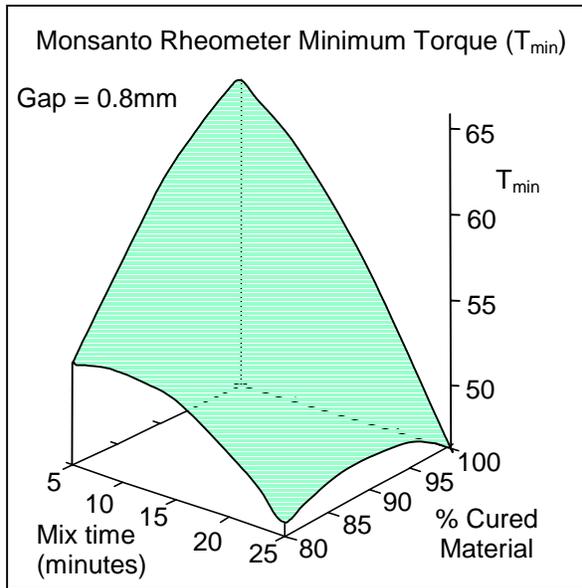**Figure 11** shows how the key variables affect the increase in torque observed over the 21 experimental trials.

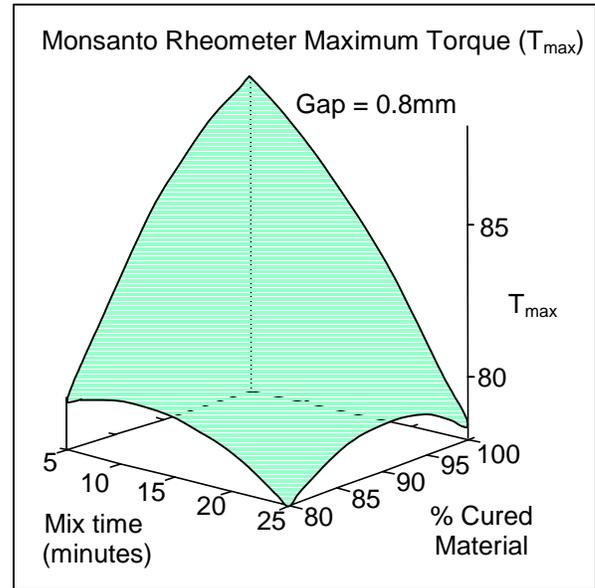**Figure 9: Monsanto Rheometer Minimum Torque (T_{min})**

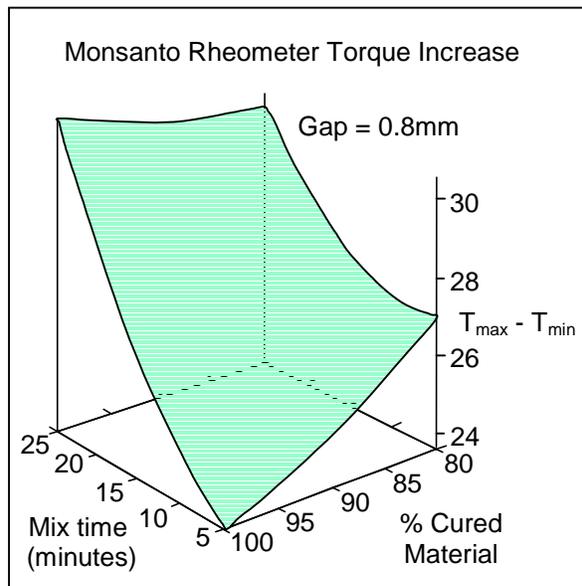**Figure 10: Monsanto Rheometer Maximum Torque (T_{max})**

Figure 11: Monsanto Rheometer Torque increase (T_{max} - T_{min})

It should be emphasised that each mix had the same amount of sulphur available for curing, added as part of the uncured component, or added according to the amount of cured material present (assuming all the sulphur used to cure the crosslinked component originally, was no longer free to take part in the curing reaction). The change in torque from the start to the end of the curing reaction ($T_{max} – T_{min}$) gives an indication of the state of cure achieved, corresponding to the number of crosslinks being formed and the subsequent stiffness of the compound. Considering the response surface plot (Figure 11), after a mix time of 5 minutes the materials containing the least cured material showed the highest increase in torque.

This suggests, perhaps, that some of the cured material present was not available to take part in the crosslinking reaction. This could be explained if there were a large proportion of large cured fragments in the mix, meaning fewer polymers chains had access to the added sulphur. This corresponds well to the appearance of the samples mixed under these conditions. As the mix time increases, the change in torque increases, regardless of the amount of cured material present, but again the increase is much more significant when there is 100% cured material. In fact, after 25 minutes, the 100% cured material shows a larger torque increase than that containing only 80% cured. This phenomenon can possibly be explained as suggested earlier, either by a decrease in the cured particle size, or by the breaking of the crosslinks present in the cured material, either way leading to a greater surface area of polymer available for reaction with the added sulphur. It may be that both of these things are happening, and certainly the samples of 100% cured material mixed for 25 minutes were the most homogeneous and lump-free in appearance.

The effect of the gap size was also a significant factor. In the case of the Monsanto cure characteristics just discussed, the smaller the gap, the larger the effect on the observed responses. Reducing the gap to it's lowest level of 0.8 mm, reduced both T_{min} and T_{max} and increased T_{max} - T_{min}, suggesting the most efficient breakdown of the cured material at this gap.

Whilst there are several important parameters for characterising the nature and quality of a rubber material, the tensile properties are nevertheless particularly useful in that they are very sensitive to changes in composition, cure state and contamination. The tensile modulus, ultimate tensile strength and elongation at break are very revealing about a material's nature. Considering first the tensile strength; figure Figure 12 shows the response surface that maps the effect of the significant variables on this parameter.
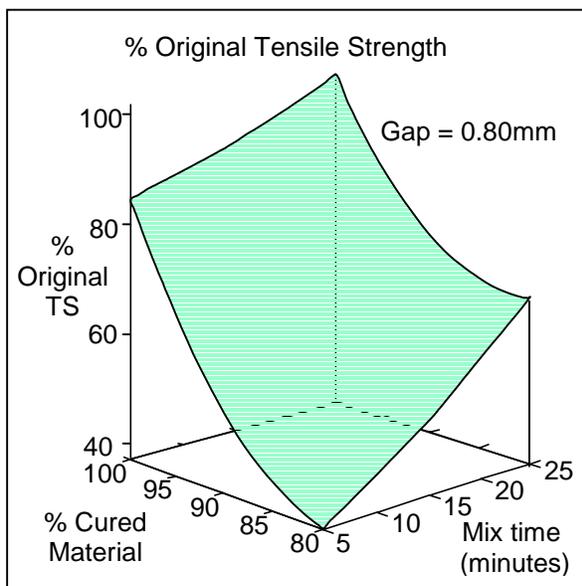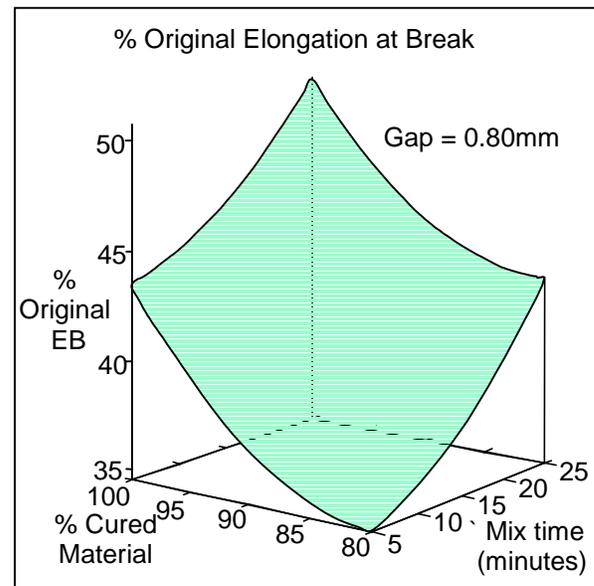

Figure 12: Tensile Strength

Figure 13: Extension at Break

The percentage of the original tensile strength achieved is plotted against the mix time and the percentage of cured material present in the sample (the original tensile strength, 17.5MPa, is that of cured material 01, containing the same amount of sulphur and cured under the same conditions as the test samples). The mix time clearly has a significant effect, with the tensile strength increasing as mix time increases. Even more significant however, is the increase in tensile strength observed as the percentage of cured material increases. After 25 minutes of mixing in the HSM with 100% cured material and subsequent re-curing, the

tensile strength achieved is similar to that of the original material. This clearly is very significant. A number of possible explanations have been proposed to explain this result, but none so far proven.

The elongation at break response surface tells a similar story (figure 12). The same trends apply, although the maximum elongation at break is only around 50% of that for the original material (360% compared to 700%), but this again is achieved with 100% cured material. In the case of both tensile strength and elongation at break, the optimum results were obtained at a gap of 0.8 mm; the smallest used in this experiment. From the results it is clear that when re-cured, the HSM processed material is not the same as the original cured material and it is likely that the current HSM process is not 100% discriminating in breaking only crosslinks. It is also possible that small cured fragments still remaining in the processed material caused weak points in the tensile specimens, preventing the elongation at break from being still higher.

There are a number of ways in which an improvement in elongation at break might be achieved; by ensuring more complete breakdown of cured fragments (or else screening them out), by modifying the cure system (the one used in the experiments was very crude), or modifying the composition after HSM processing. Letting-down with uncured material also should help improve the materials characteristics still further. In terms of mix time, subsequent experiments have shown that going beyond 25 minutes has little beneficial effect on the properties of the material. Likewise, reducing the gap further does not appear to produce any real benefits in terms of property improvement, and has the opposite effect if anything, on this particular material.

These observations permit some more positive conclusions to be drawn regarding the effectiveness of the HSM technology. The improvement in tensile properties achieved by using 100% cured material is very significant, as it is highly unlikely that such high values could have been achieved had the process only resulted in finely powdering the cured material. The inevitable conclusion therefore, is that the cured material has been modified by the breaking of a significant proportion of crosslinks, in such a way that it becomes re-processable whilst retaining, or rather regaining, a large proportion of it's original strength characteristics. In other words, it can be recycled in the true sense of the word.
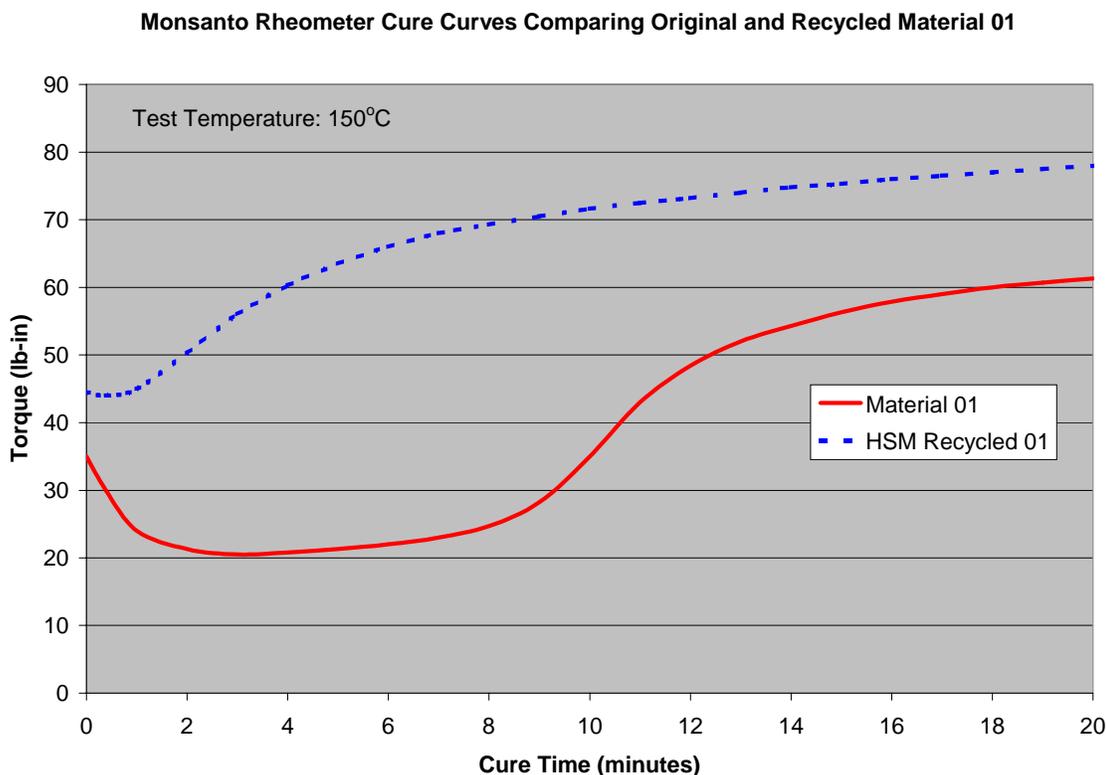
Monsanto Rheometer Cure Curves Comparing Original and Recycled Material 01

Figure 14: Monsanto Rheometer curves comparing Original and Recycled Materials

Whilst these results are very encouraging, there are a number of points worth considering. Firstly, it should be noted that the cure characteristics of the recycled material 01 are different to the original material, with a tendency to cure more quickly (Figure 14). This may require a modification to the cure system. The material viscosity for 100% cured and subsequently HSM processed material is greater than the original compound, and this may need to be accounted for by adjustment to the formulation. For example, the recycled material could be let-down by addition of a proportion of uncured compound, or processing aids or oils could be incorporated. An important point that should not be overlooked is that the model material 01 is a clean, pure material without contamination by other polymers, or other foreign material. The results obtained therefore, are likely to be amongst the best possible. It is inevitable that the recycling of scrap materials, including tyres will be fraught with problems of contamination and indeed polymer degradation. However, many of the problems can be overcome with careful segregation, separation and reformulation. Finally, this is but one material and it will almost certainly be the case that other materials will require a different set of experimental parameters, in order to achieve optimum results. How different materials behave in the process is likely to be affected by the polymer type molecular weight, compound composition and crosslink density, amongst other factors.

Work with other materials is on-going, including end-of-life scrap and manufacturing waste. Encouraging results have been obtained with elastomeric cable materials, scorched and fully cured EPDM materials and scrap tyre materials amongst others. Initial trials on the 20g machine indicate that the HSM may in fact be able to take predominantly whole tyres, tyre fragments or other rubber waste and convert this to a fine crumb or even a coherent mass. This material may then be extrudable in order to screen out any non-rubber components such as wire or cord fragments. This would simplify the whole tyre recycling process. Another point to bear in mind is that the HSM, like other internal mixers, is well suited to work in combination with a dump mill or extruder.

4   Current Research and Development Projects

4.1   CRAFT project

A 2 year European funded Craft project started at the beginning of January 2001, involving 9 European partners based in the UK, The Netherlands, Germany and Portugal, aimed at exploiting the potential of HSM technology as a means of rubber recycling. Watson Brown HSM are the technology providers, whilst the other partners will be contributing expertise in the areas of tyre crumbing, application development, polymer technology and engineering elastomers. Amongst the objectives are to build and commission 2 20kg machines to evaluate further the scale-up potential of the technology for tyre and in-house rubber scrap recycling.

4.2   Fundamental research programme

Whilst the fundamental principles of mechanochemistry are well established, much of the work in this area has concentrated on uncrosslinked systems. It has been known for many years that cold mastication can be used to break polymer chains and reduce the average molecular weight. As described earlier, it has been a logical progression to apply the same principles to crosslinked systems. With the introduction of crosslinks into the equation, the complexity increases still further. The experiments carried out so far have relied on macro properties such as tensile strength as a means of attempting to understand what is happening on a microscopic level. The results obtained with the model SBR based tyre material can be partially explained by devulcanisation, but it is unlikely that the breaking of crosslinks is happening in isolation.

A fundamental research programme is underway at Watson Brown HSM in order to understand more fully the process and material parameters critical to the mechanical devulcanisation process. Whilst the process parameters are relatively straightforward to characterise and optimise, the material parameters are equally important and somewhat more complex. From the work carried out so far it is clear that factors such as polymer type, molecular weight, crosslink density, crosslink chemistry, and compound composition (filler type and level, etc) are likely to be important. These factors are being studied from both a physical and a chemical perspective and the knowledge gained fed through into the process technology development.

4.3   Research partnerships

Along side the Craft project and the fundamental work being undertaken, Watson Brown HSM are actively seeking to extend the list of industrial partners with whom we work in order to facilitate the introduction of the HSM technology to key areas associated with rubber recycling and compounding. Discussions are already underway with a number of interested parties and initial trials with some commercial materials have been very promising.

5   Summary and conclusions

The problem caused by the inability to successfully recycle crosslinked rubber scrap and manufacturing waste, exemplified by the ever growing tyre mountain, may have a solution in the form of HSM technology. Results on a small scale have shown that rubbers can be recycled using a simple mechanical process to yield materials having close to their original physical properties, whilst containing a high proportion of previously cured rubber. The HSM process provides materials that can not only be re-processed by conventional means, but that also have properties suitable for a wide range of applications. Rubber waste may now be regarded as a valuable asset rather than something only fit for disposal or incineration. Whilst

the work so far has been on a small scale, the indications are that scale-up of the technology to a useful industrial size is feasible, both technically and economically.

It is of particular interest that for the model tyre SBR material tested, 100% of the UTS was obtained and 50% of the EB for a sample of material that had not been let down and which only had a simple curing system added.

Tyres, however, represent one of the biggest challenges in terms of recycling, due to their complex composite structure and use of non-rubber components. The quality of the scrap entering the recycling process will no doubt be reflected, at least in part, in the quality of the resulting material. Mixed tyre scrap will result in a material having a composite blend of all the rubber compounds represented in any particular batch. This will not prevent the material from having some value, but it may not be suitable, on it's own, for the original application. Reformulation, or blending in with virgin compound may be necessary in many cases.

Acting as a mixing technology, HSM fits well in existing economic models used within the Industry. The additional promised bonus of its effectiveness as a compounding mixer only improves payback times, which typically vary from 2 years to less than 6 months.

In addition to rubber recycling, the HSM may also prove to be versatile alternative to existing rubber mixing technologies, and may for example, allow a single stage mix where two stages are currently used (as in the case of curative addition), due to the efficient cooling permitted by the machine.

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