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TRUE RECYCLING OF RUBBER – MYTH OR REALITY?

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***SPEAKER**

TRUE RECYCLING OF RUBBER – MYTH OR REALITY?

Every year, the Rubber Industry scraps more than 10% of its compounds – just because they have been crosslinked. Although not normally accounted for, this material could represent additional profits of between 1.4% and 7% to any organisation capable of recovering it and returning it to the main material stream as a usable compound.

In a climate of rapidly increasing raw material costs (some grades of NR up by 60% on last year's prices), decreasing material availability and increasing competition from both low cost manufacturing areas and new classes of materials, rubber compounders must innovate to survive. Continuously tightening environmental laws and increasing recycling targets are further drivers for change that cannot be ignored.

Although this is not new, the need to address the problem is urgent. Despite the well-documented technical barriers to traditional rubber recycling approaches, a number of processes do exist that enable reuse of scrapped materials, ranging from reuse as a simple filler to reincorporation as a compatible compound.

This paper looks briefly at some of the drivers for change and the technologies available for reusing previously scrapped materials. In particular, information is provided on the novel HSM technology, including technical and economic results from its application.

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 vulcanization 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 valuable asset.

Tyres account for more than half of the rubber consumed by the industry annually. An estimated 270 million tyres reach their end of life in the US each year; over a billion throughout the world [2,5]. Each tyre constitutes a particularly difficult problem environmentally as its rubber does not break down to be recyclable (as, for example, do glass, paper and metals) its shape harbours insects, its volume encloses much air and it is dangerously combustible.

Additionally, not all new rubber materials end up in products. The Rubber Industry scraps, on average, more than 10% of its new compounds, typically as process waste. This wastage is often neither recorded nor admitted to within the industry, even though it represents a source of clean, unused material with a known history. These materials include some of the most expensive polymer compounds formulated, but they are scrapped because they are cured and often the financial effects of scrapping are not recorded.

Ideally, if vulcanised rubber could be returned to an unvulcanized state, as is the case for other recyclable materials, rubber in products could be recycled into new products of the same or similar value. This means that high quality or high performance products would require high-specification recycled materials.

Current approaches to waste rubber may have the potential to deal effectively with the volume of post consumer waste but are not effective in recovering the true investment made in the rubber material or products. A considerable further investment in energy and resources is often required that only serves to further reduce the economic and environmental return when using these approaches.

Legislative and social pressures due to 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.

The challenge is twofold – firstly, there is a technical issue as technologies must be found that enable true recycling to take place; secondly, there is an economic issue as new models need to be developed for the Rubber Industry to include significant material recycling streams.

This paper looks at some of the issues behind the growing need for the true recycling of rubber and proposes the novel High Stress Mixing (HSM) technology as a possible solution.

THE PROBLEM

BACKGROUND

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 had grown to a yearly production level of some 20.83 million tonnes by 2005 [3].

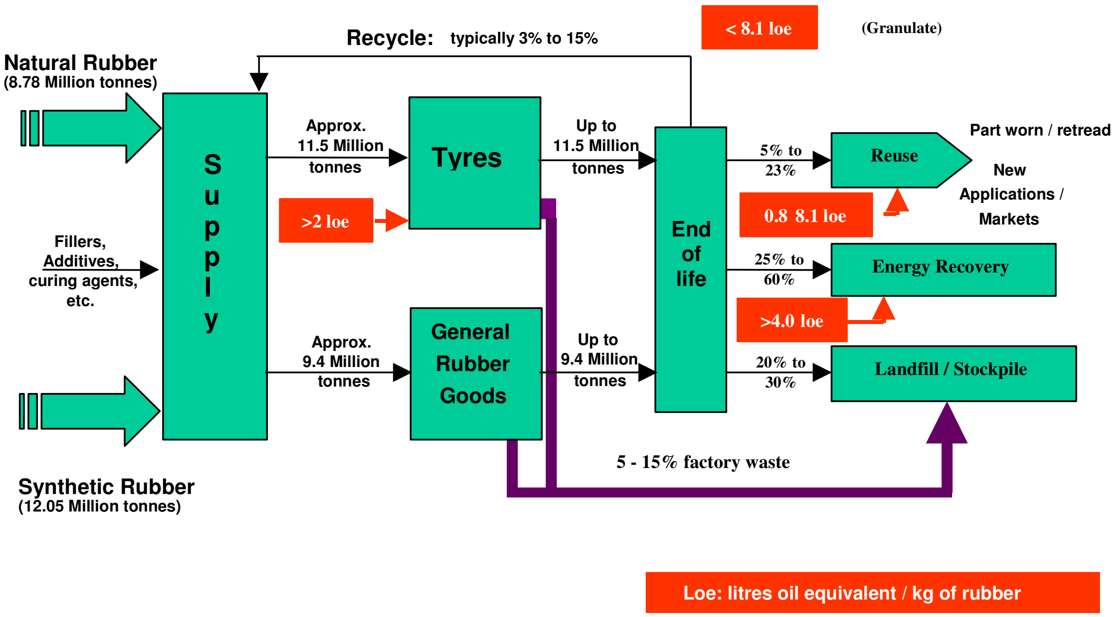


FIG. 1. – Simplified rubber life cycle analysis, partly based on figures reported by the International Rubber Study Group (IRSG), 2006.

Approximately 42% of this, some 8.78 million tonnes, was natural rubber whilst the remaining 12.05 million tonnes consisted mainly of oil-based synthetic rubbers. In the same year more than 1 billion tyres were manufactured, requiring approximately 11.5 million tonnes of rubber material, including most of the 8.78 million tonnes of natural rubber produced.

Once vulcanised rubber has reached the end of its working life it must be recycled or disposed of. For tyres, in 2005 it has been estimated that approximately 1 billion tyres were scrapped globally, weighing some 6 to 10 million tonnes[8]. Approximately 600 million tyres weighing about 5.7 million tonnes were recorded as being scrapped in Europe and the US alone[2,5,8]. Although most of the published figures report scrap tyres, it may be assumed that other rubber products are reaching their end-of life and that the total rubber waste stream may therefore tend towards the annual production totals of 20 to 21 million tonnes, with a lag equivalent to the lifetime of the product.

Recycling rubber is not simply a case of melting the material down and reusing it, as can be done with materials such as aluminium and glass. Reversing the vulcanisation process could be likened to "un-baking" a pastry and then reusing the dough. Recovery of useful, uncontaminated materials is even more complex for multi-material laminated products such as modern tyres. Because of these difficulties, scrapped rubber and in particular scrapped tyres, have traditionally been landfilled or stockpiled. The estimated quantity of known stockpiled and landfilled rubber in the US and Europe is in excess of 21 million tonnes with a further 5 to 10 million tonnes being added yearly.

Recent changes to legislation in Europe has seen the banning of tyres and tyre shred from landfill, although this is still an accepted route for non-tyre rubber products and materials. This has led to the increase in tyre incineration, (energy recovery) which is currently the preferred disposal route for 45% of US and 31% of European tyre arisings; an estimated 2.2 million tonnes.

WHAT INDUSTRY SCRAPS

In addition to the post consumer waste such as tyres, the Rubber Industry scraps between 5% and 15% of the materials that it uses annually as production waste. Globally this averages 1 million to 3 million tonnes of material. Even if the value of a low cost compound is used, for example $1000 / tonne, this results in an annual cost to industry of $1 billion to $3 billion. In reality the average cost to Industry is higher, particularly if opportunity costs and the cost of disposal are included.

Where we scrap. – It can be argued that much of this wastage is inherent in the production processes employed and that the volumes are often underestimated. Whilst tyre manufacture and continuous extrusion lines typically report 3% to 5% wastage, usually as trimmings and during planned or unplanned start-up and shut-down, this does not include product rejects and recalls. The scrapped materials are often cured or partially cured, as in machine purge. It is the very high material throughput of these processes that leads to large volumes of scrapped materials.

In compression moulding, even a carefully designed mould could generate up to 10% material loss as flash to ensure correct filling, particularly if the mould is complex. Losses in injection moulding processes, where the flash, sprue and gates are discarded, can average 35% to 50% of the materials used, depending on the mould and product design, whilst as an extreme, some transfer mouldings have been identified with 60% material loss. This material is usually cured and, in some cases, has also been through a post-cure process. These materials are often high value compounds with costs ranging up to $50 / kg and beyond.

Typical losses from stamped products also average between 35% and 50%. This is usually in the form of punched strips of fully cured materials, often determined by the geometry of the punch and gripping system.

Why we scrap. – In most cases, the material that is scrapped is good material that is within specification. The only problem with it is that it was not at the correct location to be included within a product. Once cured, the material is no longer regarded as being within specification and is scrapped, rather than recovered. This approach may be cultural although there are a number of technical reasons for regarding such materials as waste. In some cases, the material may have been contaminated with a powder, oil, glue or flock or may have been cured as a composite together with other compatible materials and these are seen as barriers to reuse. Often a large variation in formulations is cited as a reason for scrapping rather than material recovery, as is the complexity of the collection logistics.

Limited recovery of materials is practised by some within the Industry, often driven by material cost or supply limitations. Typically the waste materials are ground into fine powders and returned to fresh compounds as fillers where they often help to reduce compound cost as well as improve material characteristics such as mould release and wear. Usually up to 10% of scrapped materials can be treated this way before degradation of the mechanical properties of the material becomes an issue.

Why we do not see scrap. – There is a significant discrepancy between the real levels and the reported levels of scrap within the Industry and within a number of companies interviewed. Often scrap levels of significantly less than 1% are reported, generally only referring to losses during the compounding operation. One explanation is that the waste material is not tracked within the normal accounting procedures. If it takes 10kg of material to manufacture a product, then this is the figure that is costed and tracked within the system, even if the actual product may only weigh 5kg. Recent increases in the cost of disposal of some materials are forcing a re-evaluation of these cost models.

For both post-industrial and post-consumer cured materials, the Rubber Industry is still focussed on getting rid of a problem rather than mining the source of valuable materials close to home.

THE PRESSURE TO CHANGE

The Rubber Industry is under greater pressure than ever to change. And this pressure is set to increase over the coming years, underpinned by the developments in a number of key areas.

ENVIRONMENTAL IMPACT

There is an increasing pressure to address the problems associated with rubber waste streams. 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 not regarded as being environmentally sustainable solutions. For example, the US and UK Environment Agencies have reported a number of problems associated with the landfilling of tyres. If disposed of in large volumes, tyres in landfill sites can lead to fires which can cause serious air pollution as well as the pollution of underground water supplies. Tyres also tend to rise to the surface, affecting long-term settlement and possibly causing problems for future land use and reclamation. An underground fire that started in 1989 in a dump with 10 million tyres in Powys in Wales burnt for 10 years. Recent readings of downstream water still recorded elevated zinc levels above the regulation limits (75 μg/l) (UK Environmental Agency). An Environment Agency report[6] also indicates that the effects of the long term leaching of organic chemicals are not known.

The WHO has identified the health hazards of tyre dumps, particularly in mosquito-infested areas, as an area of concern.

Whilst the major focus has been on tyres, other rubber products and formulations are increasingly being associated with environmental problems. One example is the toxicity of fluoropolymers if incinerated or treated at elevated temperatures during their disposal.

COST OF ENERGY

Recent dramatic increases in the cost of energy, as well as the cost of energy generation, have impacted a number of manufacturers. Although it could be argued that the current levels are much higher than would normally be anticipated from the underlying factors, a clear overall trend of price increase can be observed.

In 2003, the biologist Jeffrey Dukes calculated that the fossil fuels we burn in one year are made from organic matter “containing 44×10^{18} grams of carbon, which is more than 400 times the net primary productivity of the planet's current biota"[1]. In other words, every year we consume approximately four centuries' worth of plants and animals.

With a number of sources predicting a downturn in oil production, or at least a radical change in the way that oil is recovered, the long-term trends are already clear.

At present, the Rubber Industry is a significant user of energy. It is estimated that it requires 150 to 200 GJ/tonne to manufacture products from synthetic rubber and 16 GJ/tonne for similar products from natural rubber. Of this, the physical mixing of the materials typically requires 1 to 5 GJ/tonne.

COST OF RAW MATERIALS

Parallel to the increase in energy costs has been an increase in the cost of raw materials. Whilst the increases in synthetic materials can partly be attributed to the increased cost of oil and energy as well as the effects of natural disasters in the US, it is also a reflection of the increased global demand leading to local shortages. Natural rubber, whilst not as dependant on the price of oil, has seen a 54% increase in the last year. Reasons for this include an increase in demand from industry in China and India, driven by record sales of automotive products. Despite tightening of credit controls in 2003 which reduced the growth of car sales from 75% in 2003 to 15% in 2004, with 5 million car sales annually, China is now the third largest car market in the world after the US (17 million) and Japan (5.9 million) and is set to take the number one spot sometime before 2015 [4]. India is growing at a similar rate and is forecast by Goldman Sachs to overtake China by 2050.

The International Rubber Study Group (IRSG) predicts a structural shortage of natural rubber in 2010, brought about by a predicted increase in demand coupled with a slow growth in production. As a result of this, they do not foresee a change in the current upward price trend, even with a demand shift to SBR.

LEGISLATION

As a direct response to this problem, a number of countries are legislating against the landfilling of rubber materials. For example, the European Landfill Directive has banned the burying of whole tyres in landfill sites since 2003 and shredded rubber from 2006. A number of landfill site operators have already responded by dramatically increasing the disposal cost of tyres or 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.

RESISTANCE TO CHANGE

Resistance to change the way that we treat waste rubber 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

The economics 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.

It will be only a matter of time before the Rubber Industry will be forced to deal with the issue of rubber waste without the traditional response of landfills and stockpiles.

NEW TECHNOLOGIES

CURRENT APPROACHES

The generally accepted hierarchy of measures for the management of waste materials[9] as represented in Figure 2 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.

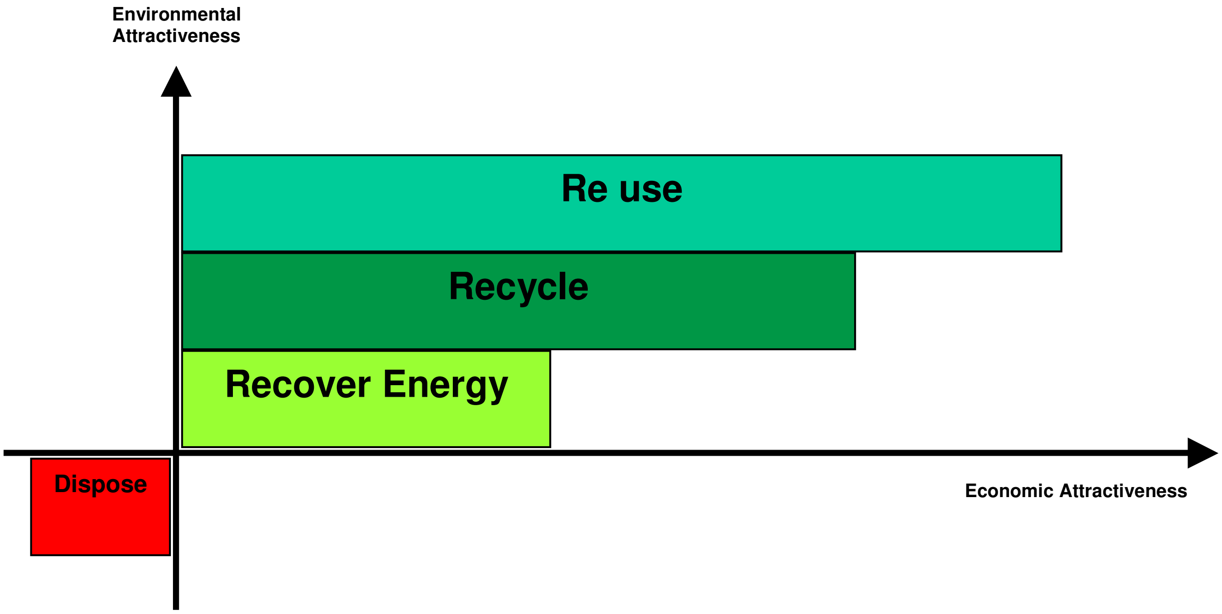


FIG. 2. – Waste management hierarchy

When positioning waste rubber products in 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 for tyre materials as new legislation is enforced. In Europe, the cost of landfill is increasing, as is disposal tax.

- Energy recovery is particularly favoured in the US, handling more than 45% of the tyre waste stream (Europe approximately 31%). It should be 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. Rubber is considered to have a similar calorific value to coal. As such, the maximum value of the rubber is set by the price of the cheapest source of fuel, which may include general waste such as animal carcasses. For a tyre, the value of TDF (tyre derived fuel) has been estimated to be less than 1% of the value of a new tyre[13].
- Recycling accounts for 5% to 15% of the waste stream, although a number of differences in terminology and classification can be seen. Recycled materials include granulates from waste tyres, which are typically sold for less than 10% of raw polymer prices even though they consume more energy during generation than the manufacturing of the tyre. Smaller particle sizes, often found in cryogenically ground materials, are considered to offer improved dispersion and therefore command higher prices. They are also considerably more expensive to produce. Reclaimed materials, which include devulcanized materials, are typically sold for up to 50% of the raw polymer price, reflecting the improved performance over granulate as well as the increased production costs. These materials are often used as compatible extenders and cost-reducing agents and their price is limited by the cost of equivalent filler materials. In some cases, the cost of proprietary formulations added to “soften” the materials and improve breakdown, have reduced the application of reclaimed materials, as have concerns related to the chemical composition of additives. The products of pyrolysis, which returns basic components such as carbon black and oils, are also price-limited by the cost of commercially available materials. Pyrolytic black must compete with carbon blacks that have evolved into complex products with a number of customised variants tuned to provide specific levels of performance. The combination of plant capital costs and low product returns have proved to be significant barriers to pyrolysis. Products can also be made from crumb using binders, such as urethane to glue the particles together. The cost of urethane is typically significant in such products and they tend to be mechanically weak when compared to rubber materials (typical UTS of 0.4 to 0.6 MPa).
- 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. Reuse is the most environmentally friendly disposal method and often provides the highest economic return for the lowest investment. It is, however, limited by market opportunities and demand.

Although recent efforts in Europe and the US have focussed on managing the disposal of scrapped tyres, a difference in the current implementations can be observed. The reliance on energy recovery in the US is much higher than in Europe, although Europe is likely to follow America along this path.

Concerns associated with the environmental impact of the incineration process, particularly in cement kilns, have 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 1970s it was estimated that it took 3.5 tonnes of oil to produce 1 tonne of SBR. Whilst manufacturing efficiencies have been improved, a high level of hydrocarbons is still involved, up to 10 times that of natural rubbers. Recent studies have estimated that a new passenger car tyre requires the equivalent of more than 30 litres of oil to manufacture, whilst an average new truck tyre requires an equivalent of more than 93 litres of oil to manufacture[8]. Approximately 30-40% carbon black filler content 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 tyre incineration.

Given the public concern generated by the topic of global warming, it may be prudent to evaluate current and future rubber recycling strategies and technologies in terms of the total energy balance throughout their lifecycle in order to determine their “environmental friendliness”. This was treated generally in a previous paper[13], as well as being the subject of life cycle analysis (LCA) research.

Whilst it is not the intention to treat the pros and cons of individual strategies and technologies in this paper, in general it has been observed that:

1. cured rubber contains a large investment of increasingly valuable resource and should not be discarded or destroyed
2. the relatively high costs and low returns of existing recovery processes and technologies often need to be overcome by subsidies and grants
3. successful technologies are economically viable without the need for external subsidy
4. a number of technologies and approaches have been proposed and tested in laboratories, but have yet to translate into viable processes at industrial scales
5. There is an overriding need to extract the maximum performance from recovered materials, for the minimum investment in resources and that all new strategies and technologies should be tested against this criteria.

HSM TECHNOLOGY

HSM TECHNOLOGY IN CONTEXT

It is argued that 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 previously 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.

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 limited strength. Acting mainly 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 convert a vulcanisate in this way. 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 previous papers[13,15,16], the authors envisioned a commercial process using 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 the last of these papers[16], particular attention was paid to the scalability and feasibility of the approach for waste tyre materials.

Whilst very early work on SBR and NR tyre compounds reported in 1998[15] indicated the potential of the technology, considerable further work has been carried out to both extend the range of applications for HSM technology and to move the technology towards commercial scales of operation.

The early work was extended to include a wide range of viscoelastic polymers, formulations and crosslinking systems, including NR, SBR, BR, EPM, EPDM, CR, NBR, HNBR, FKM, FVMQ and FFKM materials as well as to scale-up of process to 2kg and 20kg batch weights. This work yielded very promising results for both post-industrial scrap materials, as well as applications developed using post-consumer materials such as mixed tyre crumb. The cost of processing these materials into reusable compounds is a fraction of the cost of the raw materials

In 2003, the technology was first implemented at a commercial scale and in 2005 a manufacturing partnership was formed with a major Chinese manufacturer of plastics and rubber machinery. Work on a major installation, including a number of 20 litre and 200 litre HSM lines, started in 2006.

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 1950s showed[7] 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 the 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[7] 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 in preference to adjoining bonds in the chain segments.

These two predictions are illustrated in Figure 3.

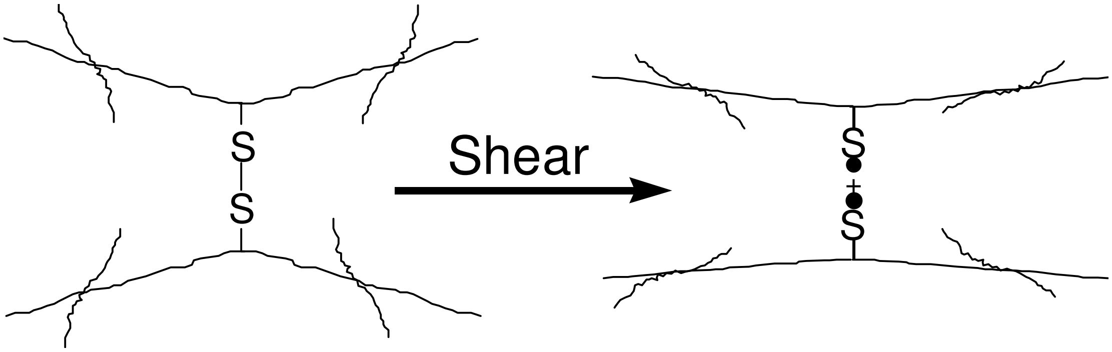


FIG. 3. – Preferential rupture of crosslinking bonds in a mechanochemical reaction

It has further been anticipated that this 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 it in an internal mixer only moves the particles within the matrix. Any rupture of crosslinks would have been discovered empirically many years ago if this was not the case.

Based on his earlier work, Watson concluded that a more effective form of mixer capable of applying higher shear was required and in the 1990s 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 at least one order of magnitude greater than existing interlocking rotor mixers, is termed a High Stress Mixer (HSM).

THE HSM PROCESS

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 4). 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 behind the rotor and stator surfaces ensures tight control of the material bulk temperature.

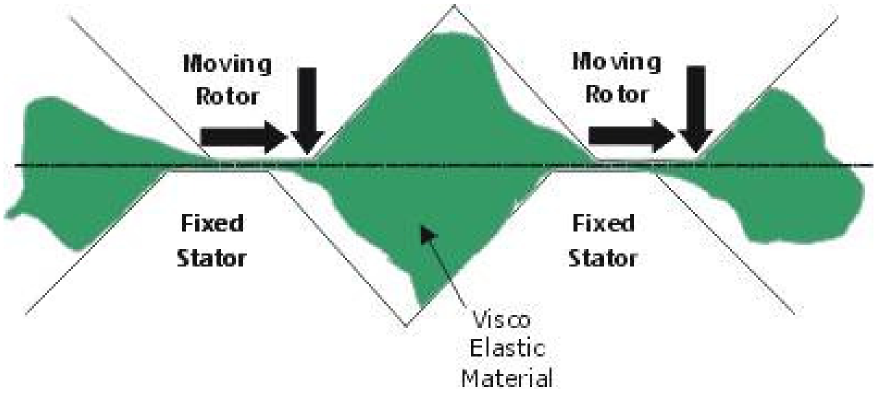


FIG. 4. – Cross-section through an operating HSM machine showing material movement between the rotor and stator surfaces

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 5) to larger 2kg 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.

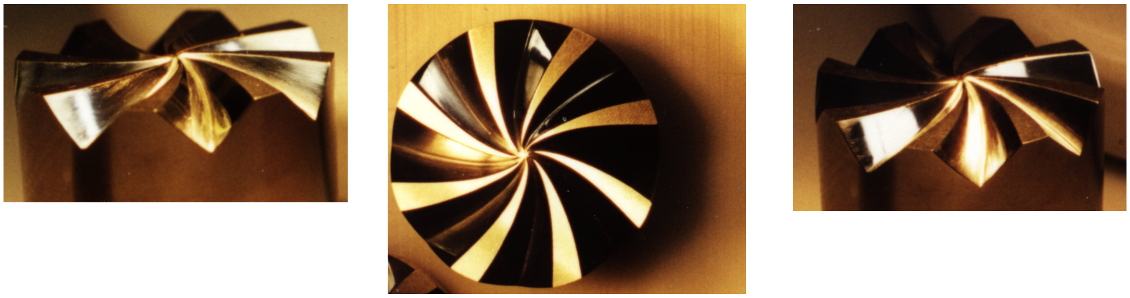


FIG. 5. – Photographs of 20g batch HSM laboratory machine rotor

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.

OPERATIONAL FEATURES OF THE HSM

In operation, the geometries and temperature controllability 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 is designed to:

- restructure crosslinked materials into un-crosslinked 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.

DESIGN OF HSM MACHINES AND PROCESSING LINES

Work on scaling HSM geometries has resulted in a range of batch machines and processing lines from 1 litre and 5 litre laboratory machines to 20, 100 and 200 litre production lines, the latter capable of producing up to 1 tonne of product per hour.

A typical HSM processing line consists of pre-processing, HSM processing and post-processing stages. During the pre-processing stage, the materials are sorted, size-reduced and weighed in preparation for HSM processing.

Materials are automatically dosed into the HSM, which can be programmed to process the material in accordance with a pre-defined recipe that includes the process time, stress, temperature, speed and quantity of material to be processed.

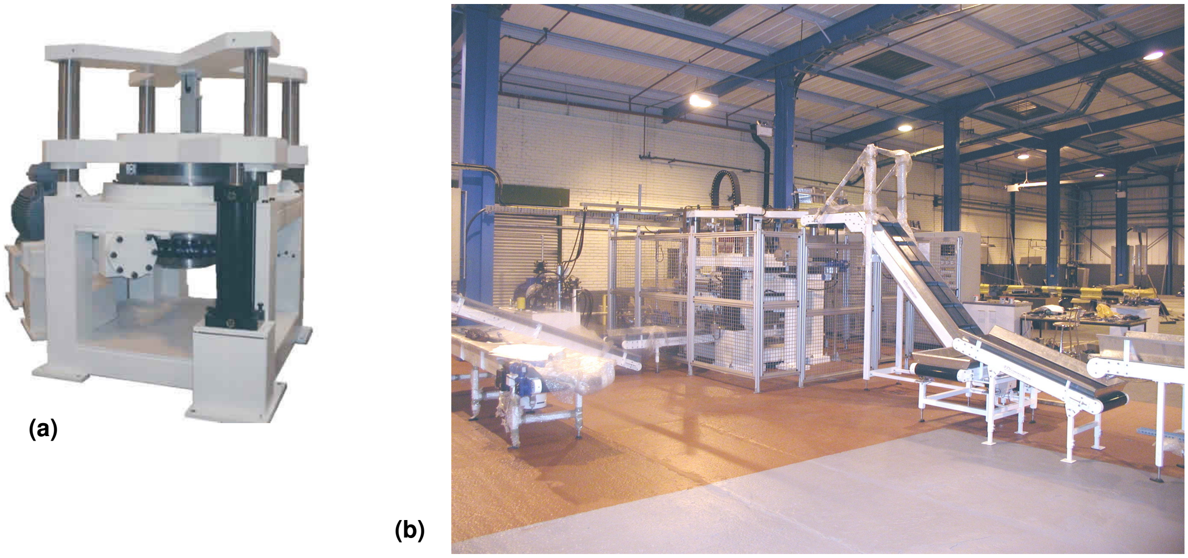


FIG. 6. – Typical 20 litre HSM production layout showing: (a) the HSM machine itself; (b) a typical factory setup with pre- and post-processing equipment

Post-processing will depend on the intended use of the processed material. Once materials have been through the HSM, they can be further processed using standard rubber processing equipment. Materials that are sourced from rubber product factories (in the form of sprue or web, for example), and which are to be returned to their original processes, need to be output in a form that is acceptable to the downstream process. This could be as milled sheet or strip, extruded cord, pellets or in some cases, bagged powder. For end-of-life consumer materials that are to be turned into product, the post-processing could also be the product manufacture, and automated press or continuous extrusion / calendaring lines can be integrated into the system.

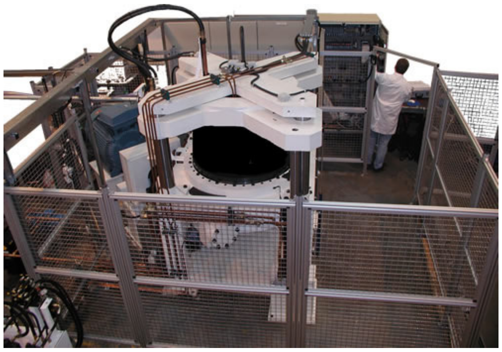


Fig. 7. – A 20 litre HSM production machine with safety cage and control panel

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 is 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.
- The main cost elements are energy, labour and the capital machine cost.
- Payback times vary depending on the scale of the process, the value of the materials being recovered and the differential local waste disposal costs. For high cost materials, payback can be within 6 months and typically a 20 litre machine would be used. For lower value materials, the economies of scale of a 200 litre line will return a material at a fraction of the cost of the original polymer.
- For many post-consumer materials, such as tyres, the HSM-processed materials can be used to develop new applications. The quality of the reprocessed rubber will enable HSM processed materials to compete with a number of virgin compounds, although at a greatly reduced cost.

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.

PROVING THE CONCEPT

The ultimate aim of 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 its original properties, both as an uncured raw material and as a crosslinked product. The material should be capable of being re-used in its 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 20kg in capacity. A wide range of materials has been investigated and the resulting HSM-processed materials evaluated by both chemical and physical testing procedures. Unfortunately, many of these tests have been carried out on proprietary materials and the results are not available for open publication. For this reason, only masked results are reported here for a few typical materials.

OVERVIEW OF TRIALS AND RESULTS

SBR-Based Model Car Tyre Tread [2001]. – A simple compound was designed to represent a typical car tyre tread based on SBR. It was chosen to characterise the HSM process and variables, as previously reported[15]. The formulation of the model tyre compound is given in Table I.

TABLE I
FORMULATION OF MODEL SBR-BASED TYRE COMPOUND

Composition	phr
Styrene-Butadiene Rubber (SBR)	75
Butadiene Rubber	25
N234 Carbon Black	60
Process oil	15
Sulphur	1.5

The Tensile Strength of the cured material was 17.5 MPa and the elongation at break was 701%.

The characterisation was done by means of a statistically designed experiment, using the following variables:

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

All other variables were fixed. In total 21 trials were carried out, including 5 replicates. Each trial consisted of 5 batch runs, with a total of 105 batches generated. Outputs such as motor current and material temperature were monitored and recorded during the trials. The resulting materials (5x16g batches for each trial) were then formed into a sheet using a two-roll mill and the sulphur curing agent added, according to the ratio of uncured:cured material present. A nip of 1 mm was used to avoid significant further breakdown on the mill, so as not to obscure the effects of the HSM process. A Monsanto rheometer was used to determine the cure characteristics of each sample, before each was cured at 150°C using a heated press to produce sheets suitable for tensile and hardness testing. The results were analysed using experimental design software to yield information about the significance of the chosen variables and to generate response surface maps.

Somewhat surprisingly, the most important variable in this experiment was found to be the ratio of cured to uncured material being processed. In all cases, the best results were obtained when 100% cured material was used, resulting in increased tensile strength. Also beneficial was a small gap and a longer mixing time, although it is interesting to note that in subsequent experiments, further decreasing the rotor-stator gap and increasing the mix time beyond 25 minutes did not result in further improvements in the physical properties of the material.

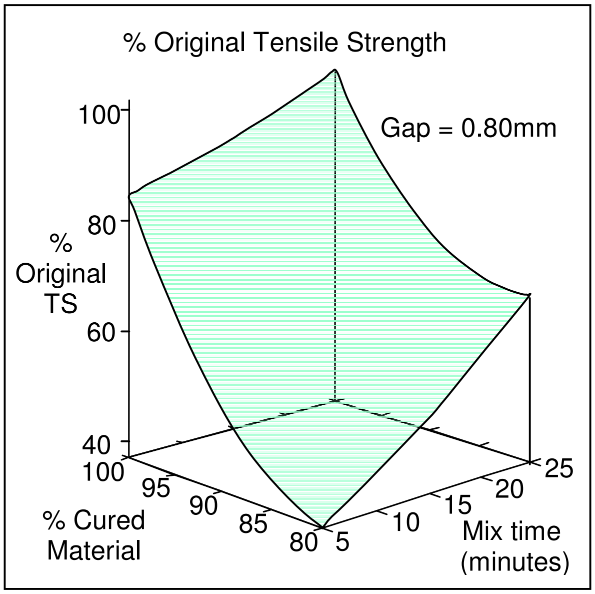


FIG. 8. – Tensile strength test results from HSM-processed model SBR tyre compound

As can be seen from Figure 8, using 100% cured material with a gap of 0.8mm and a mix time of 25 minutes, it is possible to achieve around 100% of the original tensile strength. The tensile strength was 17.5 MPa at the optimised point.

This experiment used a simple sulphur cure system. It has since been shown that improvements to the tensile strength and other properties can be achieved by optimising both the cure system and through addition of simple processing aids present in the original system.

Post-consumer (end-of-life) tyre tread [2001]. – Following on from the trials with the model car tread compound, selected parts of real scrap tyres were investigated. The tread was of particular interest as it is the component that may be most easily separated from the rest of the tyre. In terms of achieving the best possible results from any recycling process, it is desirable to have pure, uncontaminated material and this is particularly true for plastics and rubbers. The tread is a single rubber compound, although it is tightly bound to underlying layers consisting of other rubber materials, fibres and metal cord. For these experiments a number of tyres were selected and tread was carefully sliced away from the underlying layers. The tread in each case was then processed using the HSM, based on the information learned from the experiments with the model SBR-based tyre tread compound.

The HSM-processed material in each case was transferred to a 2-roll mill to observe the processability and to add the cure system. A simple sulphur cure system was again used to cure the recycled material in the form of test sheets. In addition, the HSM-processed Manufacturer **X** and Manufacturer **Y** tyre treads were let down to 50% with the model SBR-based compound, called Compound **01** on the two roll mill prior to curing.

TABLE II
TEST RESULTS FROM HSM-PROCESSED REAL TYRE COMPOUNDS

Material	Cure System	Tensile Strength (MPa)	Elongation at Break (%)	Observations
Manufacturer **X** – High performance car tyre tread 100%	1% sulphur	7.4 -10.2	161	Slightly rough surface
	2% sulphur	14.3	236	More extensively worked, higher sulphur, better surface finish
Manufacturer **X** High performance car tyre tread 50% Compound **01** 50%	1.45% sulphur	17.3	342	Very smooth surface
Manufacturer **Y** High performance car tyre tread 50% Compound **01** 50%	0.9% sulphur	18.7	473	Very smooth surface
Manufacturer **X** High performance motorcycle tyre tread (rear) 100%	0.83% sulphur	12.8	244	Good surface finish

The results, whilst not yet comprehensive, indicate what is possible with tread taken from real scrap tyres. The tensile properties achieved are particularly promising when the HSM processed materials are let down to 50% with the model tyre tread Compound **01**, even though this is an unoptimised formulation. The results were obtained using simple sulphur systems, which again were not optimised.

Work on post-consumer, NR-based tyre tread materials under similar conditions has resulted in 100% recycled materials with a yield strength of 13.7 to 14.5 MPa and extension at break of 268% to 340%.

EPDM Strip [2001]. – This material is often used in automotive applications and was supplied in a cured strip approximately 5cm wide by 2mm thick. In the HSM, the material appeared to break down very well to form a coherent, homogeneous, rubbery mass that milled well.

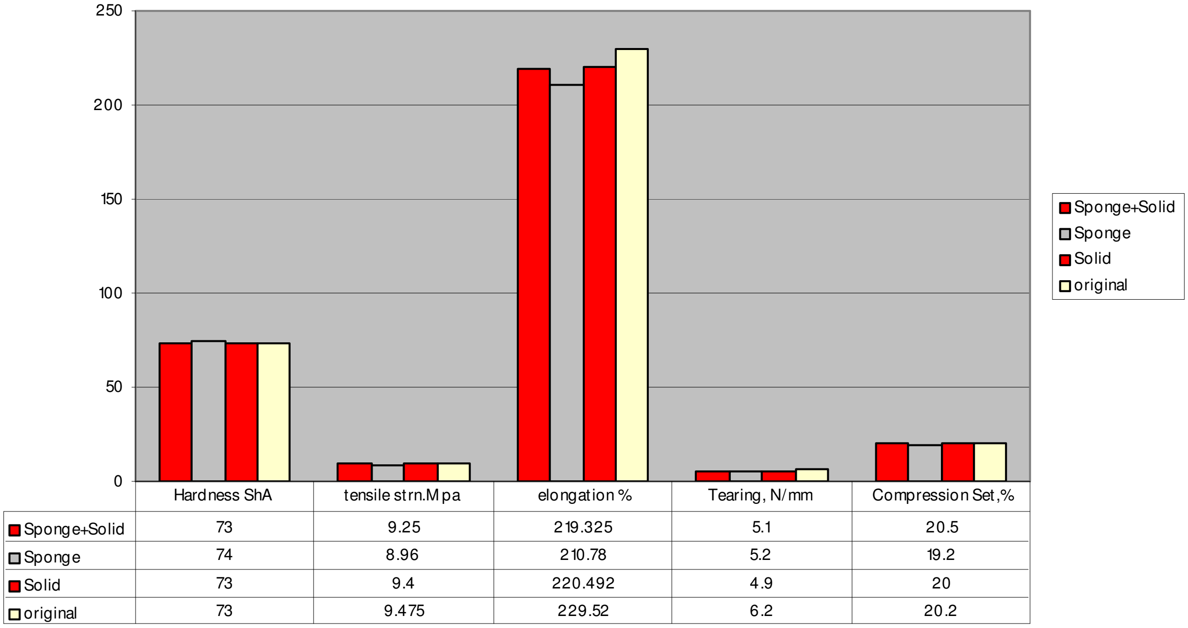
TABLE III
HSM-PROCESSED EPDM STRIP CURE SYSTEMS AND TEST RESULTS

	Cure System (phr)			
Composition	**(a)**	**(b)**	**(c)**	**Original EPDM strip**
HSM Processed EPDM Strip	100	100	100	
Sulphur	0.5	0.5	0.25	
CBS	0.25	0.25	0.25	
Zinc Oxide		1.5		
Stearic Acid		1	1	
Results				
Tensile Strength (MPa)	8.7	9.1	8.8	7.3
Elongation at Break (%)	171	169	184	368

The three cure systems used all gave similar results, with the tensile strength being the most remarkable, ranging from 8.7 – 9.1 MPa, compared to 7.3 MPa for the original EPDM strip. The elongation at break achieved was also promising at around 50% of that for the original strip. Further optimisation of the cure system has improved this performance, although this wok is not reported here. The surface finish of all of the samples was excellent and indistinguishable from the original cured EPDM strip. It was concluded that HSM-recycled material could be re-incorporated into the original product at a high level with minimal loss of properties.

Additional trials were carried out on a scorched EPDM "machine purge" of the same formulation. This material is generated when new processes are started or when old material is cleaned from a machine and forms a large percentage of the manufacturer's scrap. This material proved very easy to process in the HSM and it was difficult to identify the differences between HSM-processed and virgin materials. It was felt that the processed material would be suited to a number of applications, if it were not used in the original application itself.

EPDM door seal [2003]. – An extruded automotive door seal material was evaluated. The metal reinforcing was stripped from the product and the rubber was separated into the solid rubber surrounding the metal strip and the foamed (sponge) material that formed the seal surface. Three versions of the materials were produced, namely solid, sponge and a mixture of the two in the ratio that they occurred in the product. The HSM materials were added to a batch of virgin compound at 14phr, representing the expected scrap rate in the factory. The materials blended well to form a homogeneous material. No curatives were added to compensate for lack of curatives in the HSM processed materials.



	Hardness ShA	tensile strn.Mpa	elongation %	Tearing, N/mm	Compression Set,%
🟥 Sponge+Solid	73	9.25	219.325	5.1	20.5
⬜ Sponge	74	8.96	210.78	5.2	19.2
🟥 Solid	73	9.4	220.492	4.9	20
🟨 original	73	9.475	229.52	6.2	20.2

FIG. 9. – HSM-processed EPDM door seal test results

The variation between the virgin compound and the compounds containing HSM-processed materials were considered to be negligible and within the experimental error for the trial. It was therefore concluded that for this compound at these loading levels, no adjustment of formulation was required when returning HSM-processed material to the compound.

Nitrile sealing material [2003]. – The webbing discarded from a washer stamping operation was processed using HSM technology and then added to virgin stock at 5%, 10%, 20%, 30% and 40% of the total batch weight. No additional curatives were added to compensate for any depletion of curatives.

The materials blended well and appeared homogenous under a microscope.

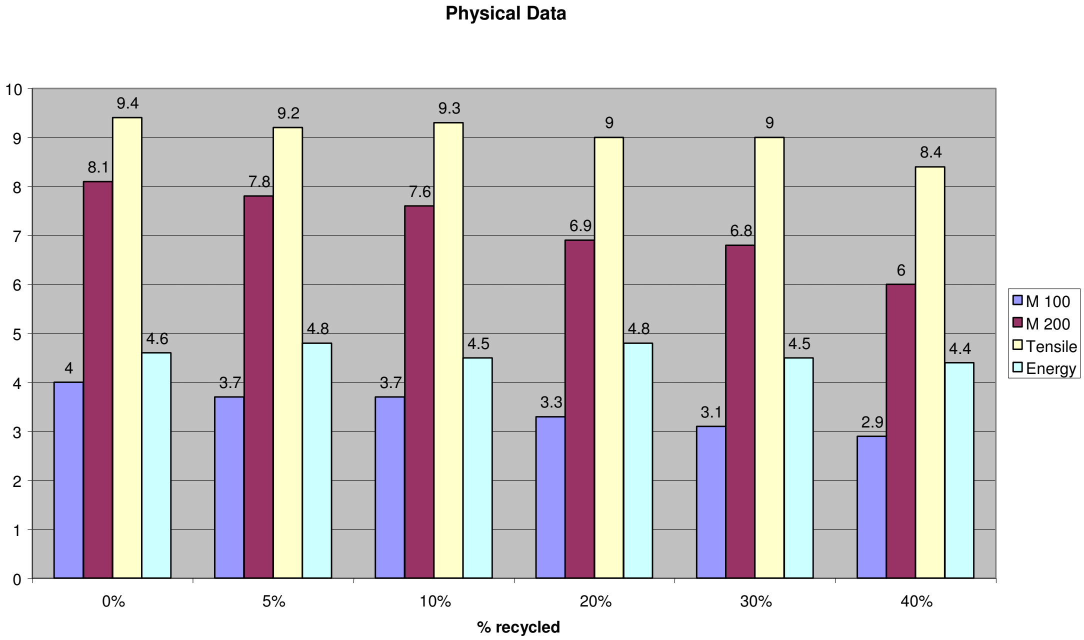


FIG. 10. – HSM-processed nitrile sealing material test results

Figure 10 shows a reduction in performance as percentage of HSM processed material is increased, although both the tensile and energy values remain good, indicating that the HSM-processed materials are well bonded within the matrix. The extent of the property drop-off could be consistent with an under-cured system.

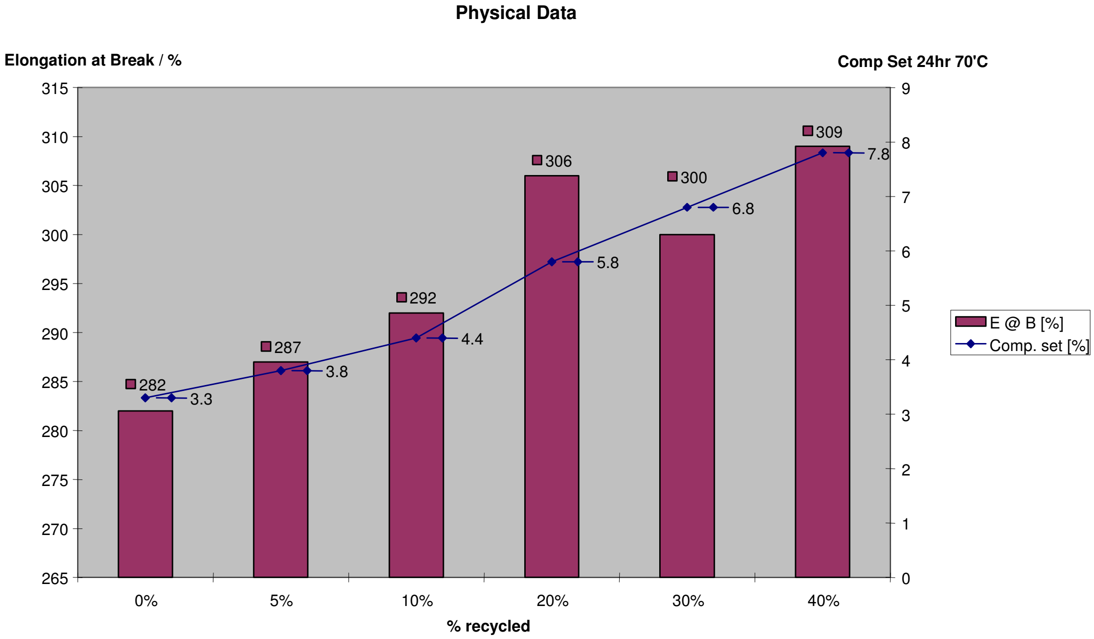


FIG. 11. – HSM-processed nitrile sealing material elongation and compression set test results

The argument that the system is under-cured is further supported by the increase in extension at break and compression set shown in Figure 11.

From this set of experiments it was concluded that HSM-processed materials behave as a compound and should not be treated as a simple filler when returned to the original system. Minor reformulation would be required for this compound at HSM material inclusion levels above 10% of the total compound.

CONCLUSIONS FROM TRIALS

Although only a small cross-section of typical results from over 8 years of experimental work is presented here, certain characteristics of HSM-processed materials can be clearly identified. Materials processed using HSM technology:

- can be regarded as compounds and not just fillers;
- do retain a large percentage of their original performance across a variety of parameters;
- do need to be reformulated to compensate for component depletion during the initial curing process;
- can be processed using standard rubber processing machinery;
- if sourced from post-industrial scrap, can be successfully returned to their original application at levels that correspond to the process scrap rate;
- if sourced from post-consumer waste, can be used as a basis for new products at inclusion levels up to 100%.

OTHER WORK

A further result, not presented in the trials illustrated here, is that partially processed materials can be re-cured to form linked networks. In these systems, materials that have broken down actually flow to form the adhesive layer between unbroken particles. In this way, granular, water-permeable or variable-density substrates and geometries can be formed. These materials can be processed and shaped using standard rubber processing equipment. A number of applications have been developed using these materials, as demonstrated in Figure 12.

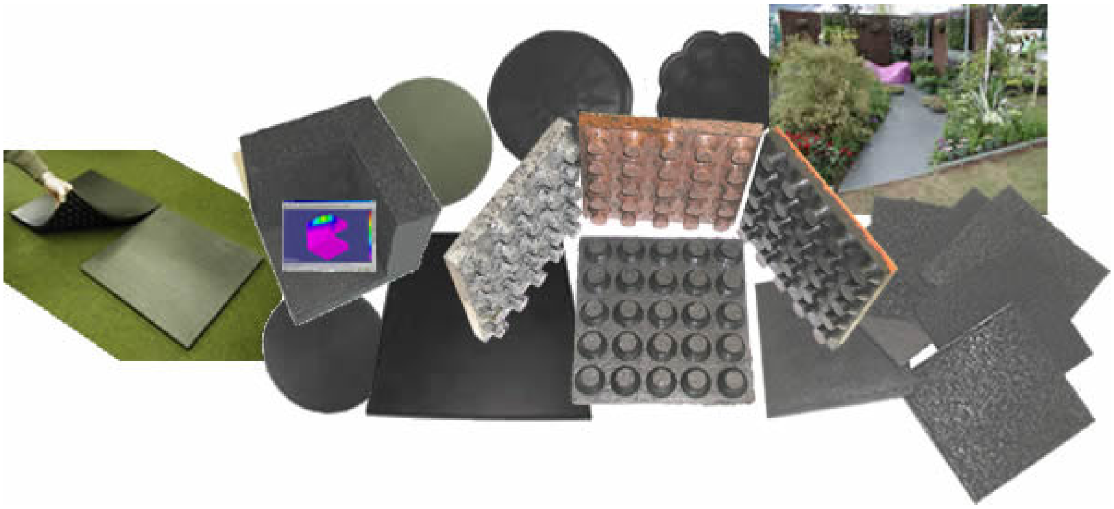


FIG. 12. – Examples of products made from 100% partially processed HSM materials

SUMMARY AND CONCLUSIONS

The increase in the cost of energy and raw materials coupled to the increasing scarcity of materials and legislative pressures all underpin the need for a re-evaluation of the Industry's treatment of scrap rubber as a waste-disposal problem and to move the industry towards a full recycling model. The maximum value needs to be extracted from a scrap material for the minimum input.

Although a number of new approaches to the recovery of value from cured rubber have been developed, very little work has been published on the relative merits of these technologies. Universal metrics for the comparison of new technologies and approaches have yet to be established and each new approach is presented in isolation. An indication of the value of the resulting processed materials both in terms of commercial value and technical properties with respect to virgin materials should be closely coupled to the cost of processing derived from a complete life-cycle view of the particular approach considered.

HSM technology provides a novel and environmentally friendly approach to the true recycling of a wide range of rubber materials and formulations. Results indicate that in-house generated scrap can be economically recovered and returned to original applications with little or no loss of product performance. Post-consumer, end-of-life scrap can also be processed to generate useful materials with performance comparable to a number of fresh compounds, but at a fraction of the cost. HSM-processed materials can therefore be used to replace existing compounds, or to extend a range of existing products to include those at lower price points.

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