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GREEN-LOOP

Sustainable manufacture systems towards novel bio-based materials

WP3 – Bio-rubber material production

D3.4 - Rubber validation trials and key findings

Version 1.0

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GREEN LOOP Consortium Partners

	Partner	Acronym	Country
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Executive Summary

Within the Greenloop project, work package 3 (WP3) is aiming to demonstrate the manufacture of multifunctional rubber panels with a reduction in vibro-acoustics transmission and an improvement in fire-retardant properties. These panels will be for use within the construction sector. By the end of WP3, TRL 5 will have been reached. The work will utilise the supply of recycled and bio-derived material feedstocks to reduce the environmental impact of the final products. The two main components of the formulation are rubber, reclaimed from waste tyres, and lignin powder extracted from waste biomass.

This report collates the work carried out to develop the formulation for use in the rubber panels. It includes details on the lignin extraction process, rubber recycling (devulcanisation), compounding trials and panel manufacture by compression moulding. Full characterisation and testing of the material will be reported in Deliverable 3.5. Further scale up of the production will occur within WP6 to take the value chain from TRL 5 to TRL 6 and will be detailed in Deliverable 6.2.

Lignin is a readily available biopolymer that is a renewable source for aromatic chemical compounds with a potential for significant valorisation as a replacement for fossil-fuel based aromatic compounds. It is the main side product of the pulp and paper industry with an annual production of 100 million. Its high thermal stability and char formation when exposed to fire mean it has potential to be used as a more sustainable additive for improved fire retardancy. Lignin powder is to be used within the Greenloop formulation to improve the fire retardancy of the material. It will be utilised in two ways, firstly as a filler that is compounded into the bulk rubber and secondly as part of a coating system that will be applied to the rubber's surface. NIC have produced 5 Kg of Kraft lignin for use in the formulation trials. This lignin has undergone NMR and FTIR confirm successful lignin isolation and to characterise the lignin produced. Full data will be disseminated within Deliverable 3.5. Fractionation of the lignin to remove lower molecular weight fractions gave an improvement in the fire behaviour of lignin by up to 20%.

For thermoset rubbers to be reclaimed and reprocessed they must go through a process called devulcanisation. This aims to break the crosslinking bonds that bind the polymer chains together without breaking the backbone of the polymer chains themselves. Ultrasound technology and sustainable chemical solvents have been used to develop a new method for devulcanised rubber production. This is currently at the lab scale (50g per batch) but the scale will be increased during WP6. A devulcanisation percentage of 72% has been achieved which compares favourably with the baseline commercial product result of 75%. Scale up results will be reported in Deliverable 6.1

The main material development within WP3 has used a supply of commercially available devulcanised rubber as it is available at sufficient scale for production of testing panels. Reprocessing of devulcanised rubber has been demonstrated both in the literature and commercially however it is usually reincorporated as a filler within a new component rather than as the matrix material itself. In this work trials were carried out to establish how the devulcanised rubber can be used as a matrix material and therefore the main component in formulation. Two formulations have been selected as the most promising and the batch size has increased for 60 g to 1.2 Kg. The mechanical results achieved so far for the formulations which contain 10-20wt% lignin are a break stress of 7.7-9.7 MPa, break strain of 311-330 %, Shore A hardness of 56-62 and a modulus at 100% strain of 2.12-2.35 MPa. These results are sufficient for a robust product that will never be required to take significant mechanical loading. Lignin is incorporated within the formulation to enhance the fire retardancy of the material however there is a limit before it impacts the mechanical properties. A loading level of 20wt% lignin was found to be the optimum loading level before a significant reduction in mechanical performance

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was seen. Fire retardancy testing is being carried out to determine the optimum level of lignin. This will inform the final upscale formulation for WP6.

Full characterisation of the final material will be reported in Deliverable 3.5. In WP6 the batch size will increase to 10-20 Kg. This will allow larger panels to be produced for large scale testing. This will include acoustic testing and fire resistance testing of full-sized panelling. The results of this will be reported in Deliverable 6.2.

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Abbreviations

DES	Deep eutectic solvents
DOE	Design of experiments
GTR	Ground tyre rubber
HBA	Hydrogen bond acceptors
HBD	Hydrogen bond donors
HMW	High molecular weight
IL	Ionic liquid
LbL	Layer by layer
LMW	Low molecular weight
MDR	Moving die rheometry
MH	Maximum torque
ML	Minimum torque
NMR	Nuclear magnetic resonance
PEI	PINETTE PEI
PHR	Parts per hundred rubber
PO	Paraffin oil
SRa	Surface roughness average
SRpm	Average Maximum Profile Peak Height
T 90	Time to 90% cure
TRL	Technology readiness level

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1 Introduction

The purpose of Green-loop Work Package 3 is to develop an optimised bio-rubber value chain and validate its deployment up to technology readiness level (TRL) 5. The target product for this material is rubber panelling with enhanced vibrational damping and fire retardancy for use in the construction industry. This report outlines the results from the work to refine the rubber composite formulation and production. It will detail the materials selected, the work to date on each processing step, key findings from the manufacturing trials and the next steps to be completed within WP6. Full characterisation and testing of the material will be reported in Deliverable 3.5.

1.1 Materials

There are two main components to the formulation: rubber and lignin. The rubber is the largest component by mass in the formulation and acts as the matrix material which binds and holds the composite together. As an elastomeric material, it is used to provide the vibration damping required for the acoustic panelling product. The lignin is incorporated into the formulation as a filler material. Lignin has been identified as an additive which can improve the flame-retardancy of a material by promoting char formation [1]. Two approaches have been taken to utilise the fire-retardant properties of lignin. The first is to incorporate the lignin into the bulk of the rubber and the second is to disperse it into a coating to be applied to the rubber's surface.

1.1.1 Rubber

The family of rubber encompasses many materials with different chemical structures. These can be from synthetic sources (e.g. butadiene rubber) and bio-derived sources (e.g. natural rubber). The supply of rubber material to be used in this work was selected to be rubber reclaimed from waste automotive tyres. Tyre waste is estimated to constitute 2% of all global solid waste per year [2] and so routes to repurpose this waste back into the economy are important to move towards a more circular economy. The average ratio of components used within passenger and truck tyres are shown in Table 1. Both synthetic and bio-derived rubbers are used in tyre formulation. Natural rubber loading is higher in truck tyres compared to passenger tyres as it increases the fatigue and tear resistance of the tyres, required for the higher load placed on truck tyres.

Table 1: Typical components within passenger and truck tyres [3]

Component	Passenger tyres percentage	Truck tyres percentage
Natural rubber	21.1	37.1
Synthetic rubber (e.g. butadiene rubber and styrene-butadiene rubber)	24.5	10.0
Process oil	4.4	0.8
Steel wire	10.8	21.1
Textile fibres	3.7	0.2
Carbon black	18.9	22.3
Silica	7.7	1.3
Antioxidant, antiozonant, curing system	8.7	7.2

To reuse the rubber from tyres the reinforcing elements of the tyre must first be removed. This is the steel wire and textile fibres. That leaves the natural and synthetic rubber blend which is filled with carbon black and

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silica. During the initial rubber processing to formulate the tyre the rubber goes through a curing process. Strong cross-linking chemical bonds between the polymer chains are formed during curing. For the rubber to be reprocessed these cross-linking bonds must be broken through a process called devulcanization. Devulcanisation aims to selectively break the cross-linking bonds without breaking the polymer backbone itself. There are several techniques to do this outlined in the literature [4] [5] [6] [7] and a number of commercially available products [8] [9] [10]. This project has used commercially available devulcanised rubber during the material formulation trials (Sections 0-5). Alongside this, work is ongoing to develop a new devulcanization approach which utilises green chemistry principles and ultrasound technology to lessen the environmental impact of the devulcanization process (Section 0). As this new devulcanisation process is scaled up the material produced will be fed into the formulation trials.

1.1.2 Lignin

Lignin is the second most abundant biopolymer in nature and as the only renewable source for aromatic chemical structures is attracting significant research in attempting to valorise it as a substitute for aromatic petroleum-derived molecules. These are mainly used as building-blocks for polymer synthesis. Lignin is the main side product of the pulp and paper industry with an annual production of 100 million tons [11]. The main role of lignin in the rubber composite formulation is to improve the response of the end product to fire exposure. Kraft lignin is a byproduct of the kraft pulping process and, unlike other types of lignin such as soda or organosolv lignin, has a higher sulphur content, a darker colour and a higher degree of condensation compared to lignin obtained by other methods. The most important characteristics of Kraft lignin (and thus a potentially renewable material for the development of flame-retardant lignin-rubber composites) are its high thermal stability, its ability to form char and its aromatic structure with many reactive hydroxyl groups. The more condensed structure of kraft lignin has a lower content of aliphatic and a higher content of phenolic hydroxyl groups, which contribute more to the formation of char and to the potential improvement of the flame retardancy of composites.

1.2 Manufacturing process overview

Figure 1 outlines the manufacturing process for the bio-rubber value chain. The sections highlighted in green are those that are being developed within the Greenloop project. The box in white shows the commercial steps required to process waste types into devulcanised rubber. These process steps will not be discussed in this report. The lignin extraction trials are detailed in section 2, the devulcanization trails in section 0, and the formulation trials in sections 0, 5 and 0.

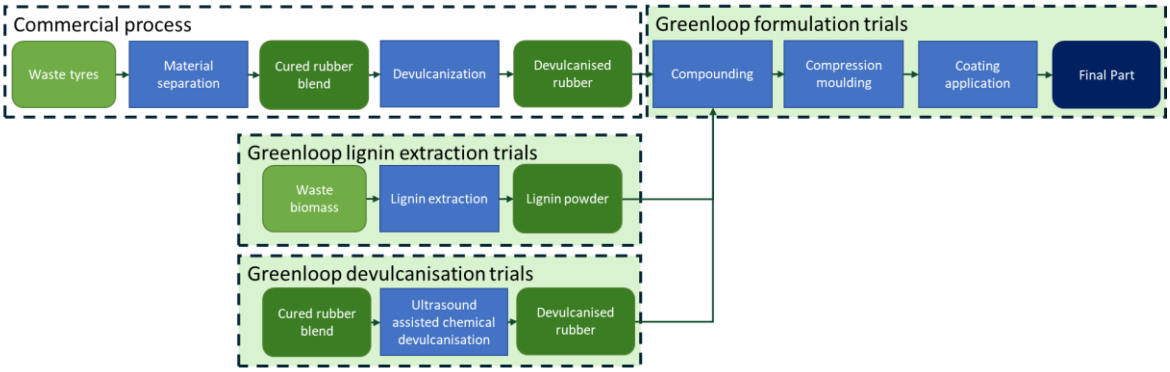

Figure 1: Process overview for the bio-rubber value chain.

2 Lignin extraction trials

2.1 Lignin extraction process

Lignin must be extracted from the biomass waste produced by the pulping industry. The isolation of Lignin at NIC facilities was carried out according to the process flow diagram shown in Figure 2 (left). Specifically, the high-pressure batch reactor (Parr; Figure 2 (right)) is filled with dry biomass (hardwood sawdust) and the required solutions: 17 % sodium hydroxide (NaOH) and 5 % sodium sulfide (Na_2S). The quantity of reagents required is calculated according to the amount of dry biomass (100 g). Thus, 17 g sodium hydroxide (NaOH) and 5 g sodium sulfide (Na_2S) were dissolved in 500 L. The reaction mixture is heated to 175 °C over 45 minutes and held at this temperature for 3 hours. The autogenous pressure rises to 6-7 bar. At the end of the experiment, the reaction mixture is cooled to ambient temperature within two hours. The reaction mixture is then filtered using vacuum filtration to remove the cellulose-rich (wood) residue. To initiate lignin precipitation, the filtrate (lignin-rich stream) is acidified to pH 2 with 75 mL of 15 % sulfuric acid (H_2SO_4). The precipitated lignin is centrifuged, washed several times with the acidic solution and freeze-dried. The lignin extraction process was upscaled and optimized to produce up to 130 g of lignin per batch.

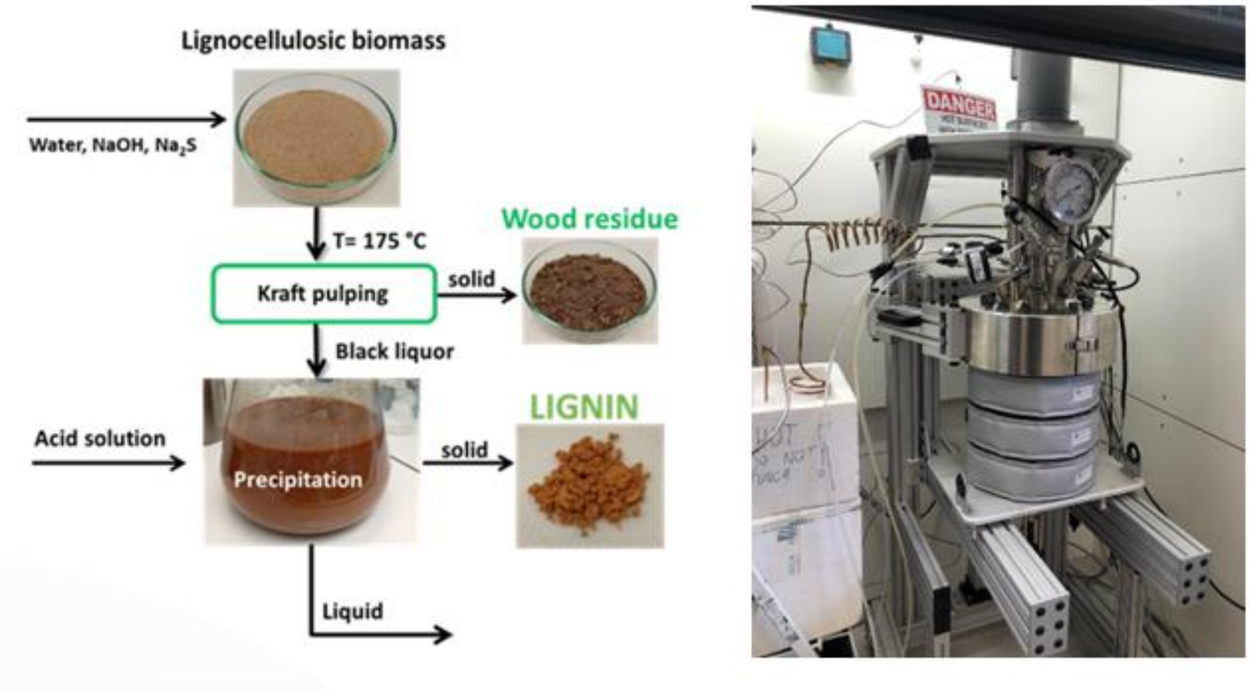

Figure 2: Kraft lignin extraction process flow diagram (left), a high-pressure batch reactor 10L (right).

Table 2: Key parameters and characteristics of Kraft lignin.

Measurement	Value
Wood residue (yield_1)	46.7 %
Delignification degree	95.9 %
Yield of Lignin (yield_2)	8.4 %
Purity of Lignin	75.1 %
Aliphatic OH group content	0.07 mmol/g
Phenolic OH group content	1.92 mmol/g
Carboxylic OH group content	0.28 mmol/g
Total OH group content	1.92 mmol/g
Average molecular weight	3500 Da
Glass transition temperature (T_g) approx.	145 °C

2.2 Lignin fractionation and testing

According to the literature, the introduction of high molecular weight lignin (HMW, 5 kDa) without small oxidized lignin fragments, which are responsible for severe combustion, could increase the flame retardant properties of the final composite [12]. To test the above approach, the low molecular weight (LMW) lignin fragments were separated from the remaining lignin by extraction with ethyl acetate, which is known to dissolve small lignin fragments [13]. For the test, 100 g of the material was suspended in 1 L of ethyl acetate and kept under constant stirring for 2 hours. After extraction, the solids were filtered by vacuum filtration to remove the insoluble components (HMW), which were repeatedly washed with pure ethyl acetate and dried under vacuum at 40 °C for 24 hours. The HMW lignin fraction obtained accounted for 85 % of the initial sample. The low molecular weight (LMW) fraction was obtained by extract concentration, solubilization in 1,4-dioxane, re-precipitation, centrifugation and freeze-drying. The recovered LMW fraction accounted for 15 % of the original lignin.

Both lignin fractions were characterized to determine the structural differences between the samples using NMR and elemental analysis. Quantitative 31P-NMR (Figure 3) experiments were performed according to the protocol reported elsewhere [14]. Measurements were performed in a 1:1.6 deuterated chloroform (CDCl3)/pyridine mixture at 25 °C, and N-hydroxy-5-norbornene-2,3-dicarboximide (NHND) was used as an internal standard. Prior to analysis, the lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP). The total content of OH groups in the starting lignin, HMW and LMW was determined to be 2.87, 2.27 and 3.09 mmol/g, respectively. Extraction with ethyl acetate successfully reduced the total content of OH groups in the lignin by 21 %.

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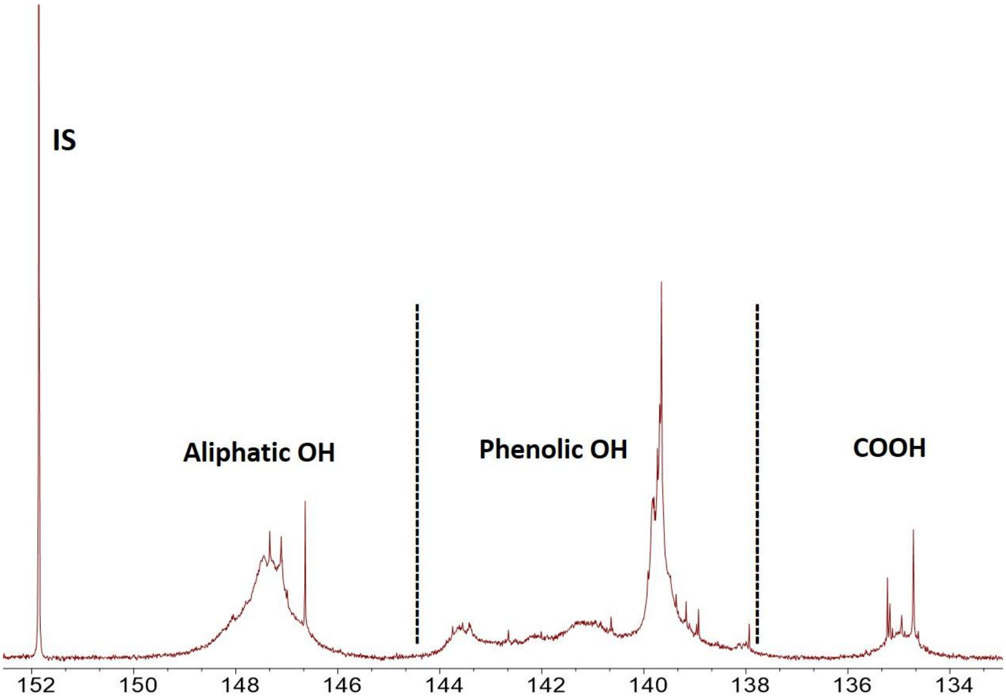

Figure 3: Quantitative 31P-NMR spectra of initial kraft lignin.

The results of the elemental analysis are summarized in Table 3. The elemental analysis showed only a slight change in oxygen content between the original lignin and the HMW lignin fraction. These results indicate that while ethyl acetate dissolves smaller lignin fragments rich in OH functional groups, significant oxygen remains present in the HMW lignin, especially in the form of methoxy end groups, ester and ether bonds.

Table 3: Results of elemental analysis of lignin samples, performed using a vario EL cube analyser (Elementar, Hanau, Germany); the presented values are averages of four measurements.

Sample	**wN (%) ±0.01**	**wC (%) ±0.03**	**wH (%) ±0.06**	**wS (%) ±0.06**	**wO (%) ±0.03**
Initial lignin	0.51	59.80	5.49	2.69	31.35
High molecular weight fraction (HMW)	0.54	60.06	5.46	2.50	31.44
Low molecular weight fraction (LMW)	0.27	63.31	5.93	2.88	27.61

Fire behaviour testing of both the starting lignin and the HMW lignin fraction was conducted at ZAG's facilities using a standard cone calorimeter (ISO 5660-1) at 50 kW/m^2 radiative heat. Approximately 66 grams of each sample were levelled on an aluminium foil tray inside a standard sample holder, with the exposed surface of 10 cm x 10 cm. Both samples ignited almost immediately after exposure and showed significant intumescent behaviour, forming a dense, foam-like structure (Figure 4). The samples showed some expected differences between original and HMW lignin fraction. The HMW lignin fraction lost less mass, released less total heat and smoke and had lower average release rates for both heat and smoke than the original lignin (Table 4). The removal of LMW lignin fraction seems to improve fire behaviour of lignin by up to 20% in some parameters.

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Figure 4: Extracted lignin during exposure on the cone calorimeter

Table 4: Selected parameters of cone calorimeter testing

Parameter	**Starting lignin**	**HMW lignin**
Mass loss %	49%	39%
Total heat release	82,2 MJ/ m^2	57,7 MJ/ m^2
Peak heat release rate	119,4 kW/m^2	122,2 kW/m^2
Average heat release rate	82,2 kW/m^2	69,5 kW/m^2
Total smoke release	438 m^3/m^2	291,0 m^3/m^2
Average SEA	118,5 m^3/kg	97,7 m^3/kg

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3 Acoustically enhanced rubber devulcanization trials

Devulcanization (i.e. reverse process of vulcanization) is a promising method for rubber reclaiming. The aim of devulcanization is breaking the cross-linking bonds, carbon-sulfur (C–S) and sulfur-sulfur (S–S) bonds, in the vulcanized rubber network without breaking the backbone, carbon-carbon (C–C) bonds. Breaking C–C bonds requires a higher energy than C–S and S–S bonds which allows the crosslinking bonds to be selectively targeted but in reality some degree of chain scission as well as cross-linking breakage will occur during devulcanization. On this basis, the best devulcanization method is a process with a high cross-link breakage to chain scission ratio.

Chemical devulcanization methods involve the use of various chemicals to break the crosslinks between rubber chains and prevent the recombination of sulphur linkages. Several chemicals have been identified as effective devulcanizing agents, including sulphides, peroxides, amines, deep eutectic solvents (DES), and ionic liquids [15].

Incorporating ultrasound technology into the devulcanization process aims to significantly enhances the effectiveness of the chemical treatment. Ultrasound waves generate localized elevated temperatures and pressures, creating cavitation bubbles that facilitate the breaking of S–S bonds within the rubber matrix. This work has combined ultrasound with two chemical reagents, deep eutectic solvents and paraffin oil. This method aims to provide an effective means of devulcanisation while minimising its environmental impact. DES, known for their low toxicity and biodegradability, can selectively target and cleave sulphur cross-links at relatively low temperatures, while paraffin oil serves as an effective medium for distributing the ultrasonic energy and chemical agents uniformly throughout the rubber material [16].

The synergy between ultrasound and chemical agents in devulcanization not only improves the speed and efficiency of the process but also helps preserve the physical properties of the reclaimed rubber. This technique aligns with sustainable practices in the rubber industry, offering a practical pathway to reduce waste and promote the circular economy by converting used rubber products into valuable resources [17].

3.1 Preliminary tests using Paraffin oil

The use of paraffin oil (PO) for chemical devulcanization of rubber has been explored previously due to its compatibility with the rubber matrix. Its inert nature ensures that it assists in the devulcanization process without introducing harmful side reactions [17]. The presence of paraffin oil helps in controlling the devulcanization process, allowing for a more selective and controlled breakdown of the S -S cross-links. This ensures that the rubber retains as much of its original properties as possible, which is essential for recycling and reusing the devulcanized rubber. PO has a high boiling point and good heat transfer properties, helping to maintain a consistent temperature throughout the rubber during the process.

To prepare the sample and soften the rubber, 5 g of the rubber crumbs (80 mesh) provided by Genan (Denmark) were soaked in paraffin oil (250 –350 parts per hundred of rubber (phr)) for 2 – 6 h at 70 °C. Once swollen, the rubber (still immersed oil) was ultrasonically treated (500 – 1000 Ws/g rubber). The devulcanization degree was determined after Soxhlet extraction using acetone and toluene according to standard ATSM 6814 [18]. Figure 5 depicts the devulcanization process enhanced by ultrasound application.

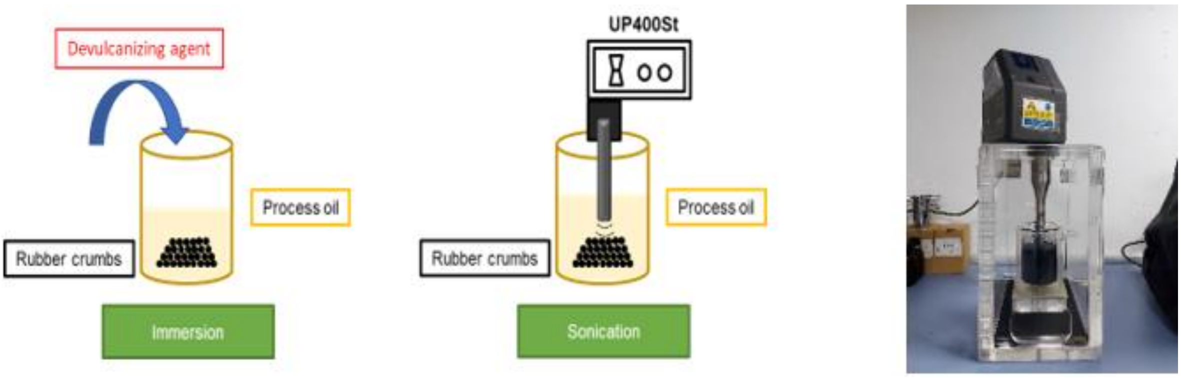

Figure 5: Acoustically-enhanced Rubber devulcanization.

Table 5 summarizes the experimental conditions and main results obtained in the design of experiments (DOE) prepared for studying the effect of the paraffin oil immersion. The variables were parts per hundred of rubber, time and applied acoustic energy (Ws/g). Commercially available devulcanized rubber was used as a control sample. The best conditions for devulcanization of the rubber was 300 phr, 4 hr of immersion and 750 Ws/g. This gave a devulcanisation percentage of 72%. Longer immersion, higher power and greater ratio of PO (350 phr, 6 h of immersion and 1000 Ws/g) gave a slightly lower devulcanisation percentage of 67%. These two best conditions were used for further scaled-up testing, using 50 g of rubber and the UIP1000hdT ultrasound device (Prototype 1).

Table 5: DOE Ultrasound-assisted chemical devulcanization of rubber.

Sample	Paraffin oil [phr]	Immer-sion [hr]	Ac. Energy [Ws/g]	Devulcanization [%]
1	250	2	1000	24.2
2	300	4	750	72.3
3	250	2	500	38.8
4	350	6	500	48.9
5	350	2	500	50.3
6	350	2	1000	2.4
7	250	6	500	63.6
8	350	6	1000	67.2
9	250	6	1000	37.1
Control	0	0	0	75.3

3.2 Preliminary tests using DES (Choline Chloride and Urea)

Deep Eutectic solvents (DESs) can be termed as a new class of solvents that have emerged as potential alternatives to conventional solvents and ionic liquids (IL) in many industrial applications. DES, made from hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), still exhibit similar properties to IL and can be tailored. Moreover, they are non-toxic, biodegradable, cheap and easy to synthesize [19]. It has been widely reported that ammonium-based DESs are applied in the process of desulphurization, with a sulphur removal efficiency of 99.48% from oil. The ammonium-based DESs are effective in reacting with sulfur-sulfur bonds and has a high possibility to act as an effective devulcanizing agent [20].

A green-chemistry approach using Deep Eutectic Solvents (DES) was trailed at UBRIS for a de-vulcanization process with a low environmental footprint. The process involved first synthesizing the DES using choline chloride and urea (molar ratio 1:2) by stirring at 100°C (300 rpm) for up to 45 minutes. For the devulcanisation process the DES/rubber ratio is 20:1. 1 g of vulcanized rubber was subjected to probe sonication for 10 minutes (12 W), followed by bath sonication for 15 minutes at 50°C (40 kHz, 50 W), and final mixing for 5 minutes at 180°C and 1400 rpm. Four rubber crumb sizes were tested 40 mesh (40 M), 80 mesh (80 M), 120 mesh (120 M) and superfine (30 mesh, 30 M).

The devulcanization percentage was determined following the ASTM D6814 test [18]. Horikx, TGA, SEM, ATR-FTIR, and EDX analysis were also carried out on the devulcanized rubbers. Horikx analysis relates the soluble fraction of the devulcanized rubber to the reduction in terms of crosslink density. Horikx theory provides a relationship between the soluble content generated as a result of degradation and the relative reduction of crosslink density caused by crosslink or chain scission [21].

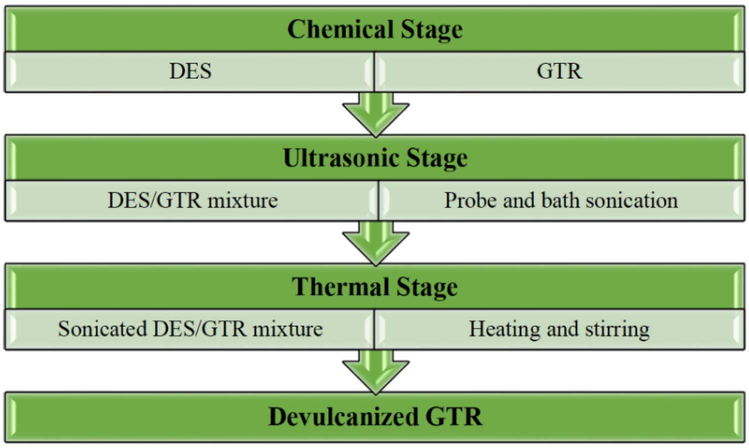

Figure 6: Schematics of the green-chemistry devulcanization process.

Table 8 shows the results of the devulcanization process. The 120 M samples have the smallest crumb dimensions and the highest devulcanization percentage (58.1%). The morphology of the devulcanized rubber was investigated using the SEM technique. The SEM images in Figure 7 showed that the devulcanized rubber's morphology is similar to plasticized polymers with a rough surface finish; the roughness increases with the percentage of devulcanization.

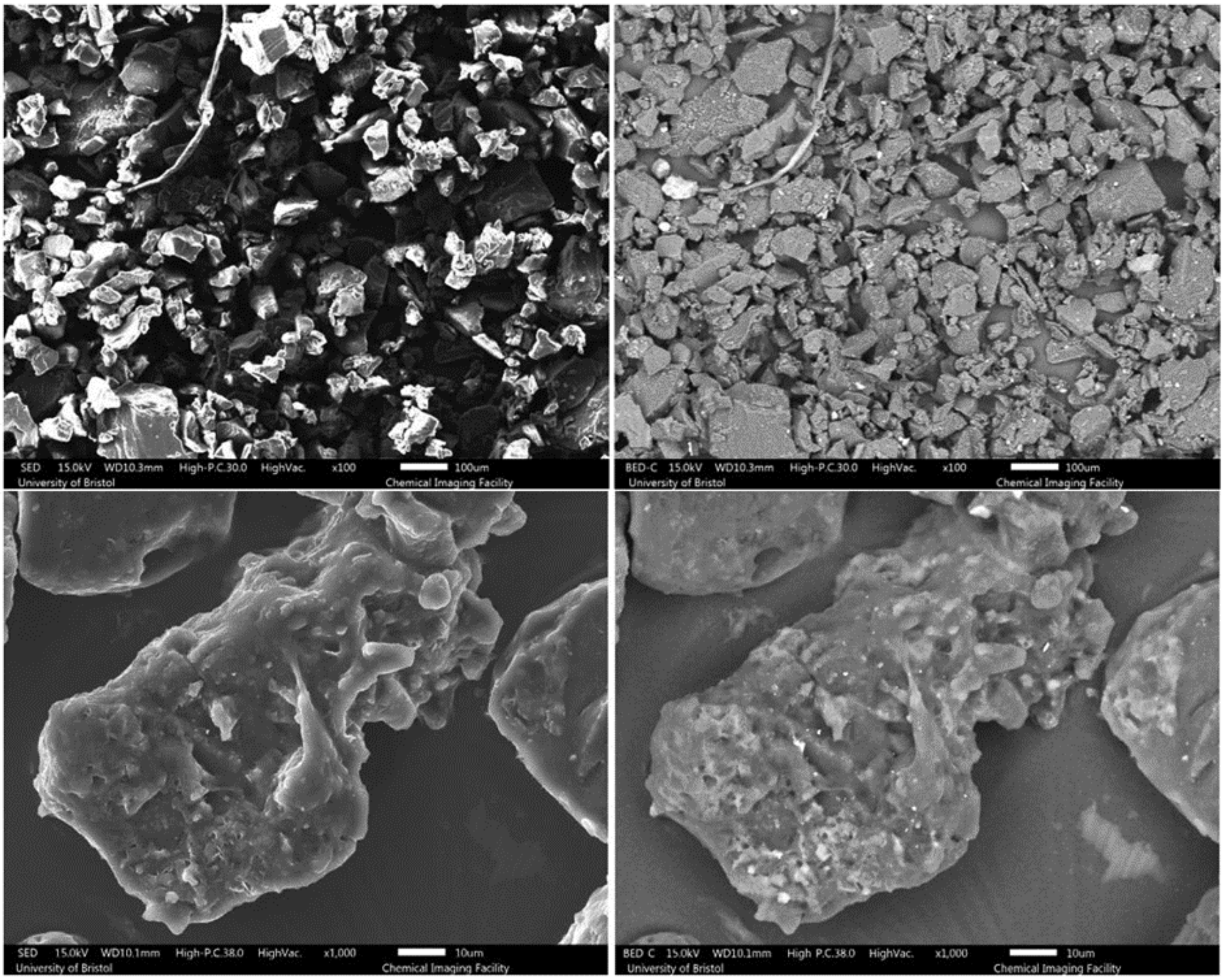

Figure 7. SEM images of the 120 Mesh samples, left column: SED and right column: BED

FTIR analysis shows that mono-, di-, and polysulfide bonds are broken during devulcanization, without breaking the C-C bonds of the polymer backbone. The band between 669 and 938 cm-1 shows the presence of the C-S bonds. All the spectra show a slight decrease in intensity when comparing GTR and the devulcanized rubber. This indicates that the mono, di, and polysulfide bonds were broken, and selective crosslink scission occurred during the devulcanization. This observation supports the successful devulcanization of the GTR samples [19] [20].

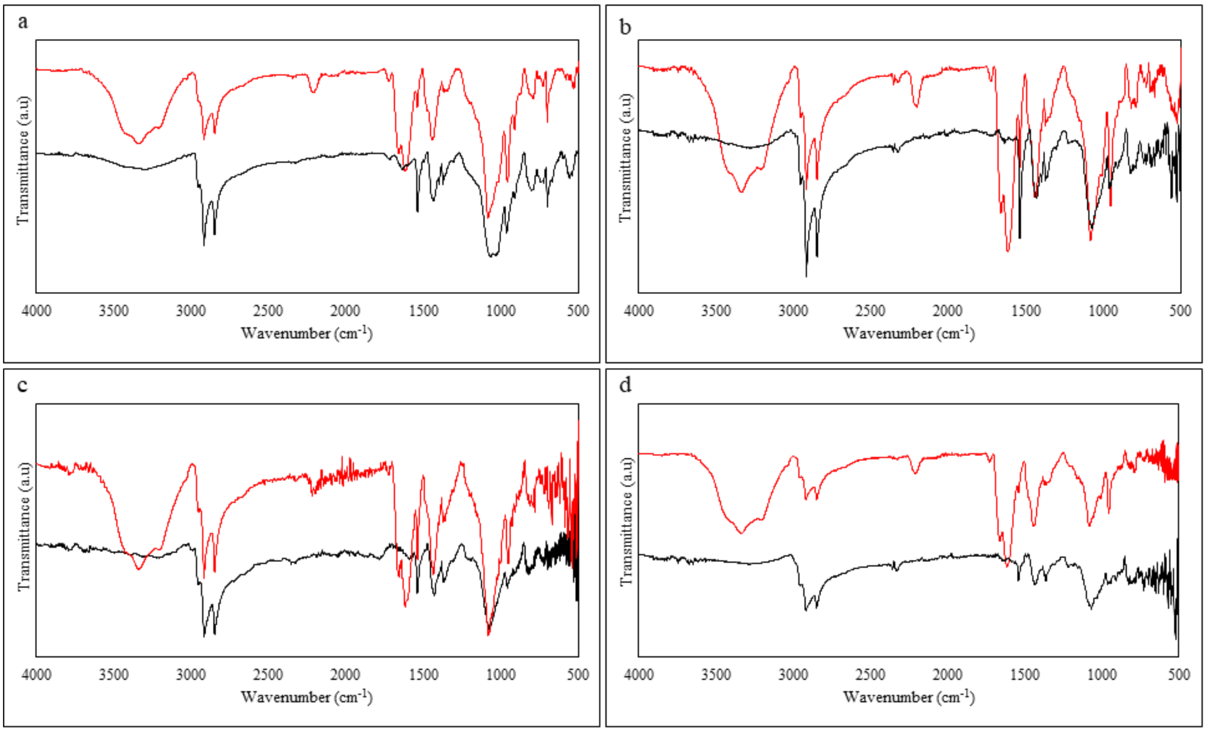

Figure 8. ATR-FTIR spectra of a) Super fine sample, b) 40 Mesh sample, c) 80 Mesh sample, d) 120 Mesh sample, the black line belongs to untreated, and the red line belongs to the devulcanized rubber

The EDX results in Table 6 and Table 7 show no evidence of backbone scission during devulcanization and the presence of nitrogen and chlorine. The nitrogen and chlorine present in the devulcanized samples are evidence that the DES reagents have formed chemical bonds with the polymer.

Table 6. Elemental analysis of the untreated GTR (At.%)

	C	**O**	**S**	**Si**	**Zn**
Superfine S.F$_u$	91.8	6.1	0.6	0.2	0.8
40 M$_u$	93.4	4.8	0.8	0.3	0.4
80 M$_u$	90.7	7.3	0.5	0.8	0.3
120 M$_u$	93	5.4	0.5	0.5	0.3

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Table 7. Elemental analysis of the devulcanized GTR (At.%)

	C	O	S	Si	Zn	N	Cl
$S.F_{dv}$	90.4	5.9	0.8	0.4	0.4	1.0	0.3
$40\ M_{dv}$	85.5	8.1	0.9	0.7	0.4	3.1	0.7
$80\ M_{dv}$	86.9	7.1	0.8	1.2	0.4	2.4	0.6
$120\ M_{dv}$	85.9	6.5	0.9	1.2	0.4	3.6	0.6

TGA shows that the devulcanized 80 and 120M have a larger mass loss than the other devulcanized rubbers. Figure 9 shows four different thermal regions attributed to volatilization, degradation of isoprene, degradation of styrene-butadiene and char residue. Within the first region (from 100 to 250 °C), low molecular weight materials, any absorbed moisture, oils, and waxes are degraded. In the following region, natural rubber (the major constituent of GTR) degrades at approximately 250 to 400 °C. In the next region, styrene-butadiene, which has higher thermal stability than natural rubber and is another major constituent of the GTR, is degraded at a temperature range of 400 to 480 °C. The char residue after 500 °C is attributed to carbon black, silica, and degraded natural rubber. The increased mass loss in 80 and 120M is due to the removal of the crosslinks leading to polymer chains becoming more susceptible to the introduced heat and consequently, increased thermal degradation.

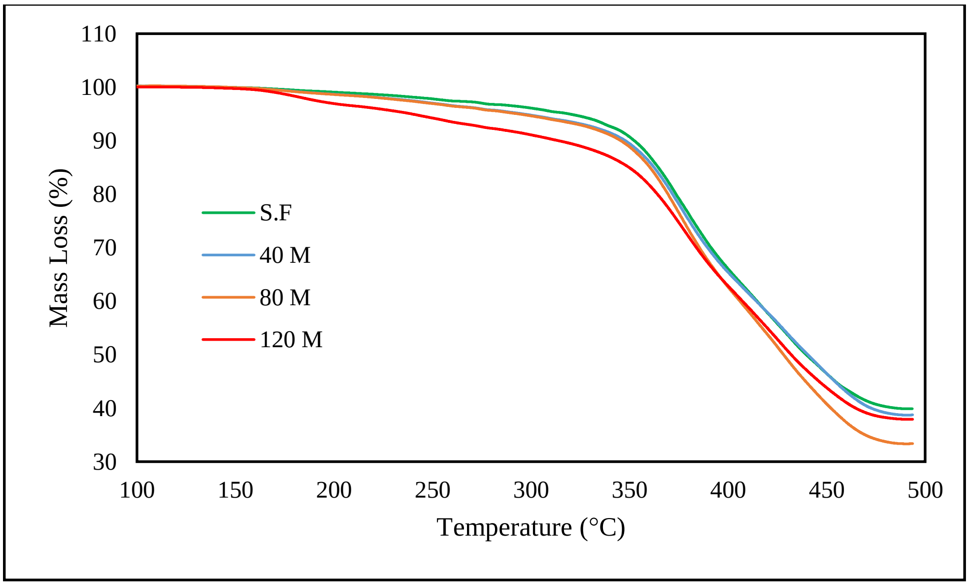

Figure 9. TGA curves of the devulcanized samples

The chemical devulcanization process of the rubber has been studied further using the previously mentioned approaches but increasing the scale to 50 and 100 g of vulcanized rubber. To reach this goal, the trials will be conducted at IRIS facilities using their ultrasonic devices (UIP1000hDT) to provide a higher ultrasonic power to maintain the devulcanization degree reached at laboratory scale.

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Table 8: Results of the devulcanization carried out using the green chemistry approach.

Rubber sample	Swelling degree Q (%)	Soluble fraction S (%)	%Dev.
S.F$_u$	49.77	15	-
40 M$_u$	50.41	11	-
80 M$_u$	55.09	10.8	-
120 M$_u$	50.12	8.2	-
S.F$_{dv}$	56.71	3.07	29.3
40 M$_{dv}$	57.68	3.45	42.1
80 M$_{dv}$	67.48	3.00	51.48
120 M$_{dv}$	75.66	4.09	58.13

3.3 Upscaled chemical devulcanization using Prototype 1 (800 W).

Based on data from IRIS and UBRIS regarding the chemical devulcanization of rubber using paraffin oil and deep eutectic solvents (DES), a series of trials were planned and conducted at IRIS. The objective was to evaluate the application of ultrasound on a larger quantity of rubber (100g) using ultrasound prototype 1 (800 W). For these trials, new samples were requested from Genan (Denmark), featuring larger particle sizes ranging from 1.4 to 3.0 mm (Medium) and 3.0 to 7.0 mm (Mega Coarse). This adjustment was made in response to unsatisfactory compounding test results obtained with the previously used fine particle size (80 mesh = 0.17 mm). This is detailed in section 4.1.

The primary goal was to optimize the solvent-to-solid ratio to minimize solvent consumption (paraffin oil, DES) while maintaining ultrasound efficacy to ensure a homogeneous mixture during swelling and sonication (Figure 10). These tests were carried out using the ground tyre rubber (GTR) medium size (1.4 – 3.0 mm).

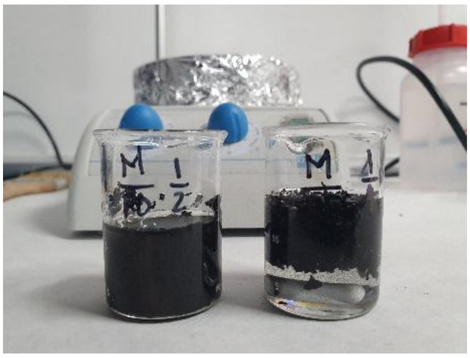

Figure 10: Optimization of the solvent to solid ratio.

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The optimization made possible a reduction of solvent in both cases. Using a larger crumb size in the mixture allowed for a significant reduction in solvent usage required for embedding. This is attributed to the decreased surface area to volume ratio of larger crumbs, which reduces the amount of solvent needed to adequately coat and integrate the mixture. Consequently, the absorption capacity of the mixture was optimized, leading to more efficient solvent utilization and improved overall process efficiency. This adjustment not only minimized solvent consumption but also contributed to a more sustainable and cost-effective manufacturing process. The new ratios were: 2.5 for PO and 4.0 for DES, saving in each case 16.6% and 80% solvent usage, respectively.

Figure 11 depicts Prototype 1, developed and configured by IRIS for the chemical devulcanization of medium-sized GTR using paraffin oil (PO) on the left and deep eutectic solvents (DES) on the right. In both experimental setups, additional accessories were employed to address specific challenges. When using PO, a low PO/GTR ratio necessitated an additional cooling system to prevent excessive heating of the sample. Conversely, when using DES, the high viscosity of the solvent required an auxiliary stirrer to facilitate the flow of the mixture during sonication and no cooling system was necessary.

Figure 11: Ultrasound Prototype 1 for Chemical Devulcanization of Rubber using PO (left) and DES (right).

Table 9 summarizes the experimental conditions evaluated using Prototype 1. To verify the effect of ultrasound application, separate control tests were conducted without ultrasound enhancement, utilizing only stirring.

Table 9: Experimental conditions for the chemical devulcanization of GTR.

Test	Solvent	GTR size (mm)	Solvent: Solid ratio	Enhancement
1	Paraffin oil	1.4 – 3.0	2.5	US
2	Paraffin oil	1.4 – 3.0	2.5	Stirring
3	DES	1.4 – 3.0	4.0	US +Stirring
4	DES	1.4 – 3.0	4.0	Stirring
5	Paraffin oil	3.0 – 7.0	2.5	US +Stirring
6	DES	3.0 – 7.0	4.0	US +Stirring

These samples have been produced on sufficient scale (100g) to enable compounding trials to be the determination of the effectiveness of the devulcanisation process. As outlined at the beginning of this section, incorporating ultrasound technology into the devulcanization process aims to improve the effectiveness of chemical treatments by generating localized high temperatures and pressures and creating cavitation bubbles that break sulfur-sulfur bonds in the rubber matrix.

Initial compounding runs have been carried out using the devulcanised rubber produced from tests 1 and 3 and Table 9. These tests used a particle size of 1.4-3.0 mm. The initial compounded materials did not bind together well, some binding can be seen in Figure 12 but it is not sufficient to form a coherent material. It is anticipated that this is because the particle size is too small. This is discussed in greater detail in Section 4.1 but in summary, work with commercially available devulcanised rubber has found that if the crumb size is too small the particles feel insufficient shear forces during mixing and therefore are not sufficiently compounded. To overcome this devulcanisation tests have been repeated on a larger crumb size, tests 5 and 6 in Table 9. These samples will be processed in August 2024 and the results will be included in Deliverable 6.1.

Figure 12: DES and ultrasound treated devulcanised rubber after compounding.

The samples will be compounded and pressed into test panels and their mechanical properties assessed to determine how successful the devulcanisation process was and therefore how the rubber has bound together during its reprocessing. The devulcanized samples (1 – 6 in Table 9) were shipped to NCC for compounding tests which will determine the success of the ultrasound assistance.

3.4 Upscaled chemical devulcanization using Prototype 2 (2000 W).

The experimental trials using Prototype 2 will be conducted at the IRIS facilities, employing the UIP2000hdT ultrasonic device. This device will be adapted to the most promising conditions identified with Prototype 1, with an increased sample load from 100 g to either 250 g or 500 g, depending on the behaviour of the mixture during sonication. The newly devulcanized samples will be sent to NCC for compounding tests. Detailed information regarding the use of Prototype 2 in rubber devulcanization will be provided in Deliverable 6.1.

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4 Formulation trials - Compounding

4.1 Material selection trials

Engagement with the supply chain was undertaken to access a robust supply of material for use in the rubber formulation trials. To minimise the risk of supply chain disruption multiple sources of devulcanised rubber were procured. Material from three suppliers of devulcanised rubber was received, the companies were J Allcock & Sons (UK), Rubber Conversion (Italy) and Tyromer (Canada). It was decided that the initial trials would proceed using the J Allcock & Sons material to minimise transportation emissions as the manufacturing was to be done in the UK. The J Allcock & Sons devulcanised rubber was supplied in a crumb format with a crumb size of 40 mesh.

All rubber received went through a quality assurance process of thermal and chemical testing. This included dynamic scanning calorimetry (DSC), thermogravimetric analysis (TGA) and infrared spectroscopy (IR). This will enable an assessment of batch consistency as the project progresses to larger scale production in work package 6.

4.1.1 Initial rubber compounding

Reprocessing of devulcanised rubber has been demonstrated both in the literature and commercially however it is usually reincorporated as a filler within a new component rather than as the matrix material itself [22]. Initial trials were therefore required to understand how the devulcanised rubber could best be processed as a matrix material.

The rubber crumb was processed alone within an internal mixer to confirm the devulcanisation process was sufficient to allow the rubber to be melted and compounded into a single homogeneous material. Compounds were produced using an a HAAKE Rheomix OS/3000 internal mixer with a 78 cm^3 chamber volume and Banbury style rotors. The initial temperature was set at 60 °C and the rotor speed was 60 rpm. Following compounding the material was passed through a two-roll mill twelve times with a nip point of 1 mm. These parameters were used as standard in subsequent mixes.

Initial trials demonstrated that the devulcanised rubber crumb did not melt during compounding within the internal mixer. It remained as a crumb as shown in Figure 13. Out of the mixer, the sample was very granular and disintegrated when removed from the mixing chamber. More forcing conditions were attempted, through increasing the mixer temperature, though again this did not produce a cohesive material. This suggested that either the devulcanisation process had not broken sufficient cross-linking bonds to allow for the material to melt and reform or that the rubber particle size was too small to be sufficiently masticated by the rotors of the internal mixer. If the latter, then the rubber particles would not experience any shear forces from the rotors and the rubber crumb would simply be moved around the mixer chamber rather than formed into one single material.

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Figure 13: Crumb material remaining on the rotors of the internal mixer after the compounding process. Individual particles of rubber can still be seen.

A proportion of virgin natural rubber was added to the blend to act as a binder to improve the cohesion of the material. This did improve the cohesion to some degree. Figure 14 shows the devulcanised rubber blend with 10 parts per hundred (phr) of natural rubber at the top and 20 phr below. The sample with 10 phr natural rubber still did not fully bind together and could not be removed from the mixer without breaking apart. The 20 phr natural rubber sample did bind together however individual particles could still be seen in the final material.

Figure 14: Top, devulcanised rubber with 10phr virgin natural rubber after compounding. Bottom, devulcanised rubber with 20phr virgin natural rubber after compounding.

4.1.2 Lignin inclusion

Lignin was incorporated using the same equipment as outlined above. Compounding experiments were required to establish the level of lignin filler which could be incorporated into the devulcanised-natural rubber blend. Filler loading levels of 10 and 30 wt% were tested. Once compounded the materials were pressed into 100 x 100 x 1 mm sheets. These are shown in Figure 15. On the left the rubber blend with 10 wt% lignin filler is shown. The material had a reasonable surface finish although teared easily when removed from the mould.

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On the right is the rubber blend with 30wt% lignin filler. The surface finish was very poor and the material readily broke apart when handled. The 30wt% material was too poorly performing to be able to conduct mechanical testing on the material and was discounted from further evaluation.

Figure 15: Left, Rubber blend with 10wt% lignin filler. Right, Rubber blend with 30wt% lignin filler.

4.1.3 Curing behaviour

The cure properties of the compounds were measured by moving die rheometry (MDR). During the MDR test the compound is held at elevated temperature and the torque required to rotate the die is monitored. As the curing reaction occurs, crosslinks form in the material and the viscosity of the material increases. This is measured as an increase in the torque reading. The testing was done in accordance with ASTM D 5289 [18] and the temperature selected was 160 °C.

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Table 10: Cure properties of the compounds

	NCC-GL-P-001 **Devulcanised rubber (DR) only**	**NCC-GL-P-002** **100 phr DR 20 phr NR 0wt% lignin**	**NCC-GL-P-003** **100 phr DR 10 phr NR 10wt% lignin**	**NCC-GL-P-004** **100 phr DR 20 phr NR 30wt% lignin**
Minimum torque (ML) dNm	11.98	3.93	6.18	2.75
Maximum torque (MH) dNm	24.11	16.23	14.67	5.07
Time for ML to double (TS2) min	0.63	0.55	0.56	24.27
Time to 90 % peak cure (T90) min	3.85	4.62	10.23	25.37

From the data in Table 10 there are clear trends. The devulcanised rubber still had residual cure activity, as shown by the significant difference between the minimum torque (ML) and the maximum torque (MH). However as the percentage of lignin is increased from 0 wt% (NCC-GL-P-002) to 30 wt% (NCC-GL-P-004) the MH decreases. This suggests a reduction in the cross-link density as the loading of lignin is increased. The time to 90 % peak cure (T90), is also extended in the 10 wt% and 30 wt% lignin filled samples compared to the unfilled. It is apparent that the cure reaction is severely impacted at 30wt% lignin, with only limited torque increase in the MH and a T90 that is extended further than that of the 10 wt% filled sample. The MDR traces are shown in Figure 16, this shows that the torque response decreases significantly with the addition of lignin. It is suspected that the functional groups on the surface of the lignin are interacting with the thiol groups in the rubber and preventing the sulfur-sulfur cross-linking bonds from forming.

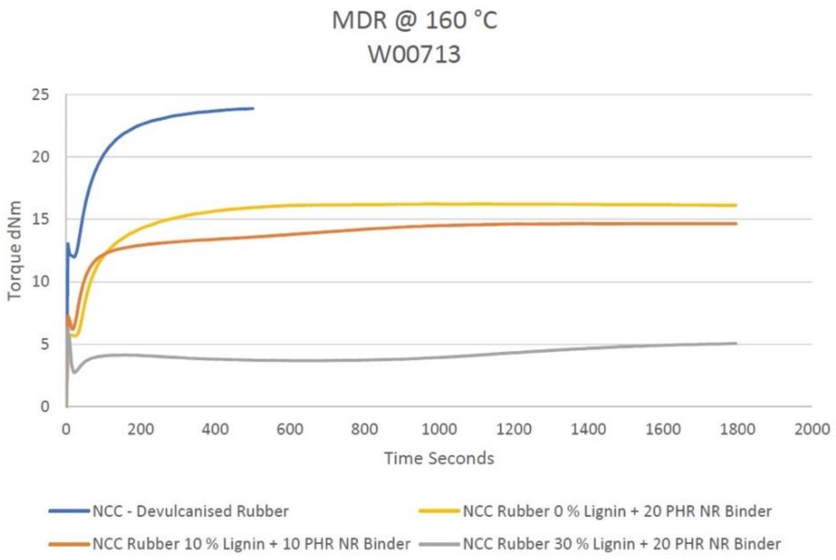

Figure 16. MDR plot for the pure rubber, and compounds produced.

To overcome the reduction in curing behaviour, additional curatives were included into the blend during the compounding phase. The solid line in Figure 17 shows the torque response of a compound with 30 wt% lignin and additional curatives compared to the grey dashed line of the 30 wt% sample without curatives. From this point forward additional curatives were added as standard to overcome the impact of the lignin filler on the curing response.

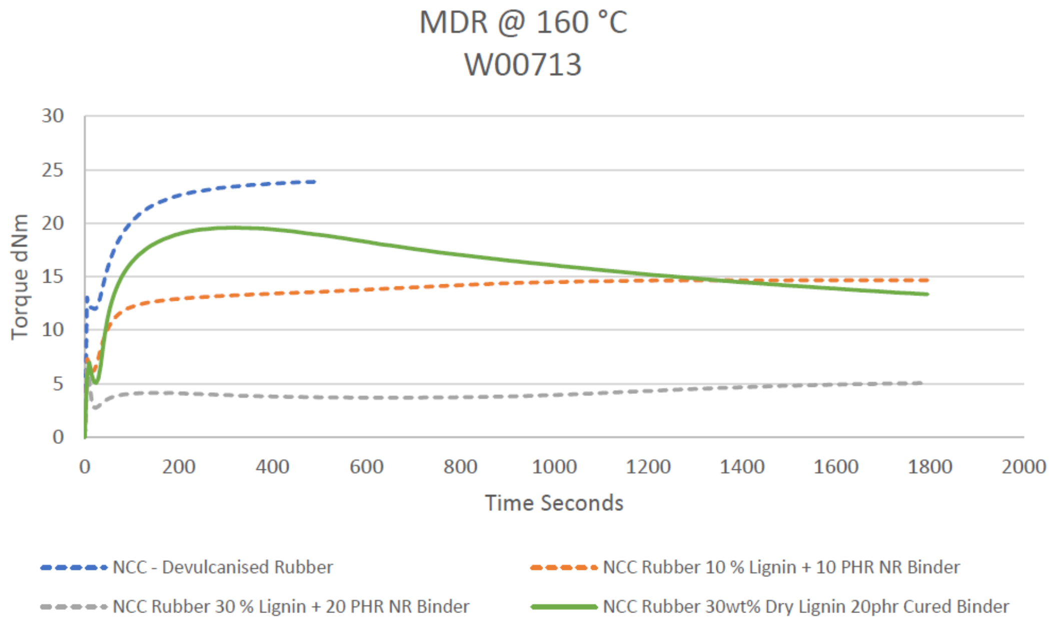

Figure 17: MDR plot for the rubber compounds and the effect of additional curatives.

4.1.4 Dispersion

A dispersion assessment was undertaken to assess how uniformly the lignin had been dispersed and how well the devulcanised rubber had been masticated. Sections of the rubber panel were imaged using a scanning electron microscopy (SEM).

Roughness was recorded using two figures, the Roughness Average (SRa) and the Average Maximum Profile Peak Height (SRpm). SRa is the arithmetic average of height deviations from the mean line. This is useful as a basic measure of roughness, but a very regularly textured surface would record a low value of SRa. Therefore, SRpm is also recorded, this is produced by sectioning the surface into five even sections and recording the largest peak in each section. This provides more information about the maximum deviations from the mean on the surface.

The values generated, and the images recorded are shown in Table 11 and Figure 18. The rubber matrix when cut does not show smooth, uniform surfaces. Rather, they appear to have pieces of the crumb visible, indicating that the particles have not been totally masticated in the mixing process which is leading to these irregular features. Individual rubber particles can be seen in the optical images in Figure 18. The poor dispersion appeared to increase with increasing lignin filler loading.

Table 11. Surface Roughness of Bio-Rubber Samples

	NCC-GL-P-002 **100 phr DR** **20 phr NR** **0wt% lignin**	**NCC-GL-P-003** **100 phr DR** **10 phr NR** **10wt% lignin**	**NCC-GL-P-004** **100 phr DR** **20 phr NR** **30wt% lignin**
Roughness Average (SRa) µm	1.27	1.74	4.06
Average Maximum Profile Peak Height (SRpm) µm	3.73	5.55	11.10

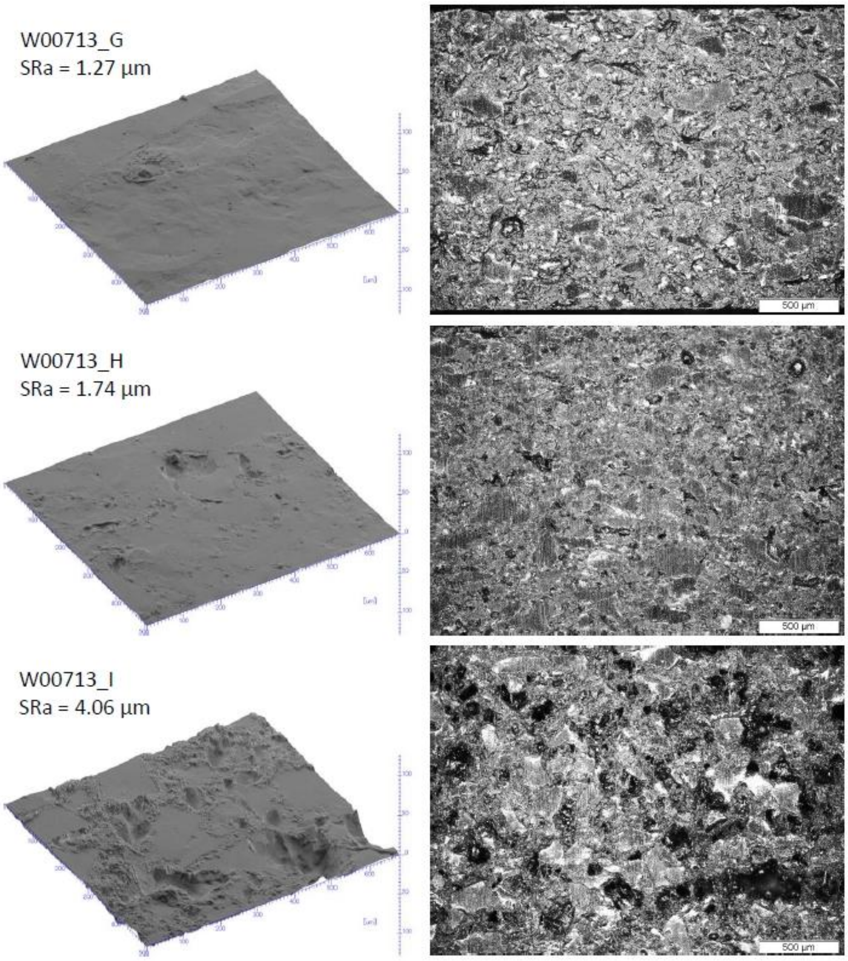

Figure 18. Dispersion images, SEM (Left) and optical microscope (Right). Large particles of devulcanised rubber that have not been broken down can be seen in the optical images.

It was concluded that the rubber crumb particle size was too small to feel significant shear force when in the internal mixer as it was smaller than the gap between the rotor and the mixer wall. This meant that the rubber was not sufficiently masticated and hence remained as particles as shown by the SEM images in Figure 18. The rubber crumb was behaving like a filler rather than a matrix material. This, combined with the lignin powder, meant the natural rubber binder was the only matrix material encapsulating both the devulcanised rubber crumb and the lignin. As such poor material handleability was seen.

4.2 Solid devulcanised material

Following the conclusions from the SEM analysis another supply of devulcanised rubber was sourced from Tyromer [8]. This was a solid material (not in a crumb form) which could be fed into the internal mixer in strips. Switching to this material provided a step change improvement in the processability. Figure 19 shows the new devulcanised rubber material blended with curatives only (no natural rubber) and pressed into a panel. This improved processability allowed a set of experiments to be designed to assess the impact of lignin and natural rubber addition on the mechanical properties of the compounds. The compounds produced are shown in Table 12.

Figure 19: Panel of the solid devulcanised material.

Table 12: Compounds produced to assess impact of lignin and natural rubber.

Compound	Lignin (wt%)	Natural rubber (phr)
NCC_GL_P_009	0	0
NCC_GL_P_010	10	0
NCC_GL_P_012	20	0
NCC_GL_P_011	30	0
NCC_GL_P_013	10	20
NCC_GL_P_014	20	20

Tensile testing on the rubber panels followed the standard BS ISO 37 [23]. The results of the tensile tests are shown in Figure 20 and Figure 21. It is apparent that the inclusion of lignin has a detrimental effect on the break stress of the material. This suggests that the lignin filler has a low interaction with the rubber, it is not binding strongly to the rubber and providing a reinforcing effect but instead is providing opportunities for stress build up and crack propagation. A similar pattern is seen for the break stress; however the lignin only has an impact above 10 wt% as there is no decrease in break strain between 0 and 10 wt% lignin.

The addition of natural rubber to the blend increases the break strain of the material at 10 wt% lignin loading but appears to have no impact at 20 wt% loading level. Whereas the break strain increases by 57% when

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natural rubber is included for both 10 and 20 wt% lignin samples. From this it was concluded that the natural rubber was important within the blend to improve the mechanical performance of the material. However as the stiffness (Figure 22) and hardness (Figure 23) were decreased when incorporating the natural rubber, there is a limit to the level of natural rubber that could be included. This hardness and stiffness decrease is due to the natural rubber being a softer material compared to the devulcanised rubber (mainly synthetic rubbers) and the dilution of fillers within the material (the devulcanised rubber is loaded with 30wt% carbon black).

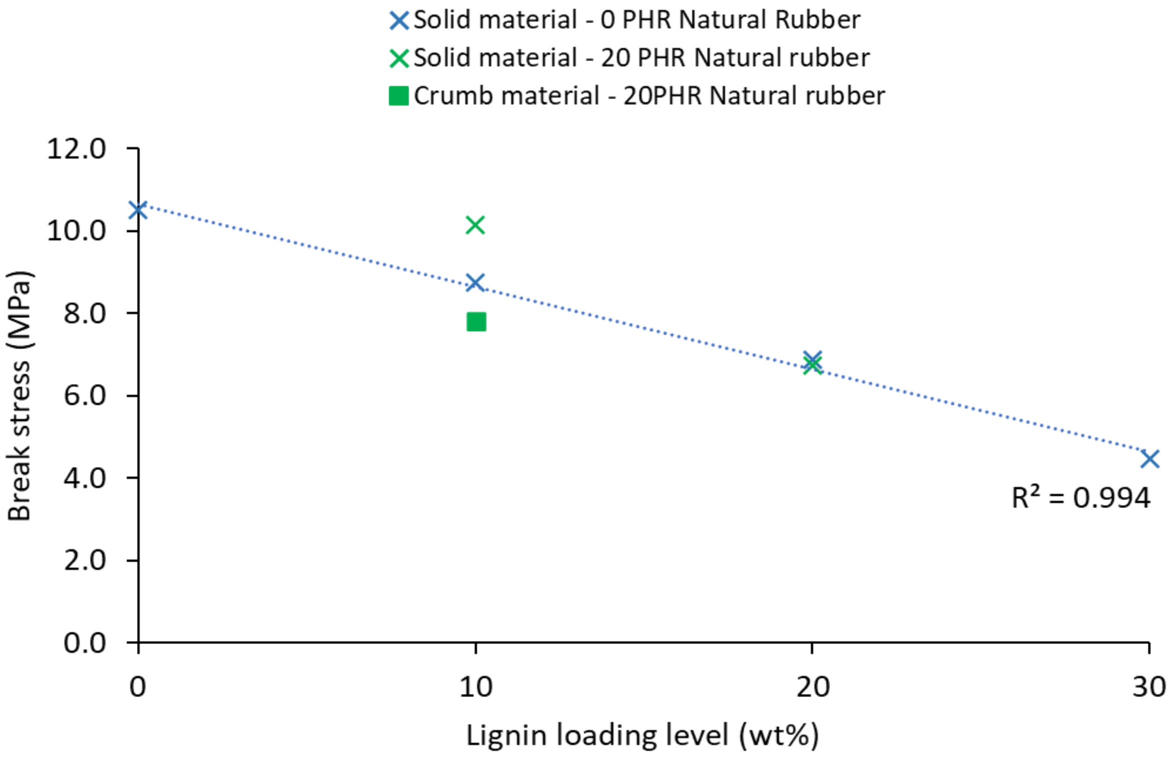

Figure 20: Break stress vs lignin loading level.

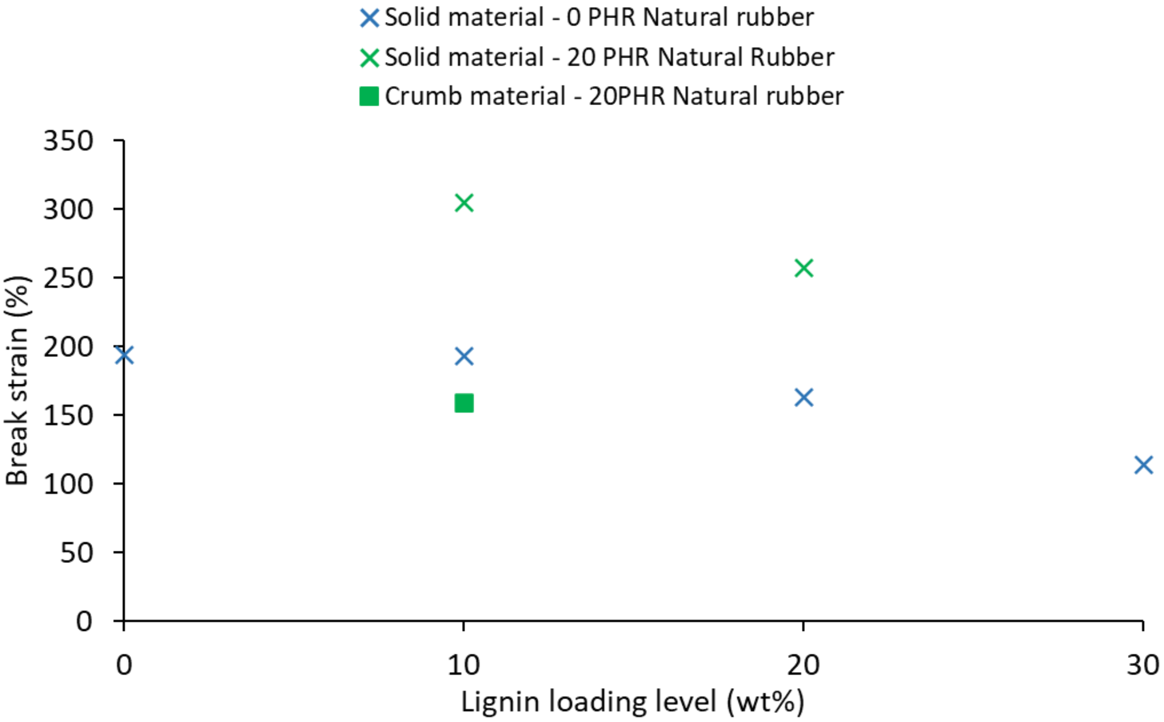

Figure 21: Break strain vs lignin loading level.

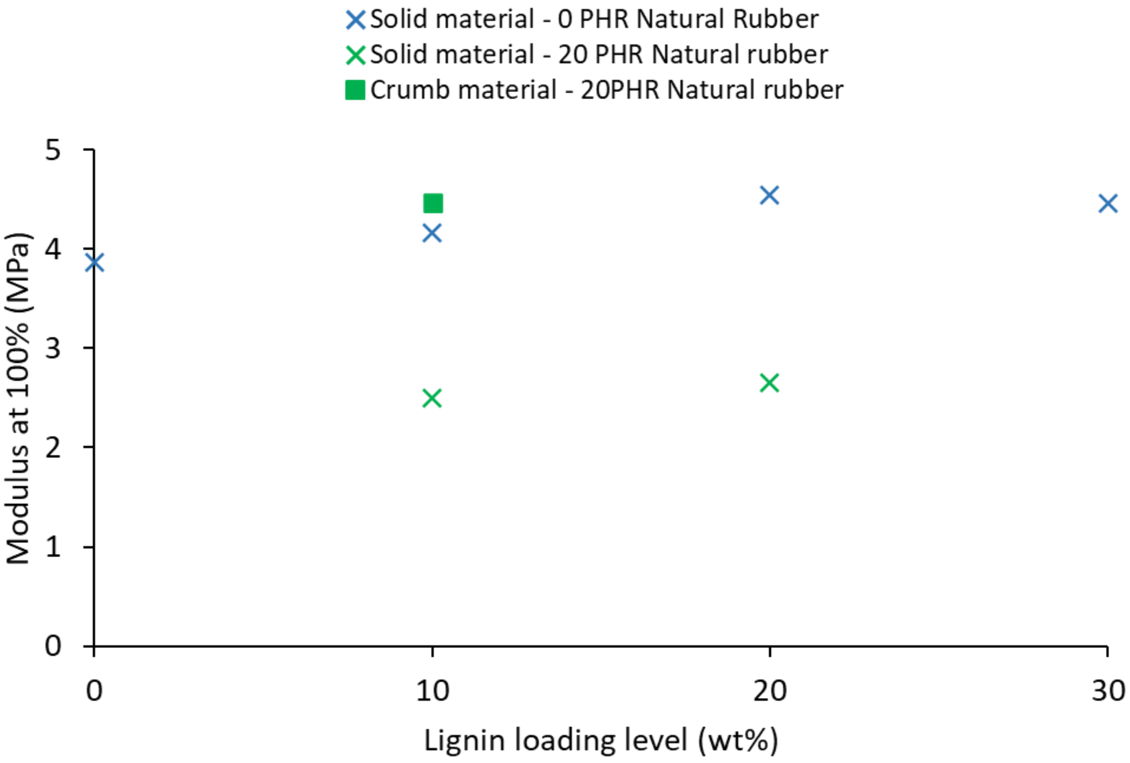

Figure 22: Modulus at 100% elongation vs lignin loading level.

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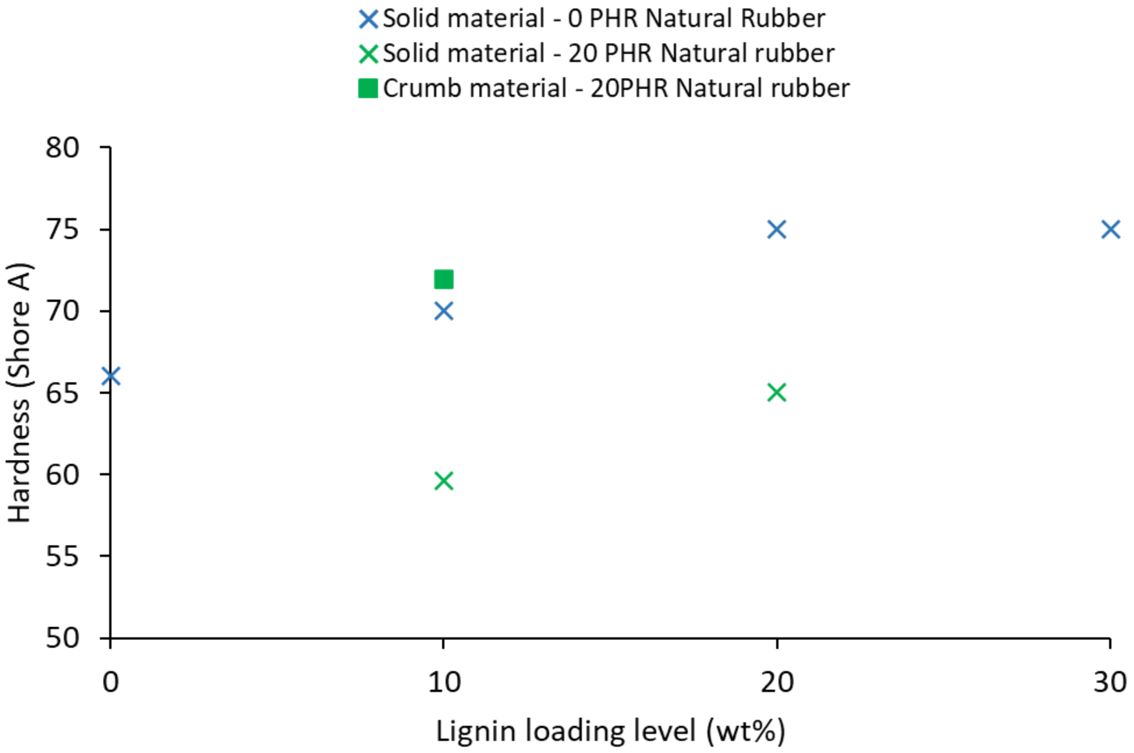

Figure 23: Hardness (Shore A) vs lignin loading level.

These results demonstrated that with the addition of lignin and natural rubber the devulcanised rubber could be used as the matrix material within the formulation rather than just as a filler. These positive results allowed the project to move on to the next stage of the process which was to increase the scale of production.

4.3 Larger scale processing

The compounding trials described above used an internal mixer with a batch size of 60g. To enable full characterisation of the material larger batch sizes were required. Scaling up polymer compounding processes can be challenging as the shear force and temperature profile during processing can vary. For an extrusion process, this is often because the shear heating and the rate of thermal loss changes between different extruder sizes. This was factored into the decision to process this material using an internal mixer instead of an extruder. The scale up using an internal mixer is often less challenging due to their reduced complexity relative to extruders.

To minimise the risk, the scale up will be completed in two steps. Several 1.2Kg batches have been produced and their properties assessed. Once the process is optimised for 1.2Kg batches, a second scale up will be undertaken with 10-25Kg batch sizes. This will be completed in Task 6.1.

The 1.2Kg batches were produced using a Banbury 1.6L laboratory internal mixer. The processing steps were kept identical to the 60g batches. The initial temperature was set at 60 °C and the rotor speed was 60 rpm. Following compounding the material was passed through a two-roll mill twelve times with a nip point of 1mm. These parameters were used as standard in subsequent mixes. No additional processing challenges were identified between the 60 g and 1.2 Kg batches.

From the 60g results, two candidates were selected for larger scale compounding. Both contained 20phr natural rubber, one with 10wt% lignin and one with 20wt% lignin. Table 13 compares the mechanical results between the 60g batches and the 1.2 Kg batches. There is a slight improvement in the break stress and break strain of the 1.2 Kg batches and a slight reduction in the modulus and hardness. A new batch of devulcanised rubber was used for the 1.2Kg trials. It was speculated that the older devulcanised rubber used for the 60g trials had begun curing over time and therefore its stiffness has increased. A shelf-life assessment is ongoing to test this theory. The results of this will be reported in Deliverable 6.2.

Table 13: Comparison between mechanical results of 60 g and 1.2 Kg batch sizes

Property	**60 g batch**		**1.2 Kg**	
	10 wt% lignin	**20 wt% lignin**	**10 wt% lignin**	**20 wt% lignin**
Break stress (MPa)	10.16	6.74	9.66	7.70
Break strain (%)	305	257	330	311
Modulus at 100% (MPa)	2.50	2.65	2.12	2.35
Hardness	60	65	56	62

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5 Formulation trials - Compression moulding

Once compounded the material must be shaped into its final geometry. This is done here by compression moulding. Heat and pressure are applied to the material to form it into shape and cure it in place. It is at this point that the crosslinking bonds broken during the devulcanisation process are reformed and the rubber panel holds its final shape.

5.1 Processing conditions

An 1100 tonne hydraulic press (PEI) at the NCC was used for the rubber composite compression moulding.

Part width = 365 mm

Part length = 335 mm

Part thickness = 2.9-3.1 mm

Curing temperature = 160 °C

Dwell time = 10 minutes

To inform the optimised processing conditions the curing results from the MDR testing outlined in section 4.1.3 were used. A curing time of T90 + 5 minutes was selected to ensure full curing without exposing the material to elevated temperature for longer than required. This is the time to reach 90% of the maximum torque plus a further five minutes. The PEI press used at the NCC is shown in Figure 24.

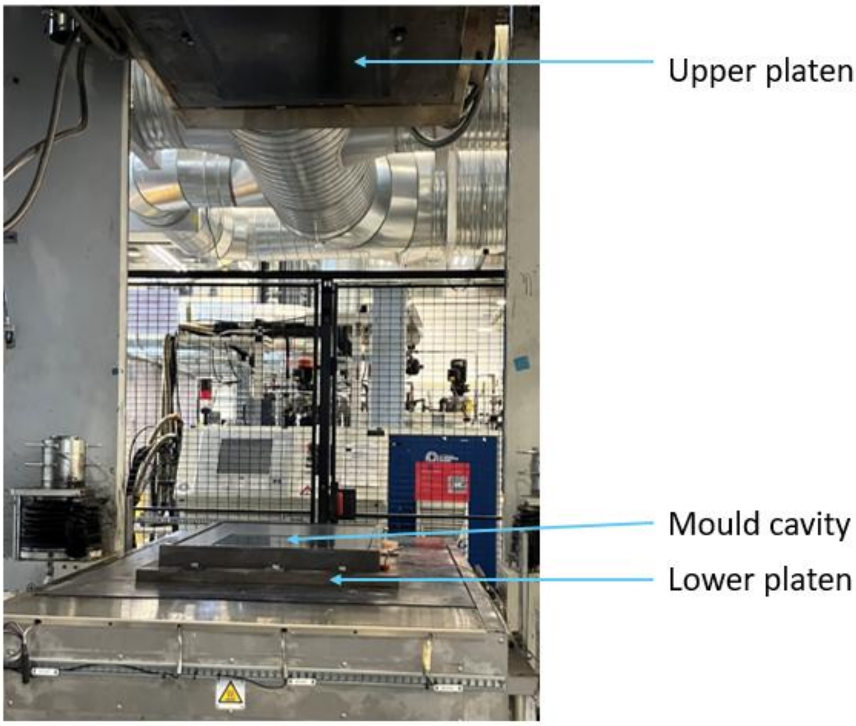

Figure 24: PEI pressed used at NCC for rubber compression moulding.

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5.2 Pressing trials

Two panels of each material type (10 wt% lignin and 20 wt% lignin) were pressed using the parameters described above. The rubber blank was loaded into the mould cavity (Figure 25, left) then pressed and cured into a single rubber panel (Figure 25, right). The parts were left to cool in the mould while still under pressure. Any excess flash material was cut away by hand.

Figure 25: Left, rubber blank loaded into mould cavity before pressing. Right, rubber panel after pressing.

The compression moulding trials proceeded very successfully. As can be seen in Figure 26 and Figure 27 the rubber panels produced had a sharp edge and a good surface finish. The panels are undergoing further testing to assess mechanical performance, fire resistance and acoustic dampening at ISQ and ZAG. The results will be disseminated in Deliverable 3.5.

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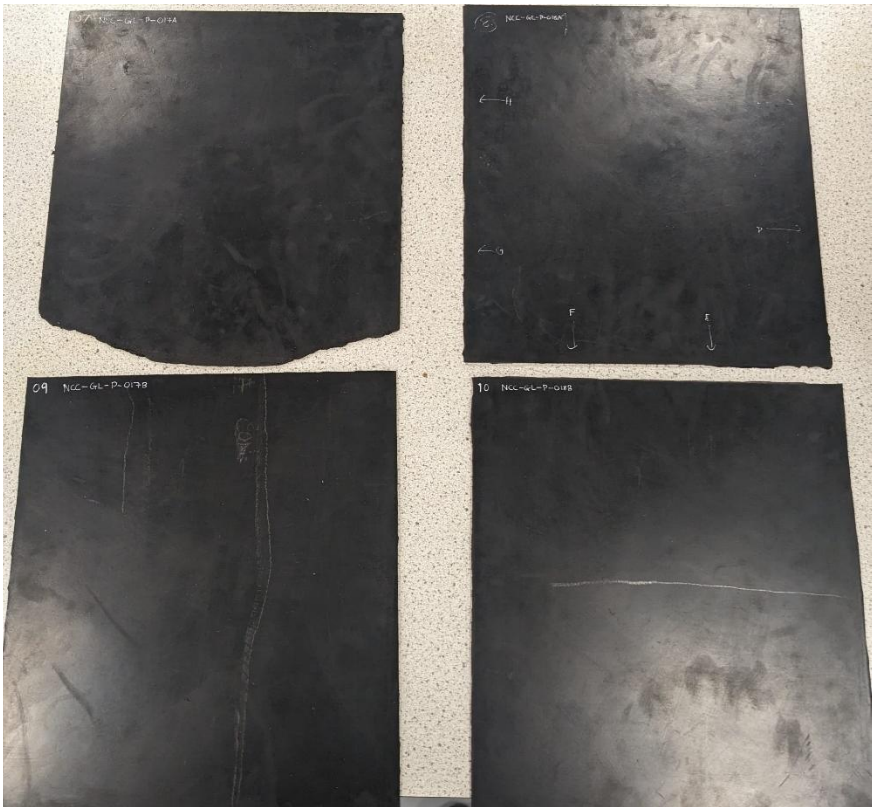

Figure 26: Panels after compression moulding. Left, 10 wt% lignin filled. Right, 20 wt% lignin filled.

Figure 27: Edge of rubber panel.

It was found that cooling within the mould, while still under pressure, gave the best surface finish. The material could be removed while still at elevated temperature. This would minimise the cycle time to produce a part as the mould could stay at elevated temperature rather than cooling and then reheating ready for the next part. However when the panels were removed at elevated temperature the surface finish was poor exhibiting pitting and blistering.

Figure 28: Panel removed at elevated temperature rather than colling under pressure. Pitting and blistering can be seen on the surface.

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6 Multilayer coatings

In the work outlined above lignin has been incorporated into the rubber composite with the aim of improving the fire retardancy. Another approach to this is to incorporate the fire-resistant component within a coating layer and apply the coating to the rubber panels. Here, commercially sourced rubber sheets were coated using a layer-by-layer (LbL) method. In this process, multiple layers of rubber are cut to specific dimensions and after being coated with a biobased coating solution (polyacrylic acid (PAA), lignin, and sepiolite), they are joined together using hot press equipment. The methodology, materials, and details are discussed in the upcoming sections.

6.1 Rubber Panels Production

The rubber panels were produced by stacking multiple 10 × 10 × 0.3 cm layers of ready-made recycled rubber sheets. ECO Recycled Rubber Matting Roll was procured from Polymax Ltd, UK. The height of the layers is governed by the thickness of the rubber sheets used, which in this case is 0.3 cm. The mould can accommodate up to 10 layers. The properties of the rubber used are in Table 14.

Table 14: ECO Recycled Rubber panel properties

Material	NR/SBR
Hardness (Shore A)	70
Density (g/cm^3)	1.35
Tensile Strength (MPa)	4
Elongation at Break (%)	250
Abrasion Resistance (mm^3)	400

The mould is required to hold the rubber layers in alignment when in the hot press. The dimensions of the mould should be the same as the rubber layers, except for the height. The suggested mould height is 3 cm, meaning it can hold up to ten stacked layers. The final height of the resulting rubber part can also be controlled by the amount of applied pressure during thermoforming and the number of rubber layers. It is suggested to set the rubber thickness to 1 cm to have an easy-to-use part for different applications and reduce the required pressure during thermoforming.

6.2 Coating process

The coating formulation is based on previous research to improve the mechanical properties of foams [24]. In the previous research PAA, lignin, and sepiolite were used to coat polyurethane foams using an LbL dip coating method.

The proposed method for this project is to use a similar coating based on PAA, lignin, and sepiolite. The mentioned fillers can improve the mechanical, thermal, and flame retardancy of the end part and PAA can provide mechanical enhancement and act as the binder for the fillers [24]. The formulations of the coating solution that were synthesised are outlined in Table 15.

Table 15: Coating formulations

Mix	PAA (wt.%)	Lignin (wt.%)	Sepiolite (wt.%)	DI water (wt.%)
A	1	1.5	1.5	96
B	1	3	3	93
C	3	1.5	1.5	94
D	3	5	1.5	90.5
E	3	10	1.5	85.5

To prepare the solution, PAA, lignin, and sepiolite were measured and added to a container while DI water was added to increase the total weight to 100 g. The solution was mixed using a homogeniser at various speeds depending on the lignin loading which heavily affects the viscosity of the solution. As the viscosity increases the homogeniser's speed must be increased to achieve a homogenous solution. To achieve this, the IKA T25 digital Ultra Turrax homogeniser with a was used, and the mixing speeds are presented in Table 16.

Table 16: Sample preparation speeds.

Mix	Speed (RPM)
A	8000
B	10000
C	10000
D	14000
E	18000

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Figure 29: Mixing stage of the coating solution E, using IKA T25 digital Ultra Turrax at 18000 RPM

Afterwards, degassing was performed to obtain a more uniform coating on the rubber surface to reduce or eliminate air bubbles (Figure 30).

Figure 30: Degassing chamber.

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The degassed solution was then poured into a shallow container and the rubber sheets were dip coated. A spatula was used to cover uncoated parts of the rubber. Figure 31 and Figure 32 show the rubber before and after coating.

Figure 31: Rubber sheets before coating with solution E.

Figure 32: Rubber sheets after coating with solution E.

The samples were then placed in an oven at 80 ℃ overnight to cure the PAA and evaporate the water. After this stage, the samples can be processed by hot pressing. The panels after drying are shown in Figure 33.

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Rubber was coated to improve the end product's fire retardancy. A flame attack test will be carried out at ZAG to investigate the effectiveness of the synthesised coating.

Figure 33: Dried sheets coated with solution E.

6.3 Moulding

The coated rubber layers were then stacked on top of each other and moulded using a JRD Bipel Laboratory Compression Press equipment (Figure 34) with a platen size of 40×40 cm and a maximum pressing force of 400 kN.

Figure 34: Bipel Press equipment.

The procedure consists of a preheating stage at 100-120 °C The pressure that was applied to the layers after reaching the desired thickness is 10 MPa for 10 minutes. In the moulding stage, the temperature was increased

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to 160 °C at 10 MPa for 20 minutes and then under constant pressure, the part was allowed to cool down to room temperature before being removed from the mould. Using this method a rubber panel could be compressed into a multilayer panel with the fire-resistant coating layers. The final panel is shown in Figure 35.

The final product has good dimensional stability and handleability like the original rubber sheets. Its flexibility is shown in Figure 36.

Figure 35: Final multilayer rubber panel.

Figure 36: Demonstration of rubber part flexibility.

6.4 Next steps

The coated rubber panels produced so far will undergo mechanical and fire resistance testing to understand their performance. These panels have been made using commercially available rubber panels with the lignin-containing coating applied after their manufacture. The performance of these panels will be compared against the rubber panels manufactured using the Greenloop rubber formulation as laid out in Section 4. In this way a comparison between using lignin as a fire retardant in a coating layer or as a filler within the bulk of the material can be compared.

The coating will be further optimised to explore higher weight percentages for lignin (10 - 20 wt%), sepiolite (5 – 10 wt%), and PAA (5 – 10 wt%) to achieve the highest possible filler loadings in the coating, while obtaining

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a uniform rubber part through hot pressing. Furthermore, shapes will be added to the rubber surface to investigate their potential effects on various properties of the end part.

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7 Concluding Remarks

This report outlines the work undertaken to demonstrate a bio-rubber value chain by formulating a material suitable for use as acoustic panelling within the construction industry.

Lignin extraction has been carried out up to a scale of 130 grams per batch. This material has been characterised and fed into the formulation trials. To date, 5 kg of Kraft lignin has been produced. The lignin generated was characterised by NMR to determine the oxygen content before and after fractionation. Little difference in oxygen content was noted between the samples. This aligned with results from flammability testing that suggested the impact of fractionation had little impact on the time to ignition.

Formulation trials have identified two formulations for the rubber panels which have sufficient mechanical strength for the targeted application. These formulations are NCC_GL_P_013 and NCC_GL_P_014 which contain 10 and 20 wt% of lignin respectively. This balances the mechanical properties with the level of lignin which is anticipated to improve the fire retardancy. Flammability tests are ongoing to assess the impact of lignin on the time to ignition. The results of this will be reported in Deliverable 3.5. Batch sizes of 1.2 kg have been achieved for both the NCC_GL_P_013 and NCC_GL_P_014 formulations. Their mechanical properties were as follows: break stress of 7.7-9.7 MPa, break strain of 311-330 %, Shore A hardness of 56-62 and a modulus at 100% strain of 2.12-2.35 MPa. Compounding with fine rubber crumb was found to have very poor processability when compounded in an internal mixer. For that reason larger crumb sizes have been targeted for the Greenloop devulcanisation process.

Ultrasound technology and green chemical reagents (deep eutectic solvents) have been utilised to devulcanised rubber granulate sourced from waste tyres. The devulcanisation percentage achieved varied significantly between 2 and 72%. The best performing treatments compared favourably with the baseline material, a commercially available devulcanised rubber, which had a devulcanisation percentage of 75%. The process has been scaled up to 50 g which is on a sufficient scale to be compounded. Work is ongoing to establish the scaled up process' efficacy and environmental impact compared to existing devulcanisation techniques. Compounding tests will be carried out to understand how the devulcanised material behaves during processing and how it performs once compression moulded. These results will be reported in Deliverable 6.1.

Following the conclusion of validation testing results a final formulation will be selected for upscale. Full characterisation of the final material will be reported in Deliverable 3.5. Production will move to a 10Kg minimum batch size to demonstrate production at scale and generate sufficient material for real world testing. This will include acoustic testing and fire resistance testing of full-scale panelling. The results of this will be reported in Deliverable 6.2.

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