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Effect of solid-state shear milled natural rubber particle size on the processing and dynamic vulcanization of recycled waste into thermoplastic vulcanizates

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ABSTRACT

Natural rubber (NR) and crosslinked polyethylene (XLPE) waste streams were devulcanized by solid state shear milling (S3M), producing a fine powder that may be more easily reprocessed. Understanding devulcanization and the nature of decrosslinked thermoset materials is of utmost importance for turning these waste steams into functional products. It was found that the devulcanized powders contained significant concentrations of radicals, which may be active in the subsequent revulcanization process. The produced devulcanized powders were converted into recyclable thermoplastic vulcanizates (TPVs) by twin screw extrusion. Reprocessing of these powders into value-added products is an important step in recycling and the use of extrusion allows for high throughput and industrial viability. Herein, we demonstrate that the optimal conditions for reprocessing are dependent upon the particle size of the devulcanized powder. Furthermore, dynamic vulcanization is affected by the nature of these recyclate powders. The successfully prepared TPVs showed similar properties to virgin materials, with a high elongation to failure. Therefore, the conversion of waste rubber into the rubber phase of a TPV shows significant promise in moving towards sustainable products, providing the revulcanization step can be well controlled.

1. Introduction

The importance of recycling can be clearly demonstrated by the increased media coverage, publications and governmental policy relating to waste materials [1,2]. However, difficult to recycle materials, such as thermosets, still require extra attention. A significant portion of end-of-life rubber is burned as fuel [3]. Amari et al. demonstrated that the burning of rubber only recovers 37% of the embedded energy from the manufacture of the product [4]. Environmentally, the devulcanization and reuse of thermoset rubber, rather than their destruction, would be highly beneficial.

Devulcanization of thermoset materials via mechanical means produces a reprocessable powder. The intensity of the deformation mechanisms within these mechanochemical processes leads to reduced crosslink density and reduced particle size. The resultant recyclable powder is often characterized in terms of its particle size. Therefore, we should seek to establish how the particle size effects subsequent reprocessing.

The target product for these thermoset waste streams is thermoplastic vulcanizates, which offer good reprocessability and thus an environmentally beneficial move towards a circular economy. In order to arrive at that point, a number of critical parameters must be established including the particle size of the recycled powder, the level of devulcanization, the concentration of radicals, the cure package required to revulcanize, the ideal extrusion parameters including rpm and temperature, the optimal rubber/plastic blend, and the subsequent compression moulding conditions. Meanwhile, energy and cost should also be considered for each parameter.

The first step along this path is to establish a set of benchmark properties and parameters for the thermoplastic vulcanizates produced. In addition, we will consider how the particle size of the produced recyclate powder affects reprocessing and revulcanization.

The difficulty in recycling rubber comes from the nature of thermoset crosslinks. For conventional sulphur-cured rubber, it is difficult to

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discriminate between the flexible C—S linkages that form the crosslinked network and the C—C bonds that makeup the polymer chains, despite differences in bond energy. Therefore, when grinding and devulcanizing the 3D crosslinked network, the C—C bonds are often damaged, resulting in a lower average molecular weight of the polymer chains [5,6]. This reduction in the molecular weight of the polymer backbone may be expected to lead to reduced properties. Furthermore, the composition of crosslink types (ratio of mono/di/poly-sulphidic linkages) may be affected [7].

Several technical approaches to recycling of thermosets have been considered, such as microwave devulcanization [8], chemical devulcanization [9], low temperature devulcanization [10] (such as cryo-milling), high temperature devulcanization (typically by extrusion) [11] and mechanical devulcanization [5,7,12]. Elastic strain-assisted technologies have proven effective in pulverising polymeric materials at different temperatures and pressure profiles. High shear stresses applied during these processes are capable of physically fragmenting the polymer to produce a fine powder and achieving bond scission, hence the mechanochemical label attached to these methods [13]. Solid-state shear milling (S3M) is one of the most promising methods in its field. Based on traditional pan-milling [14], the waste is sheared between two uniquely surface-structured plates at room temperature [15,16]. It offers a great processing flexibility since the final powder properties correlate to pan speed, applied force and number of passes.

S3M can transform even hard-to-recycle materials into an easy to process, useable powder form. Recently, this S3M technique has been shown to effectively devulcanize rubber [17,18]. Similarly, S3M was successful in partially decrosslinking XLPE and producing a thermoplastic product [19]. This was demonstrated by the reduction in gel content of XLPE and rubber alike. Utilising S3M for devulcanization eliminates the need for chemical processing and the thermoset powder can then be processed either as a filler material, a matrix material or as one phase of a thermoplastic vulcanizate [20].

In order to produce a more readily recyclable product from the waste, a devulcanized thermoset can be converted to a thermoplastic vulcanizate (TPV) by blending with a thermoplastic and dynamically vulcanizing [21]. This acts to reduce the cost and improve the toughness compared with a traditional thermoplastic. Thermoplastic vulcanizates are the fastest growing form of elastomers being used to replace traditional thermoset rubbers [21]. These thermoplastic elastomers are made up of a thermoplastic as the continuous phase with a crosslinked rubber as the dispersed phase. Typically, the ratio of rubber to plastic (R/P) will be between 50/50 and 80/20. Higher plastic content gives a higher modulus, while higher rubber content improves elongation at break. Blends of EPDM and PP are the most successful thermoplastic vulcanizates to date, but many different thermoplastic/rubber blends can be produced providing there is a reasonable compatibility between the phases. In order to achieve good compatibility, a viscosity match is considered desirable [22,23].

The microstructure of the TPV product depends upon many factors, including; the crosslink density and resulting domain size of the rubber (after dynamic vulcanization), the interface between the R/P phase components, and the structure of particles within the network; all of which may be influenced by the devulcanized rubber's particle size and state [21]. Degree of crosslinking and domain size can be easily measured and evaluated for the S3M materials. Additionally, crosslink density and reaction rate are major factors in dynamic vulcanization affecting the final morphology, both of which will be dependent upon the S3M devulcanization.

L'Abee et al. demonstrated that a reduction in TPV rubber domain size resulted in increased fracture toughness, tensile strength and elongation at break [24]. The authors suggested that matrix yielding is the main deformation mechanism. Therefore, reduced particle size improved mechanical properties by reducing interlamellar void formation. Crucially, they suggest that above some critical domain size, the particles cannot influence the mechanism for elastic recovery. Subsequently, other works have discussed how to influence the domain size of the rubber network and the influence on TPVs [21,25–27].

The particle size of the devulcanized rubber is expected to affect a number of factors, including; the viscosity of the rubber phase (and hence compatibility with the plastic phase), the degree of devulcanization of the particles, the surface area of the particles, the ratio of mono/di/poly-sulphidic linkages and the molecular weight of the rubber. Since these are modified by the S3M process concurrently, there is a compromise between competing phenomena. For example, a greater degree of devulcanization may positively influence re-processability and thus properties but with a reduced molecular weight, which may, conversely, be expected to reduce properties. Zhang et al. found that increasing the number of S3M passes led to a reduced and narrowed molecular weight distribution of the devulcanized rubber [5]. Overall, this may result in some optimum particle size, which may be dependent on the use of the particles (as a rubber phase of a TPV, as a filler or a matrix). Typically, reduced particle size leads to increased elasticity, tensile strength and elongation at break but reduced tear strength and flexural strength [28–30].

Macsiniuc et al. investigated the effect of particle size distribution (125 to 500 μm) of SBR on its regeneration [31]. They found that crosslink density was a function of particle size and important to the process of regeneration itself. Additionally, the authors highlight the importance of controlling processing conditions to effectively reduce crosslink density because of complications from radical reaction mechanisms. It has been demonstrated that during the S3M process the oxygen content of the devulcanized rubber increases, which is likely due to reactions between atmospheric oxygen and the radicals generated from bond scission [17].

Devulcanization results in radical generation and may proceed via a radical assisted mechanism [7]. Despite these assertions, limited work has been done to quantify the concentration of radicals generated or the variety of radical structures that may exist within these rubber recyclate powders [32]. Furthermore, the effects of these radicals upon the reprocessing of waste rubber are not yet fully understood. Some works have suggested the structures that may be formed by reactions between radicals and other chemicals present under the devulcanization conditions, but the measurement of these structures remains difficult [7].

In this study, thermoplastic vulcanizates were produced from recycled waste streams (crosslinked polyethylene and natural rubber) without the need for any virgin material. This was achieved using a combination of solid-state shear milling, extrusion, and compression moulding, all of which can be performed at industrial scale with high throughput. We seek to understand how the two different rubber particle sizes, achieved by different numbers of S3M passes, affects reprocessing and vulcanization in the production of these TPVs. Particle size of the devulcanized natural rubber was measured by SEM, whilst EDX was used to measure the elemental composition of the rubber. Electron paramagnetic resonance (EPR/ESR) was used to investigate the radicals generated by the milling process and how their concentration changes upon heating to the vulcanization temperature. The S3M powders of crosslinked polyethylene (XLPE) and natural rubber (NR) were converted into TPVs by twin screw extrusion under different conditions and the resulting mechanical properties were measured by tensile testing. Rheology of the produced blends was measured using oscillatory rheometry. Finally, the effect of crystallinity was considered using DSC and the thermal stability was measured by TGA.

2. Materials

The materials processed herein were Natural rubber from disused shock absorber and crosslinked polyethylene from waste electrical cables. Pre-shredded natural rubber, of approximately 2–5 mm size, was obtained from recycling facilities in China. Waste XLPE (peroxide crosslinked) was obtained from a cable factory in Deyang China.

Zinc oxide (ZnO) reagent grade, Stearic acid (SA) 95%, Sulphur, and tetramethyl thiuram disulfide (TMTD) 97% were procured from Sigma Aldrich. n-cyclohexyl-2-benzothiazole sulfenamide (CBS) was procured from Santa Cruz Biotechnology.

3. Experimental

3.1. *S3M*

The materials were passed through the solid-state shear milling process to obtain a homogeneous rubber powder, as described by Xu et al. [14]. The solid-state shear milling process reduces the size and crosslink density of the materials with each pass. Therefore, different numbers of passes can be used to obtain powders of different size. In this case, 3 and 4 S3M cycles were used, named NR50 and NR100, respectively (a reference to the corresponding mesh size).

XLPE was converted to a powder form following 10 cycles of the S3M equipment. The crosslinked polyethylene contained approximately 20% ethylene vinyl acetate (EVA) and 5% additives.

3.2. *Direct compression moulded samples*

To demonstrate the activity and initial state of the recyclates after S3M devulcanization, the NR50 and NR100 as-received powders (AR) were directly compression moulded using a Moore press at 160 °C to 180 °C and 8 MPa to produce sheets of approximately 2 mm thickness. The mechanical properties of these sheets were tested to give benchmark minimum properties.

3.3. *Extrusion*

Extrusion was used to convert the powders into a processable and mouldable filament, as well as to blend materials and add vulcanization agents. Extrusion was performed using an APV twin screw extruder with a screw diameter of 19 mm and an L:D ratio of 25:1. The screw configuration can be seen in Fig. 1, with further technical details provided in the supplementary information.

For the preparation of an XLPE masterbatch, the powder was extruded at 140 °C and 20 rpm to give a filament of approximately 3 mm diameter, which was then cooled in a water bath and pelletised.

3.3.1. *Preparation of thermoplastic vulcanizates*

For the preparation of the rubber/plastic blends, the XLPE masterbatch pellets were mixed in a bag with the natural rubber powder and any curing agents (as listed in Table 1), the resulting powder covered pellets were then extruded according to the temperature and screw speed indicated. In all cases, the rubber-plastic blends were produced using a 50/50 by weight mixture.

3.4. *Compression moulding*

The blended materials were compression moulded according to the temperature given in Table 1, the maximum pressure used was 8 MPa in all cases. The three different mould temperatures, 120, 160 and 180 °C refer to different specimens. For XLPE and rubber/plastic blends, materials were moulded for a total of 12 min, during the first 7 min the pressure was gradually increased under high temperature, followed by cooling under pressure for 5 min. For rubber matrices, the materials were compression moulded for 6–10 min and the maximum pressure was applied immediately after degassing.

Table 1
Prepared materials.

Recycled materials	Ext. temp. (°C)	Ext. rpm	Curatives	Mould temp (°C)
XLPE masterbatch	140	20	–	–
XLPE	160	20, 80, 140	–	120, 160, 180
NR50	–	–	–	160, 180
NR100	–	–	–	160, 180
XLPE/NR100	160, 180	20, 80, 140	0, Half	120, 160, 180
XLPE/NR50	160, 180	20, 80, 140	0, Half	120, 160, 180
Control materials				
LDPE/vNR	160	20, 80, 140	Full	160, 180
XLPE/ vNR	160	20	Full	160, 180
LDPE/ NR100	160	20	Half	160, 180
vNR	–	–	Full	160, 180
LDPE	140	20	–	160, 180

'Half' cure package = 1.5 phr ZnO, 0.5 phr Stearic acid, 1 Sulphur, 0.5 CBS.
'Full' cure package = 3 phr ZnO, 1 phr Stearic acid, 2 phr Sulphur, 1 phr CBS

3.5. *Characterisation*

3.5.1. *SEM and EDX*

SEM was performed using an FEI Quanta400 environmental SEM at 20 kV on samples coated with 10 nm of carbon. ImageJ was used for particle size analysis.

For Energy dispersive X-ray spectroscopy (EDX) measurements, the uncoated as-received powder was spread onto aluminium tape. To prevent accidental repeated measurement of a particle, a grid was printed onto the aluminium surface. 100 particles were measured with at least 100 point-measurements taken per particle. The detector used was an Oxford instruments Explore 30. Aztec 4.4 was used for analysis of the spectroscopy results.

3.5.2. *Differential scanning calorimetry (DSC)*

A TA Discovery DSC connected to an RCS-90 cooling system (New Castle, USA) was used to study the melting and crystallisation thermal transitions. An average sample size of 8 mg was loaded into standard aluminium pans and scans were performed from −90 to 250 °C at a standard heating rate of 10 °C/min. DSC thermograms were used to determine phase temperatures before further characterisation experiments and guide processing conditions.

3.5.3. *Rheology*

Rheometry experiments were conducted on Anton-Paar Physica MCR 301 rheometer (Graz, Austria) using a parallel plate measuring system PP25 ($R = 12.5$ mm). Temperature was controlled using a P-ETD400 plate and an H-ETD400 hood. Measurements were performed on disks compression moulded at 120 °C. Frequency sweeps were performed at 160 °C, the strain value was kept constant at $\gamma = 0.1\%$ and angular frequency $\omega = 100$–0.1 rad/s. The produced curves are an average based on two.

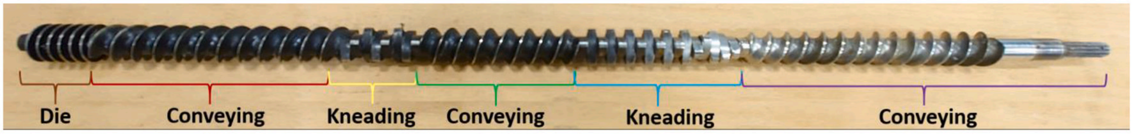

Fig. 1. Screw configuration for each screw in the APV extruder used to prepare the TPV blends.

3.6. *Tensile testing*

Tensile testing for rubber materials was performed according to ISO 37 with an extension rate of 500 mm/min using a 1kN load cell.

For XLPE and XLPE/NR blends, tensile bars (ISO34-4) were stamped from sheets using a cutter to produce specimens with overall length = 35 mm, gauge length = 10 mm and width = 2 mm. Experiments were performed using Instron 5564 (Norwood, USA) with 1kN load cell at room temperature and a rate of 50 mm/min.

4. Results and discussion

4.1. *Powders*

Firstly, the recyclate powders were characterized. The ability to reprocess the natural rubber may depend upon its particle size, flow behaviour and the extent to which it has been devulcanized. These properties will also be important for reprocessing with the decrosslinked XLPE. Additionally, the radicals produced by the S3M process and contained within the powders may affect the revulcanization of the prepared materials.

4.1.1. *Particle size*

The particle size and morphology of the S3M powders was measured using SEM, and ImageJ was used to measure the area of the visible particle surface. Since the number of milling cycles is greater for NR100 than for NR50 the particle size distribution is expected to shift to lower values. Although, the particle area measurements could be converted to traditional particle diameters using assumptions about the shape, this would increase the measurement error. Therefore, Fig. 2 shows the measured cross-sectional area. Example images of the SEM micrographs used to measure these values are provided in the Supplementary Information and further data is available to download as highlighted in section 7.

As shown in Fig. 2, NR100 has a greater concentration of small particles compared with NR50. For NR100 there are few particles above 20,000 μm^2, and less than 1% of particles have an area greater than 50,000 μm^2 compared with 3.7% for NR50. This results in the average measured particle area almost halving going from 3 to 4 S3M cycles. Assuming circularity, the average particle area measured herein for NR50 (3 cycles) would give a diameter of 120 μm and for NR100 (4 cycles) would give 87 μm. Additionally, the deviation in particle area was much greater for NR50 than NR100.

This demonstrates that each S3M cycle reduces the particle size and narrows the distribution. Previously, the particle size of a ground tyre rubber pre-milling was found to be reduced from approximately 300 μm to 200 μm and then 40 μm after 5 and 20 cycles, respectively [33]. Furthermore, degree of devulcanization (reduction in crosslinking) was previously found to increase with number of milling cycles [34].

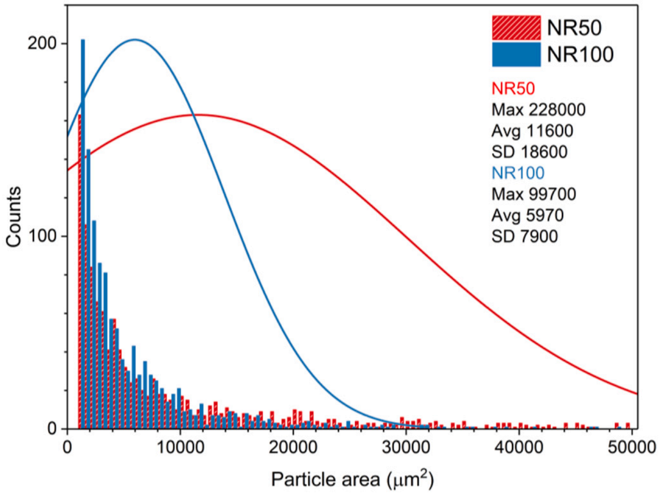

Fig. 2. Particle size distribution of NR100 and NR50 as measured by SEM, measured over 1200 particles each.

4.1.2. *SEM-EDX*

EDX was used to determine the elemental composition of the NR powder. Since the rubber was sourced from recycling plants, it is important to understand the variation within the powder and determine the concentration of impurities present. Additionally, zinc, sulphur and filler concentrations (such as Ca and Si) may be important to the revulcanization process and mechanical properties obtained. Table 2 gives the EDX analysis for 100 particles of NR100 (over 10,000 individual measurements); since the source for NR50 was the same and S3M cycles are not expected to introduce impurities, the composition of NR50 may be assumed to be similar. An example SEM image used for EDX with the line data is provided in the Supplementary Information.

As expected, the primary element is carbon, which forms not only the backbone structure of the natural rubber (and any other contaminating rubbers) but also the structure of carbon black, the most common rubber filler. Judging from the low concentrations of calcium and silicon present (which could result from fillers such as silica, talc and calcium carbonate), it is safe to assume that the primary filler was indeed carbon black.

The second most abundant element was oxygen, at 6 wt%, which is too high to be accounted for by oxides of calcium and zinc, therefore this may suggest that some of the radicals produced during the S3M process have reacted with atmospheric oxygen. Zhang et al. had previously noted that the concentration of oxygen increased following S3M [17,20].

The measured concentrations of zinc and sulphur are in line with expectations for a standard sulphur vulcanized formulation and may help with revulcanization.

Finally, there are several trace metals that would not be expected in rubber compositions and likely arise from the recycling facilities themselves. Additionally, significant concentrations of bromine and chlorine may indicate that some contamination with chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR) has also taken place. Their concentrations are low enough that they may have limited effect on the processability of the rubber. However, heavy metals and their oxides, such as antimony trioxide, may be toxic and carcinogenic [35] therefore suitable respirators and gloves should be worn when reprocessing these rubber powders. Once in the compounded state, the recycled rubber may be considered no more hazardous than a virgin rubber compound.

4.1.3. *EPR*

Electron paramagnetic resonance/Electron spin resonance (EPR/ESR) was used to measure the concentrations and types of radicals produced by bond scission from the S3M process. From the EPR spectra, electron spin g-values can be compared with the literature to identify the

Table 2
Elemental composition of NR100 as determined by EDX.

Element	Composition (wt%)
Carbon	86.91
Oxygen	6.09
Calcium	2.53
Silicon	1.02
Sulphur	0.99
Zinc	0.96
Chlorine	0.65
Bromine	0.28
Aluminium	0.27
Titanium	0.10
Antimony	0.07
Fe, Mo, Mg, Pb, Na, F, P, K, Yb, Te, Ta, Mn	<0.05

radicals present. Additionally, from double integration of the first-derivative peaks, the relative concentrations of the radicals can be compared between different samples. It is worth noting that radical concentration is expected to decrease with increasing storage time [36]. In this case, the rubber powders were stored for a period of months prior to their measurement and processing. However, this may represent a real-world scenario for recycled rubber powders.

First, we may consider the types of radical structures that we expect to be present from the milling of the crosslinked natural rubber, as demonstrated by Fig. 3. These structures may be classified into three types; main chain breakage, crosslink breakage and accelerator by-products. Main chain breakage of crosslinked cis-isoprene should result in an allylic carbon radical, which is the most stable carbon radical due to resonance stabilization by the nearby double bond. The breakage of crosslinks will result in sulphur radicals of varying lengths, which may be indistinguishable by EPR due to a similar chemical environment. Similarly, accelerators form sulphur radicals, typically of mono- or di-sulfidic length, may be difficult to distinguish from broken sulphur crosslinks. Additionally, the reaction of these radicals with atmospheric oxygen may result in oxy- radicals, as indicated by the EDX results.

In EPR spectroscopy, the spin of an electron is flipped by using a magnetic field, and the g-value corresponds to the resonance condition that causes this flip of the electron, which will depend upon its chemical environment. The XLPE and NR powders were measured by EPR using Q-band and X-band at both high and low temperature. The Q-Band curves for NR50, NR100 and XLPE, recorded at 10G and room temperature, can be seen in Fig. 4, alongside the X band spectra recorded at 140–160 °C.

The measured EPR peaks were found to be much broader than expected due to contamination from metal impurities, as identified by EDX. This limits the ability to accurately identify peaks. For analysis of the concentration of radicals, it was assumed that both NR50 and NR100 contained similar quantities of impurities, which were not introduced by the S3M process.

All sample spectra contained a peak with a g-value of approximately 2.004, this appears at approximately 3370 G for X-band and approximately 12,100 G for Q-band. The sharpness of the peak and consistency between the peak shape for XLPE and NR suggest this to be attributed to allylic carbon-centred radicals. Peaks were also identified with g-values from 2.06–2.3. However, due to the metal impurities present in the recycled rubber, it was not possible to give more precise values.

Posadas et al. suggest g-values of 2.0048 and 2.012 for allyl and alkyl carbon radicals respectively [32]. Alkyl radicals are expected to be shorter-lived due to the lack of stabilization and so may be more difficult to detect and would not be expected after such a long storage time.

Notably, a few authors have suggested that sulphur radicals from crosslink scission may also be found at $g = 2.004$. Relating to the early stages of vulcanization, Posadas et al. observed radicals with g-values of 1.974, 1.978, 2.004 and 2.024, which are then partially consumed by the crosslinking reaction [32]. In our case the measured radicals result from devulcanization, rather than accelerator chemistry.

The second integral of the Q-band curves was used to evaluate the concentration of radicals in the powders relative to one another. The second integral between ~11,900 and ~ 12,400 G, corresponding to a g-value of 2.004 can be seen in Fig. 5.

The natural rubber gives a greater concentration of radicals with a g-value of 2.004 than XLPE. There are a few possible reasons for this. Firstly, $g = 2.004$, as described earlier may arise from both sulphur radicals and allylic carbon radicals, therefore the natural rubber has two types of radicals that could give rise to this peak, whilst the XLPE only contains carbon radicals. Differences in bond energy suggest that S—S bonds may be more easily broken by the milling process than C—C bonds. Additionally, the radical concentrations for XLPE and NR may also be disproportionately affected by storage ageing. The S3M process may decrosslink XLPE and NR differently due to their material properties such as relaxation time.

The smaller particle size (NR100) has a greater concentration of radicals. The second integral recorded at a g-value of 2.07, possibly from sulphur radicals, was also found to be greater in concentration for NR100 than NR50.

The concentration of radicals is temperature dependent. At 160 °C, the difference in concentration of radicals between NR50 and NR100 becomes insignificant, as demonstrated by Fig. 5c. This suggests that the radicals in NR100 will be more susceptible to revulcanization than NR50.

At the processing temperature, 140 °C, the quantity of radicals related to $g = 2.004$ for XLPE becomes immeasurably small. The carbon-centred radicals seemingly react or recombine at the extrusion temperature. Whereas reaction of radicals with oxygen would lead to degradation products, which reduce mechanical properties. Therefore, recombination of XLPE radicals is desirable and this is considered a positive result for the recycling of XLPE.

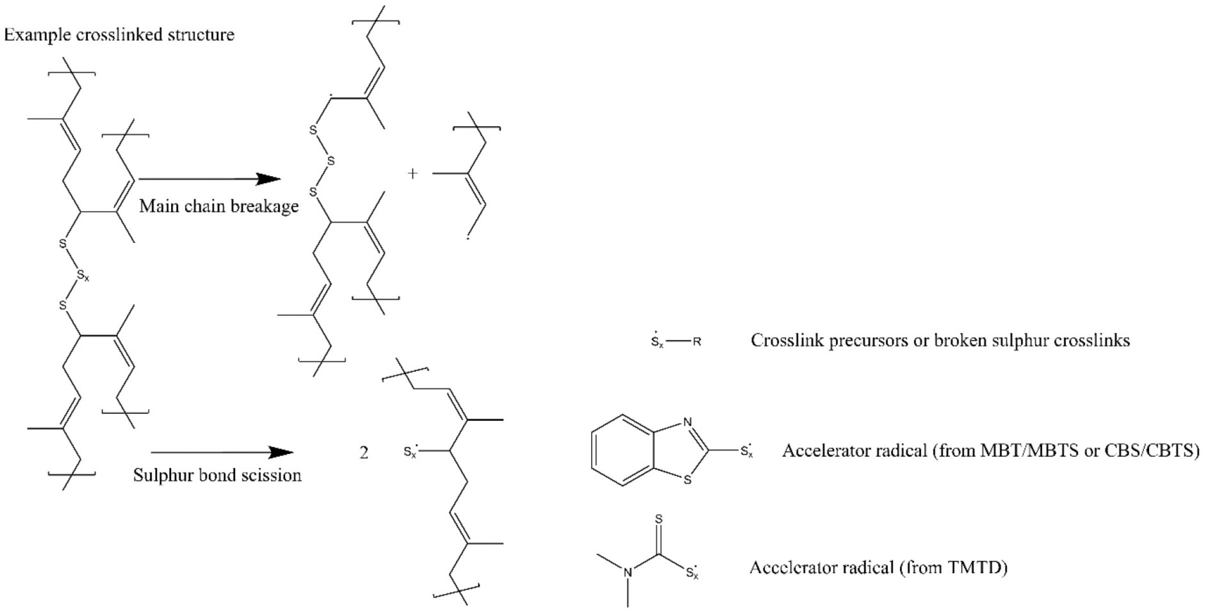

Fig. 3. Expected radical structures from milling of natural rubber (where x can be any number due to presence of mono−/di−/poly-sulphidic bonds and radicals).

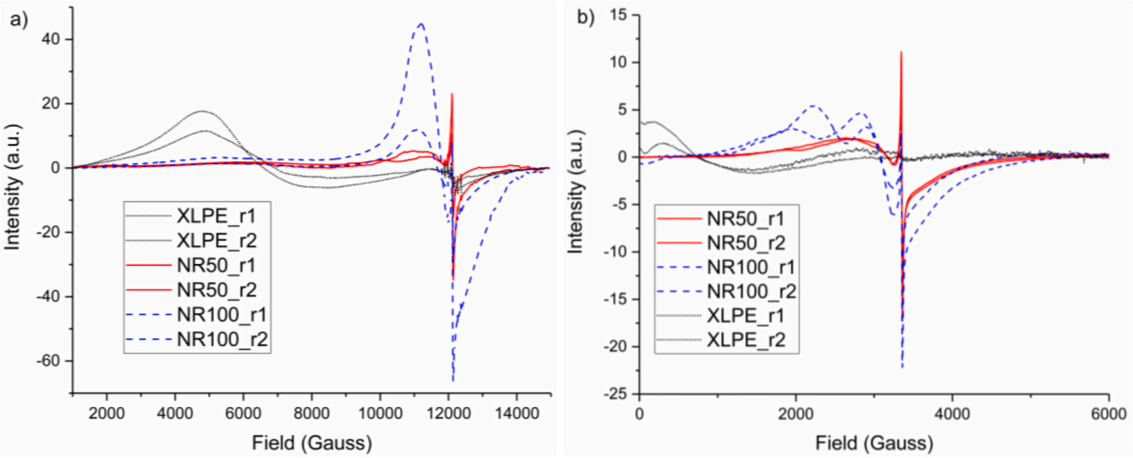

Fig. 4. EPR signal of NR50, NR100 and XLPE, a) Q-band measured at 25 °C and b) X-band measured at 140 °C for XLPE and 160 °C for NR. r1 and r2 correspond to the first run and the repeat.

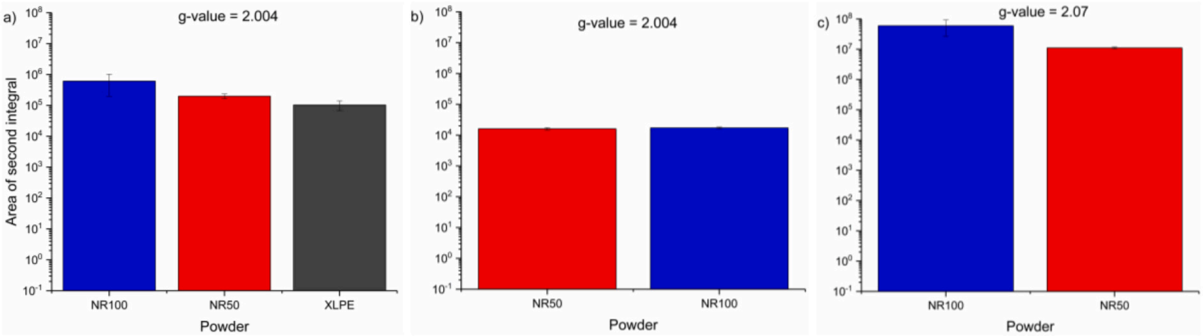

Fig. 5. Concentration of radicals as measured by EPR, for a} Q-band NR50, NR100 and XLPE at 2.004, measured at 25 °C b) X-band, NR50 and NR100 at 2.004, measured at 160 °C c) Q-band, NR50 and NR100 at 2.07, measured at 25 °C.

The results indicate that radicals are present in the S3M powders even after long storage times. Additionally, the concentration of these radicals and their activity increases with the number of milling cycles. Furthermore, these radicals, produced by the S3M process due to bond scission, could be active in any subsequent revulcanization when reprocessing the S3M powders.

4.2. *Reprocessing and blends*

The XLPE and NR powders were converted to XLPE/NR thermoplastic vulcanizates by extrusion. The production of thermoplastic vulcanizates, as opposed to a plastic filled rubber or rubber filled plastic, requires dynamic vulcanization. Dynamic vulcanization during extrusion leads to a thermoplastic matrix with crosslinked rubber domains throughout.

Since the S3M rubber exhibits a crosslink density of approximately 70%, it may be suggested that TPVs could be produced without the need for a full cure package to be added. Additionally, it has been suggested that the rubber phase of S3M rubber can be re-crosslinked with half the concentration of curatives required compared with a virgin rubber [37]. Therefore, XLPE/NR TPVs were prepared with both no additional curatives and a half cure package to investigate the necessity of curatives for dynamic vulcanization in recycled blends.

A range of extrusion rates were also investigated. Although extrusion using higher rpm may be industrially desirable, too high an rpm may lead to inadequate time within the process for vulcanization. de Sousa et al. suggest that the optimum cure time (t_{90}) should ideally match the extrusion mixing time and suggest that the temperature or feed point of the rubber phase may be altered to achieve this [38]. Sulphur vulcanization typically takes place in the temperature range 150–180 °C, higher temperature may allow for a greater degree of vulcanization, therefore extrusion at both 160 and 180 °C was investigated. The control of this dynamic vulcanization process can allow for rubber domains of smaller sizes to be produced, resulting in greater mechanical properties.

Micrographs for the prepared blends can be found in the Supplementary information in order to visualise the micro-structure of the successfully prepared thermoplastic vulcanizates.

4.2.1. *Viscosity*

The rheological behaviour of the prepared XLPE- and NR- based materials was studied at temperatures above melting, T_m, for XLPE and thermal 'softening' for rubbers. For the preparation of TPVs, a viscosity match between the rubber and plastic phases is considered desirable. However, since the viscosity of the rubber powder is not easily measured, the viscosity of the prepared XLPE/NR TPVs were compared with the prepared XLPE. XLPE demonstrated a shear thinning behaviour, as shown by Fig. 6. The rate of extrusion and processing temperature had little effect on the XLPE viscosity (data not shown).

The addition of natural rubber to XLPE and their conversion to TPVs served to increase the complex viscosity. The fact that the S3M XLPE was found to have a lower viscosity, and thus flow more easily than the S3M NR, may help to explain why the EPR measured radicals were found to be more prone to recombine upon heating XLPE than NR. The mobility of radicals is less restricted, thus the chance of radical reactions taking place may be improved.

At low frequency, the XLPE/NR blends all show a significantly higher

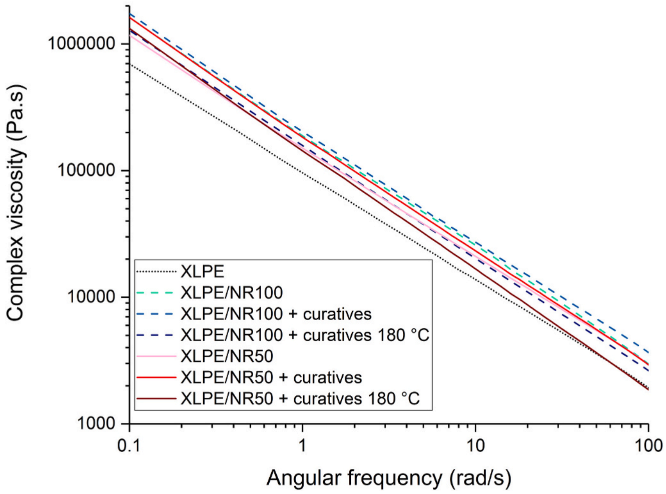

Fig. 6. Viscosity of XLPE and XLPE/NR blends, samples extruded at 20 rpm and moulded at 120 °C, showing the effect of the addition of curatives and extrusion at higher temperature.

complex viscosity than XLPE, whereas at high frequency the viscosities are typically closer. For XLPE/NR50 with curatives and extruded at high temperature, the high frequency viscosity matches that of XLPE. This may allow for improved compatibility between the phases.

4.2.2. DSC

For uncured rubber, a small endothermic peak is seen in the differential scanning calorimetry thermogram between 60 and 100 °C, corresponding to the thermal softening of the material. However, this pales in comparison to the endothermic peak resulting from the melting of XLPE at approximately 105 °C. For uncured natural rubber, there is an exothermic peak between 160 and 180 °C due to vulcanization, which is then absent post curing.

The production of TPVs containing 50/50 NR/XLPE results in a thermogram that closely resembles that of neat XLPE, as shown by Fig. 7. The successfully prepared TPVs were melt-processable at the selected extrusion temperatures from 160 to 180 °C. T_g and T_m values for the prepared blends are presented in Table 3. Only a small change was seen in the melt peak for PE following the addition of the rubber. The addition of curatives led to a slight increase in the glass transition temperature.

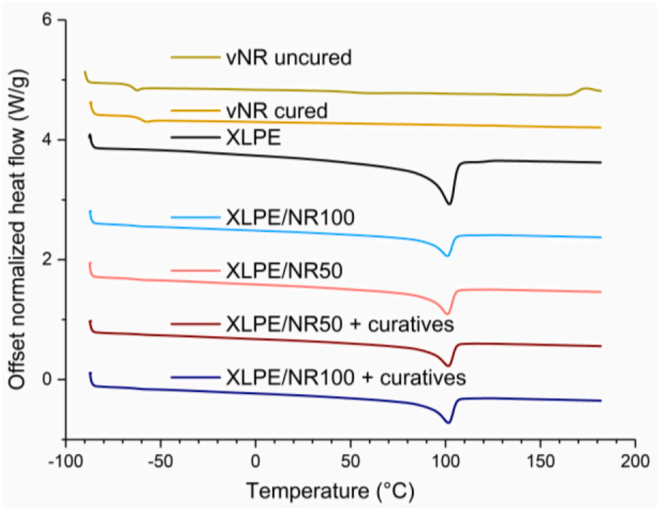

Fig. 7. Thermograms of the second heating step for vNR, XLPE, XLPE/NR100 and XLPE/NR50 as measured by DSC, exothermic upwards.

Table 3
T_g and T_m for the presented materials as measured by DSC.

Material	T_g (°C)	T_m (°C)
vNR uncured	−65.9 ± 0.1	–
vNR cured	−61.4 ± 0.1	–
XLPE	–	102.3 ± 0.3
XLPE/NR100	−63.8 ± 0.2	101.6 ± 0.2
XLPE/NR50	−64.1 ± 0.5	101.4 ± 0.1
XLPE/NR50 + curatives	−62.4 ± 1.0	101.1 ± 0.3
XLPE/NR100 + curatives	−61.4 ± 3.1	101.0 ± 0.5

4.3. Properties

4.3.1. Tensile properties

4.3.1.1. Raw devulcanized recyclate. Initially, the as-received S3M NR50 and N100 were directly compression moulded to give sheets with the benchmark minimum mechanical properties. Since the rheology of these natural rubber powders could not be measured accurately without prior reprocessing, 6-, 8- and 10-min cure cycles were performed at both 160 and 180 °C, in place of the t_{90} ordinarily used. Changing cure time typically led to insignificant changes with the powder having short cure and scorch times. However, increasing the cure temperature led to a significant increase in elongation at the expense of the modulus, as demonstrated in Table 4. This result is in line with previous reports on efficient and semi-efficient vulcanized natural rubber, where higher cure temperature can lead to a reduction in overall crosslink density resulting in higher elongation at break and lower modulus for 180 °C compared with 160 °C [39]. Representative stress-strain curves for each material can be found in the supplementary information.

The highest tensile strength was obtained for NR50 under a high temperature for a long time (180 °C, 10 mins), which also resulted in the greatest elongation at break. However, the highest modulus was obtained for the smaller particle size at lower temperature (NR100, 160 °C, 6 mins). In all cases, the elongation at break and tensile strength were considerably reduced compared with what would be expected from a virgin natural rubber. SEM images of the fracture surfaces of these samples revealed internal voiding, which may be partially responsible for the reduced properties (available in supplementary information). Therefore, for most applications, the post-processing of S3M rubber powder is considered essential.

4.3.1.2. Extruded XLPE. The effects of extrusion rate and temperature on mechanical properties were first considered for the S3M XLPE before evaluating blends of XLPE and NR. An extruder with two mixing zones and high L:D was used to increase the overall mixing time for the powder. Fig. 8 shows the effect of extrusion temperature on the properties of XLPE, the properties for XLPE with low mixing (lower L:D and single mixing zone, denoted low Rt) are also included.

With increasing extrusion temperature, the elongation at break (EB), modulus and ultimate tensile stress (UTS) of the XLPE increased. This

Table 4
Tensile properties of natural rubber powders, directly compression moulded without prior processing, min. avg. of 3.

Material	Temp. (°C)	Cure time (mins)	Modulus at 100% (MPa)	Elongation at Break (%)	Tensile strength (MPa)
NR100	160	6	1.70 ± 0.02	174 ± 6	2.46 ± 0.05
NR100	160	10	1.68 ± 0.04	194 ± 15	2.76 ± 0.09
NR100	180	6	1.33 ± 0.03	229 ± 19	2.68 ± 0.12
NR100	180	10	1.29 ± 0.04	242 ± 21	2.71 ± 0.22
NR50	160	6	1.62 ± 0.02	205 ± 23	3.07 ± 0.19
NR50	160	10	1.44 ± 0.02	207 ± 10	3.10 ± 0.16
NR50	180	6	1.14 ± 0.04	268 ± 7	3.29 ± 0.05
NR50	180	10	1.19 ± 0.04	312 ± 13	4.14 ± 0.13

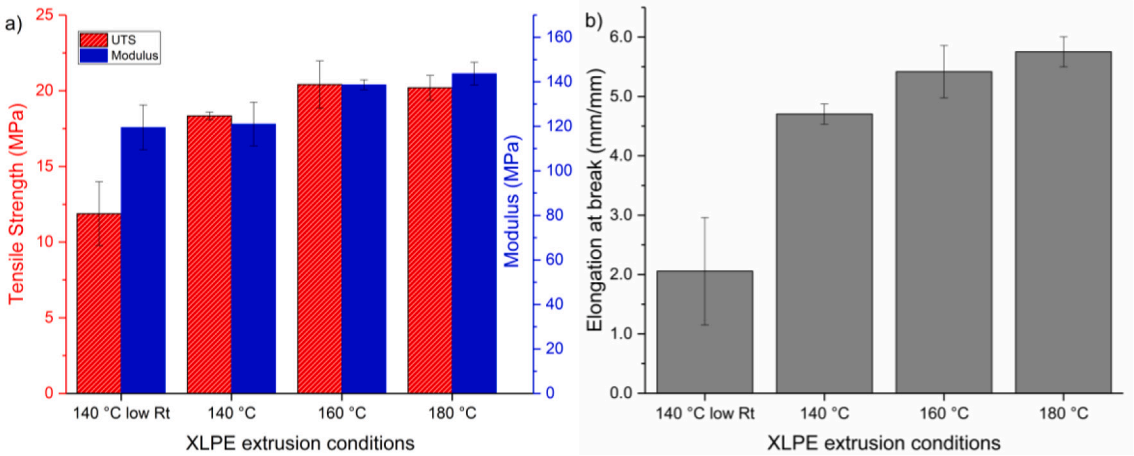

Fig. 8. Tensile properties of XLPE with different extrusion temperatures, a) Tensile strength and modulus, b) Elongation at break - low Rt (low residence time).

suggests that processing the XLPE and NR blends at the temperatures required for dynamic vulcanization, should have no negative effects on the XLPE phase. The limited benefit of moving from 160 °C to 180 °C may be outweighed by the increased energy cost, therefore 160 °C was chosen as the primary extrusion temperature for the production of TPVs. Stress-strain curves for the data presented are available in the Supplementary Information.

4.3.1.3. XLPE/NR TPVs. Reprocessed XLPE and NR blends (50/50) from 4.2 were compounded to produce TPVs. Fig. 9 shows the effect of both temperature and the addition of curatives on NR100/XLPE and NR50/XLPE.

For XLPE/NR50 and XLPE/NR100, the modulus and tensile strength (UTS) increase with the addition of a cure package, whilst the change in elongation at break is negligible. This suggests that some dynamic vulcanization took place, which was aided by a cure package. The highest mechanical properties were observed for XLPE/NR100 with a cure package. Compression moulding at 120 °C, there is no opportunity for further vulcanization or rearrangement to take place upon moulding.

If we contrast this with the same samples compression moulded at 180C, the effects of further vulcanization and rearrangement of the polymer and elastomer networks can be seen, as shown by Fig. 10.

Whilst the samples compression moulded at 120 °C showed plastic-like properties with high modulus and low elongation at break, the samples moulded at 180 °C showed more rubber-like properties with a significantly increased elongation at break, at the cost of the modulus. Tensile strength was broadly similar between the two compression moulding conditions, suggesting that rearrangement of polymer and elastomer chains was the key reason for these property differences. (Compression moulding at 160 °C was also investigated and showed intermediate properties, not shown).

When compression moulding at 180 °C, the XLPE/NR100 extruded at high temperature (180 °C) shows a reduction in properties, with significantly lower tensile strength and elongation at break than its counterpart extruded at 160 °C. This suggests that the crosslinking process had surpassed the optimal crosslink density and degradation mechanisms had begun taking place, a phenomenon known as reversion in rubber vulcanization that leads to reduced mechanical properties.

It is known that high vulcanization temperatures can lead to reversion. However, this reversion-like behaviour was not seen for XLPE/NR50. This could be related to the surface area of the particles. Since the NR100 particles are smaller, as evidenced by the SEM particle analysis, they have a greater specific surface area, allowing for more facile revulcanization. They also have a greater concentration of radicals, as evidenced by EPR, which may also help revulcanization. It is also possible that the surface area of the particles leads to differing shear intensity in the mixing zones, with the greater surface area particles resulting in higher shear and subsequently increased temperature.

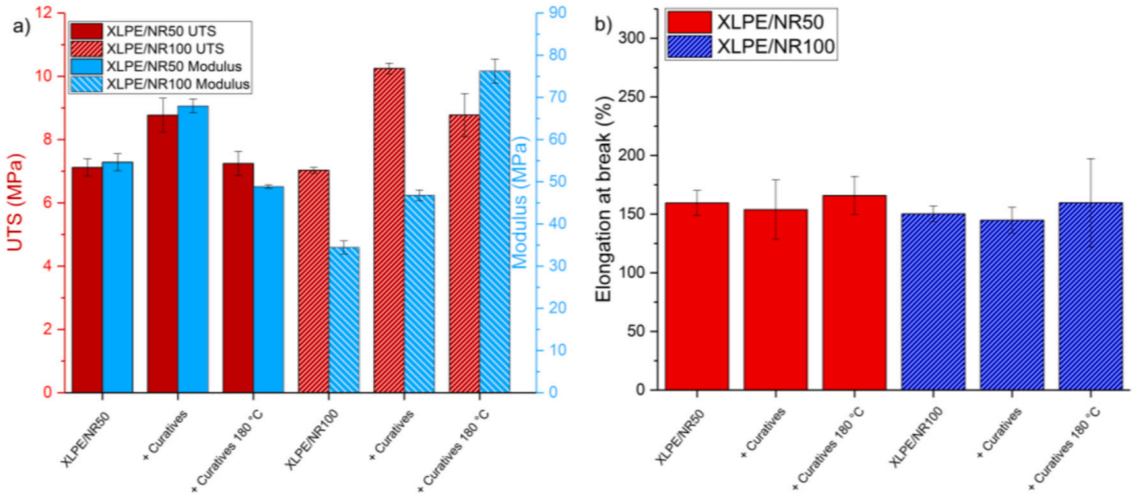

Fig. 9. Tensile properties of XLPE/NR50 and XLPE/NR100 neat and with a ‘Half’ cure package (+curatives) extruded at 160 °C (as standard) and 180 °C (where indicated) – extruded at 20 rpm, compression moulded at **120 °C**. a) modulus and tensile strength b) elongation at break.

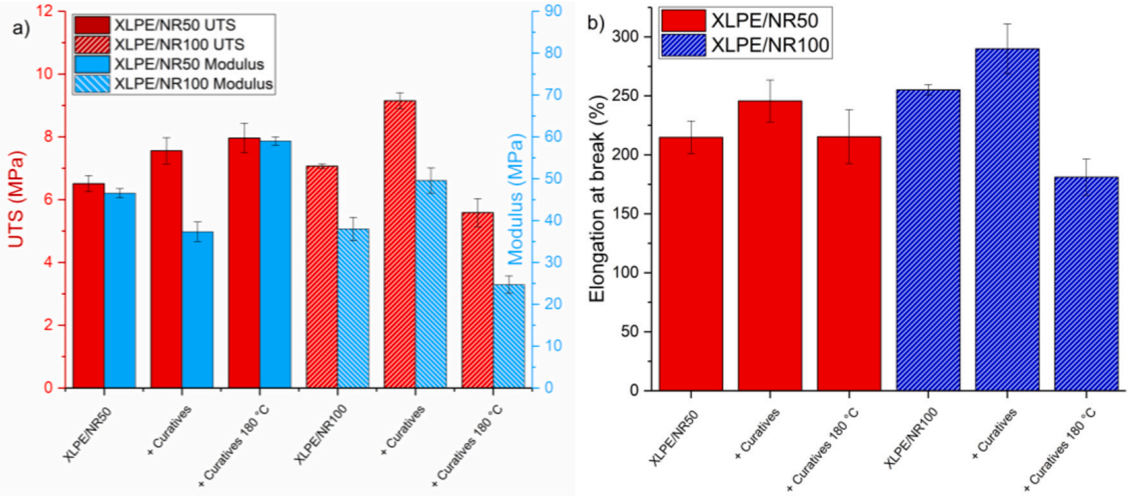

Fig. 10. Tensile properties of XLPE/NR50 and XLPE/NR100 neat and with a 'Half' cure package (+curatives) extruded at 160 °C (as standard) and 180 °C (where indicated) – extruded at 20 rpm, compression moulded at **180 °C**. a) modulus and tensile strength b) elongation at break.

Therefore, the optimal crosslink density was achieved for NR100 at the extrusion temperature of 160 °C, whereas the NR50 showed improved crosslink density at the higher extrusion temperature (180 °C).

The tensile results indicate that the optimal temperatures for extrusion and compression moulding are dependent upon particle size. This may be a consequence of the ease with which the material can be revulcanized. Larger particles benefit from higher temperature, whilst smaller particles may be better crosslinked at 160 °C. The best combination of properties was observed for XLPE/NR100 extruded at 160 °C and compression moulded at 180 °C, which resulted in a tensile strength of 9.1 MPa, elongation at break of 290% and modulus of 50 MPa.

We may now consider the effect of extrusion rpm on mechanical properties. This may be important since reduced processing time is economically desirable. Higher rpm will give enhanced shearing in the mixing zone but lower residence time. Shorter residence time may reduce the degree of crosslinking, however higher shearing may help to reduce the domain size of the rubber phase in the TPV. Both of which are expected to affect the resultant mechanical properties.

For XLPE/NR50, increasing rpm led to an increase in both UTS and EB for the specimens compression moulded at 160 °C, with 140 rpm giving the greatest mechanical properties, as shown by Fig. 11a. However, when compression moulding at 180 °C, the prior effect of extrusion rate was negligible. Previous rheological work has indicated that rubber particle networks in TPVs may strengthen with temperature due to either further crosslinking or an entropy increase [40]. Higher extrusion rpm results in greater shear forces in the mixing zone, which may help in reducing the particle/domain size of the rubber phase in the TPV and could aid revulcanization for highly crosslinked materials. It is accepted that the high shear achieved by twin screw extrusion results in finer particles compared with similar processing techniques, which typically enhances mechanical properties [41].

For XLPE/NR100, the greatest mechanical properties were found for the lowest extrusion speed, as shown by Fig. 11b, which may evidence the ease with which the reduced particle size may be recrosslinked. Therefore, again it must be reiterated that the optimal extrusion conditions are influenced by the particle size of the rubber.

As a reference, samples were prepared using LDPE in place of XLPE and virgin natural rubber in place of NR50 and NR100. The mechanical properties for these materials are summarised in Table 5, along with the recycled XLPE. For XLPE, increasing extrusion rpm from 20 to 140 led to a decrease in tensile strength and, more significantly, elongation at break. Since the drop in properties between 20 rpm and 80 rpm was relatively small, the increased rate may outweigh the reduced properties. The S3M XLPE shows good properties after being extruded, whereas

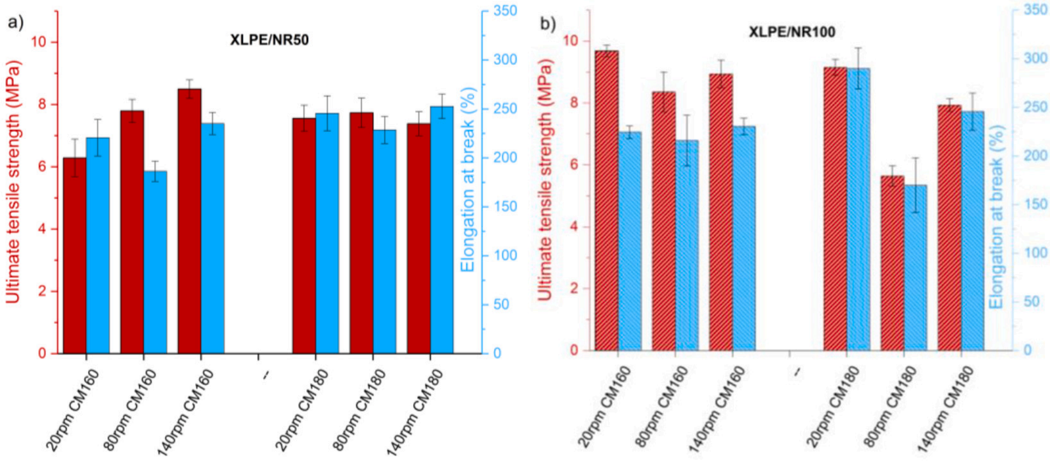

Fig. 11. The effect of extrusion rate and moulding temperature on tensile strength and elongation at break for blends of a) XLPE/NR50 with a cure package and b) XLPE/NR100 with a cure package.

Table 5
Tensile properties of control materials, XLPE, LDPE, XLPE/vNR, NR100/LDPE and LDPE/vNR.

Compound	UTS (MPa)	EB (%)	Modulus (MPa)
XLPE 20 rpm	18.6 ± 1.1	540 ± 27	129 ± 4
XLPE 80 rpm	17.8 ± 1.6	506 ± 42	133 ± 1
XLPE 140 rpm	16.1 ± 0.6	408 ± 28	119 ± 3
LDPE	30.4 ± 1.8	1300 ± 50	273 ± 5
XLPE/vNR 20 rpm Moulded 160 °C	2.4 ± 0.8	46 ± 25	16 ± 6
XLPE/vNR 20 rpm Moulded 180 °C	4.9 ± 1.2	138 ± 23	7 ± 1
NR100/LDPE Moulded 160 °C	7.9 ± 0.1	251 ± 15	72 ± 1
NR100/LDPE Moulded 180 °C	7.6 ± 0.2	249 ± 12	97 ± 1
LDPE/vNR ext. 20 rpm Moulded 160 °C	7.1 ± 3.0	264 ± 106	27 ± 3
LDPE/vNR ext. 80 rpm Moulded 160 °C	11.8 ± 1.0	196 ± 25	29 ± 6
LDPE/vNR ext. 140 rpm Moulded 160 °C	14.7 ± 1.6	132 ± 28	48 ± 6

the S3M natural rubber cannot be easily reformed alone.

It is worth noting that although the elongation at break for LDPE appears very high, the specimen begins necking at less than 10% elongation, therefore their elasticity is significantly lower than for the other prepared samples. The application of TPVs is typically closer to that of thermosets than thermoplastics. The mechanical properties indicate that it may be best to recycle the S3M XLPE back to XLPE and to recycle the S3M natural rubber into a TPV, possibly using a recycled LDPE as the thermoplastic phase.

For vNR/LDPE, increasing the extrusion rpm led to higher modulus and tensile strength at the cost of reduced elongation at break. At high rpm, the tensile strength for the virgin materials is greater than the recycled blends. At low rpm, the EB of virgin materials was similar to S3M XLPE/NR blends, however at high rpm the elongation at break was significantly reduced.

Blends of XLPE and vNR showed poor properties, with an elongation at break less than 140% and a tensile strength of less than 5 MPa. The virgin materials have significantly larger variation associated with their production due to the difficulty in uniformly incorporating the cure package. The cure package is better distributed within the recycled materials because both the curatives and the rubber are powders, which are easily dispersed into the thermoplastic matrix. As a further test, virgin rubber that was pre-compounded with the curatives on a two-roll mill was extruded with LDPE, however this did not improve properties nor error, attributed to greater difficulty in blending the rubber and plastic phases. Yet, blends of LDPE and NR100 showed strong mechanical properties, exhibiting a higher modulus than any other blend. Overall, the properties of the recycled blends are similar to virgin materials. However, the virgin materials do not contain any filler, which could be used to enhance the mechanical properties.

5. Conclusions

Thermoplastic vulcanizates were successfully prepared, entirely from waste materials, using solid state shear milling followed by extrusion and compression moulding. This novel combination of processing routes requires low energy input and high throughput allowing for economically viable products. Although recycling of thermoset materials often leads to reduced mechanical properties, these XLPE/NR TPVs showed similar properties to virgin LDPE/NR TPVs, once the processing conditions had been optimised. Crucially, the prepared TPVs showed high elongation at break, close to 300%, allowing use in elastomeric applications.

The benefit of producing TPVs was well highlighted by the mechanical properties for the XLPE/NR blends compared with compression moulded devulcanized rubber powders. Yet the benefit of producing TPVs from waste thermosets is not just their mechanical properties but also their ability to be remoulded. The production of thermoplastic vulcanizates from waste streams offers an environmentally beneficial move towards a more circular product. Given that the use of waste rubber powder in polymer and even elastomer matrices often only serves to match filler properties, and it would struggle to compete economically with carbon black, improvement of the revulcanization and in particular dynamic vulcanization of waste rubbers is an obvious area for further research.

One mechanism for degradation of the recycled materials was identified. The prepared powders showed significant and enduring radical concentrations. Their reaction with oxygen may lead to degradation and reversion if the dynamic vulcanization process is not well controlled.

The effect of particle size on the reprocessing of waste streams into thermoplastic vulcanizates was evaluated. It was found that the optimal processing conditions for each recycled rubber were dependent upon its particle size, which is a consequence of the milling history and can be controlled by the S3M process. The difference in their reprocessing is suggested to arise from the ease with which the rubber can be revulcanized and its effects upon dynamic vulcanization. Smaller particles were seemingly easier to dynamically vulcanize. As a result, the smaller particle size, NR100, typically showed improved mechanical properties, which likely results from reduced domain size in the TPV product. Whereas the larger particle size and less devulcanized rubber powder required more intensive post-processing by extrusion to achieve similar properties. For XLPE/NR50, higher extrusion rate appeared beneficial, which may be due to the high shear allowing further breakup of the rubber domains.

Overall, the greatest mechanical properties arose from the XLPE/NR100 TPVs extruded at low rpm and moulded at high temperature. However, the greater S3M input required to produce NR100 could mean that the most economically efficient property/cost trade-off results from blends using NR50. Therefore, it is pertinent to ask whether it is better to produce finer powders in the first instance, requiring more energy, or whether to use reduced power at the S3M stage and then higher energy in the subsequent reprocessing, we will seek to evaluate this in subsequent studies.

Data availability

The data required to reproduce these findings is available to download from Mendeley data: https://doi.org/10.17632/2dywwz9xsj.1

Raw data required to reproduce these findings are available to download from: https://data.mendeley.com/public-files/datasets/2dywwz9xsj/files/a9e357a0-e55c-4879-83c8-8141c7dcde57/file_downloaded

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.susmat.2022.e00424.

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