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Experimental study on the optimisation of chemical treatment to reduce waste rubber aggregates absorption properties

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Abstract

Utilisation of abundant waste rubber generated from scrap tyres in pavement engineering applications could be a useful route to consume large extent of the waste from the scrap tyres. It may contribute towards maintaining a greener environment by reducing the associated environmental and social impacts as well as improve the properties of bituminous mixture used for pavement engineering applications. This paper focuses on the upgrading of waste rubber aggregates surface properties by identifying and applying optimised chemical treatment (oxidation and cross-linking). The focus was to increase the life span of bituminous mixtures containing waste rubber as an aggregate by reducing a phenomenon of migration of light fractions (maltenes) from bitumen to rubber which occur at elevated temperatures ranging between 160-180ºC. The results of various tests conducted showed the potential of the treatment to reduce the absorption of maltenes into rubber. The existence of the surface treatment was verified through the Scanning Electron Microscope (SEM) analysis of the rubber aggregate. The reduction in the absorption properties of rubber due to the existence of the treatment was verified using the Microwave Spectroscopy technique. The results of both the tests were promising in terms of indicating the durability of the treatment and the reduction in the absorption properties of rubber. Mechanical tests such as Indirect Tensile Stiffness Modulus (ITSM) and Repeated Load Axial (RLA) tests were conducted on the newly devised bituminous mix design with 10% of added rubber (by mass of the sample). The results were promising in the case of the aged samples with both the stiffness and load bearing capacity being higher for the aged samples. However, the results need improvement in terms of its applications on the light traffic areas through the replacement of the ordinary filler with the mineral filler. Also, a higher percentage of waste rubber should be added to study the suitability of its use in the flexible surface applications such as children's playgrounds, sports pitches and surfaces, etc.

Keywords:

Waste rubber; scrap tyres; pavement engineering; sustainable environment; chemical treatment; microwave analysis; bituminous mix; bitumen analysis; mechanical testing.

1. INTRODUCTION

1.1. Scrap tyres, their environmental impact and applications

The waste rubber from scrap tyres poses an environmental threat if not utilised efficiently. Since 2006 legislation such as End of Life Vehicles (ELV) salvage, waste incineration and EU directives on the waste landfill management prohibited the disposal of waste tyres arising to the landfill and similar waste disposing routes, etc. [1, 2]. Also, stockpiling of the scrap tyres is not allowed because of it being a potential source of fire hazard, cause of environmental damage and other health risks associated with it. It also does add to the disposal costs of the scrap tyres [3-5]. In Europe 95% of the scrap tyres are recycled [6]. The emphasis on recycling the scrap tyres encouraged the introduction of new end use market applications as well as alternative recovery options. Although the market for scrap tyres and its material usage has been established, the amount of tyres that reach their end-of-life cycle worldwide significantly exceeds the end use market of the scrap tyre material. The only exception to this is the UK market of scrap tyres as it is meeting 100% of the recovery target through various routes such as recycling, recovery and reuse [1].

One of the potential applications to utilise a significant number of scrap tyres is to use them in rubberised asphalt pavements surfaces, pavement engineering and flexible rubberised surfaces whereby large quantities of scrap tyres can be consumed. This could potentially reduce the amount of waste generated and can improve some of the engineering properties of the pavements such as fatigue resistance, reduced low temperature surface cracking, improve tensile strength, adhesion, resistance to rutting, elasticity, noise reducing characteristics, safety in wet conditions, flexibility to reduce injuries in the case of playground surfaces, and many more [4, 5, 7-15] .

1.2. Brief problem statement and the literature

Applications of waste rubber aggregates in bituminous mixtures, both in the wet and dry process, resulted in two main problems identified by researchers and professionals [4, 5, 7-9, 11, 16-19]. At elevated temperatures (140-170°C) the migration of light fractions (constitute resins, aromatics, and saturates) from bitumen to rubber occurs. This causes the swelling of rubber between 3-9 times its original size causing it to lose its rigidity and shape. Also, the residual bitumen becomes brittles and hard resulting in the breaking of the bond between the rubber, bitumen and aggregates. This causes the particles of rubber to become loose and become distributed in the bitumen in the case of fine particles (wet process) and on the surface of the pavement leaving gaps on the surface in the case of crumb rubber (dry process). This adversely affects the performance and durability of the surface.

Shakhnazarli [20] has utilised secondary polyethylene, polyamide fiber waste, and crumb rubber to modify bitumen. Airey et al [7] pointed out the use of modifiers like sulphur, rubbers, thermoplastic polymers, and thermosetting resins to modify the bituminous mixture to improve mechanical properties of the bituminous mix. Stabilising agents such as cellulose and mineral fibers have been used to prevent the drain down [21]. Polymers such as styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), Elvaloy, ethylene vinyl acetate (EVA), polyethylene, and others have also been used to modify asphalt binders [22, 17]. Frantzis [23] discusses methods to modify rubber including a devulcanization process, heavy paraffinic distillate solvent extract and a water activated method. Additives like Poly phosphoric acid and vestenamer were also used for improving the properties of crumb rubber modified bitumen [24]. Although these treatments, up to an extent, improve the performance in terms of mechanical behaviour and engineering properties (resistance to deformation, low temperature cracking, flexibility, stiffness, etc.) of bitumen and bituminous mixtures that ultimately has an influence on the service life of pavements, the problem of migration of maltenes has not been explicitly addressed by any of the above.

1.3. Waste rubber aggregates treatment

This paper demonstrates the use of suitable chemical additives and their optimised quantities to modify the rubber surface properties to subsequently reduce the migration of maltenes from bitumen to rubber. This could potentially result in a strong adhesive properties of rubber which subsequently helps in improving the bonding between the bitumen and rubber. If successful in reducing the migration of light fraction from bitumen to rubber, the proposed treatment is also expected to improve the resistance to permanent deformation, reduce low temperature surface cracking, and improve the flexibility of the material over a long period of time for the applications such as use in school playgrounds and sports stadiums, shock absorbing surfaces, walkways/pathways, artificial turf for football stadiums. Additionally, it could have potential to be used on light traffic road surfaces [4, 5, 7-9, 11, 13, 16-19] (Al-Nageim and Robinson 2007; Rahman et al 2003; Huang et al 2007; Cao 2007; Navarro et al 2005; Lee et al 2008; Rahman et al 2005; Airey et al 2002; Read and Whiteoak

2003; Xiao et al 2009; Hernández-Olivares et al 2009). A Microwave spectroscopy technique was used to analyse the absorption properties of rubber through indirectly studying the properties of bitumen and changes incurred in the spectrum of bitumen after its interaction with the treated rubber. This technique has been demonstrated in previous studies by the same author as this article [25, 26] to analyse bitumen properties. The mechanical properties were tested using the Indirect Tensile Stiffness Modulus (ITSM) test and Repeated Load Axial (RLA) test.

Ateeq et al [25] and Ateeq et al [26] attempted to carry out the chemical treatment, however, the optimum chemical treatment parameters were not achieved. This study extends the work by identifying the optimum chemical treatment (percentage of oxidation and cross-linking agents). It also presents the mechanical testing of the bituminous samples prepared in the laboratory with the treated rubber and its results. Despite the attempt to identify and explore optimum chemical treatment in the current study, further work is required to improve the mechanical behaviour from the test results as well as to optimise the chemical treatment in large size samples. This can either be achieved at the chemical treatment stage (through other quantities of chemical treatment systems), at the time of manufacturing the laboratory test samples and/or through field trials. More detailed testing is also required including the use of more established analysis techniques to study the migration of light fractions from bitumen to rubber.

2. MATERIALS AND METHODS

2.1. Materials

The crumb rubber utilised to carry out the treatment was 1-6 mm size aggregates from truck scrap tyres. The size range of the sample was obtained using a set of sieve by passing through a 6 mm sieve and retaining on 1 mm particle size sieve. It was supplied by J. Allcock & Sons based in Manchester, UK. The sample of waste rubber is shown in Figure 1 and its physical properties are presented in Table 1.

Figure 1. Crumb rubber from scrap tyres of the size 1-6 mm used in the study using 1-6 mm sieve set

Table 1: Physical properties of coarse waste rubber aggregates

Properties	Value
Bulk specific gravity, gm/cm^3	2.79
Apparent specific gravity, gm/cm^3	2.82
Water absorption, %	0.4
Dielectric constant (20°C)	8.0

The bitumen was 100/150 penetration grade (pen) supplied by Nynas UK AB. The typical properties of the bitumen used in the study is shown in Table 2.

Table 2: Properties of 100/150 pen bitumen used in the study

Parameters	Bitumen (100/150 pen) values
Penetration at 25°C	100-150x0.1 mm
Softening point	39-47°C
Penetration index	-1.5 to +0.7
Dynamic viscosity at 60°C	NPD
Fraass breaking point	≤ -12
Dielectric constant (20-25°C)	2.55-3.5

The chemicals used for the oxidation were potassium dichromate, ≥ 99.5% supplied by Sigma Aldrich and potassium permanganate, 99% supplied by BDH Laboratory, England. The cross-linking agent used was polyethyleneimine supplied by Sigma Aldrich. Petroleum (petrol special) with aromatic basis (~18%, bp. 180-220°C) was supplied by Sigma Aldrich that was used to replicate the interaction effect of bitumen (because of their similar properties). This was to analyse the polyethyleneimine coating and its durability in petroleum.

2.2. Design of the chemical treatment

- The modification of waste rubber surface was a two stage process. In the first stage, oxidation of the crumb rubber was carried out. It was followed by the cross-linking of the rubber in the second stage. The most important factor in the current study was to optimise the chemical treatment and to identify the combination of the oxidation and cross-linking agents and their suitable percentages to obtain the treated rubber to be used in the preparation of the bituminous mix design. It follows the previous work carried out by Ateeq et al [25] and Ateeq et al [26]. From the detailed combination of chemical treatments and their analysis the most suitable and effective treatment identified was as follows: Waste rubber aggregates were treated with the oxidising solution comprising 0.1 mol/L of potassium dichromate ($K_2Cr_2O_7$), 0.5 mol/L of sulphuric acid (H_2SO_4) and water (H_2O). The oxidation was carried out at 60-70°C for 90 minutes to accelerate the oxidation reaction on the hot plate and thereafter kept at room temperature for 24 hours for further reaction to take place. The process is shown photographically in Figure 2.

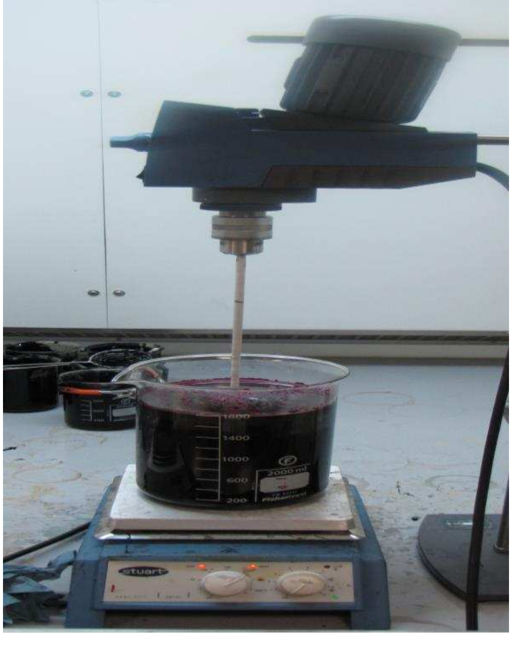


Figure 2. Oxidation of the waste rubber using potassium dichromate, sulphuric acid and water

- The oxidised rubber was then cross-linked using 3% of the polyethyleneimine in the rubber-bitumen blend. The blend was mixed for one hour and further cured for 6 hours at 160-170°C in an oven.

2.3. Testing and analysis

Two types of analyses were carried out to confirm the sustainability, durability and effectiveness of the chemical treatment. They included a surface analysis as well as an absorption analysis of rubber. The surface analysis of the treated waste rubber was carried out using a Scanning Electron Microscope (SEM). It was important to obtain evidence of the existence of the cross-linking agent (polyethyleneimine) on the surface of the treated waste rubber aggregates after the treatment at high temperature (160-170°C). The key factor was the existence of the thin film coverage on the rubber surface and to examine if the harsh temperature environment still left the thin film intact during and after the treatment. Since it was difficult to analyse the surface of the treated rubber out of the rubber-bitumen blend due to the bitumen coating on rubber particles, a suitable and alternative approach was designed. Petroleum (petrol special) was used to simulate the effect of bitumen. The oxidised rubber was mixed with petroleum and heated to 160-170°C. For the purpose of this paper, the results of two samples treated with polyethyleneimine was presented and compared with the untreated rubber sample. Cross-linking agent at 6% and 9% by weight of the rubber was added in the blend and mixed thoroughly for 1 hour to produce the uniform coating on the rubber surface. The blend was further mixed for additional 2 hours until all the petroleum evaporated. Rubber particles from the blend were then analysed under SEM.

The analysis of the absorption properties of rubber was carried out using the Microwave Spectroscopy (MS) analysis technique. The technique has been proven effective, accurate and repeatable in the analysis of the absorption properties of bitumen when it interacts with rubber [25, 26]. This was achieved through the indirect analysis of the bitumen taken from the rubber-bitumen blends with and without oxidised and/or cross-linked rubber. The aim was to monitor the surface resistance of the rubber to bitumen by indirectly measuring the changes in the bitumen properties extracted from the blend. Based on the theory of the microwave analysis technique it was assumed that if the treatment was effective the spectra obtained from the microwave analysis of the bitumen would be similar or close to the pure bitumen curve because of the least change having taken place in the dielectric properties of bitumen. This is because the two bitumen samples will have almost identical percentage of light fractions and will exhibit similar properties. Otherwise the spectra would shift away from the pure bitumen sample result. For results to be accurate and repeatable, the bitumen samples were kept in a temperature controlled chamber for 24 hours before conducting the analysis. Furthermore, the weight of the bitumen samples to be analysed need to be precisely the same to produce accurate results because of the instrument sensitivity.

The samples were analysed in the frequency range of 2.329-2.347 GHz. This is because of the effective response of the physical properties of bitumen at this band of frequencies. The results analysed were for the reflected power also known as reflection coefficient (S_{11}) due to the detailed and accurate information available. The samples were repeated twice to prove the validity of the results.

2.4. Sample preparation for microwave spectroscopy analysis

The aim of the surface treatment of coarse waste rubber was to use it as an aggregate replacement in the bituminous mix (dry process). However, to study the absorption properties of waste rubber (treated & untreated), blends of rubber-bitumen were prepared in a similar fashion as in the wet process where the fine rubber is mixed with the bitumen and heated. This approach was adapted to study and confirm the direct effect of the treatment on the surface of waste rubber and to analyse the impact in terms of absorption of bitumen into rubber through its surface. Treated and untreated rubber was mixed at 10% by weight to 100 mL of the bitumen sample at medium shear strain to bring a solution to a continuous phase. The mixing was carried out for an hour at 160-170°C. It was then followed by further 6 hours of curing for the maximum absorption of light fractions from bitumen into rubber. After the blend was ready, bitumen was extracted off the blend into the sample tube (15 mL) to be analysed using the microwave spectroscopy analysis technique.

The experimentation was carried out in a temperature controlled chamber and the temperature was set at 20°C. All the samples were kept in the chamber for 24 hours to stabilise the temperature before any analysis tests were conducted.

2.5. Microwave spectroscopy analysis theory

Microwave analysis monitors the changes in the molecular structure of the material under consideration via measuring the changes in the permittivity of the material. Any changes in the molecular structure of the material affects its permittivity. This change in the permittivity of the material can be captured in the form of microwave spectra when the microwaves interact with the material [27-29]. These response signals could be in the form of a reflected power, also known as the reflection coefficient or S_{11} parameter as well as the transmitted power, also referred to as the transmission coefficient or S_{21} parameter [30]. Collectively, they are termed as S-Parameters (scattering parameters) [31]. Permittivity simply measures the response of the material to the applied microwaves in the form of a change in the complex electric permittivity, termed as ε_r and is defined as, [31]:

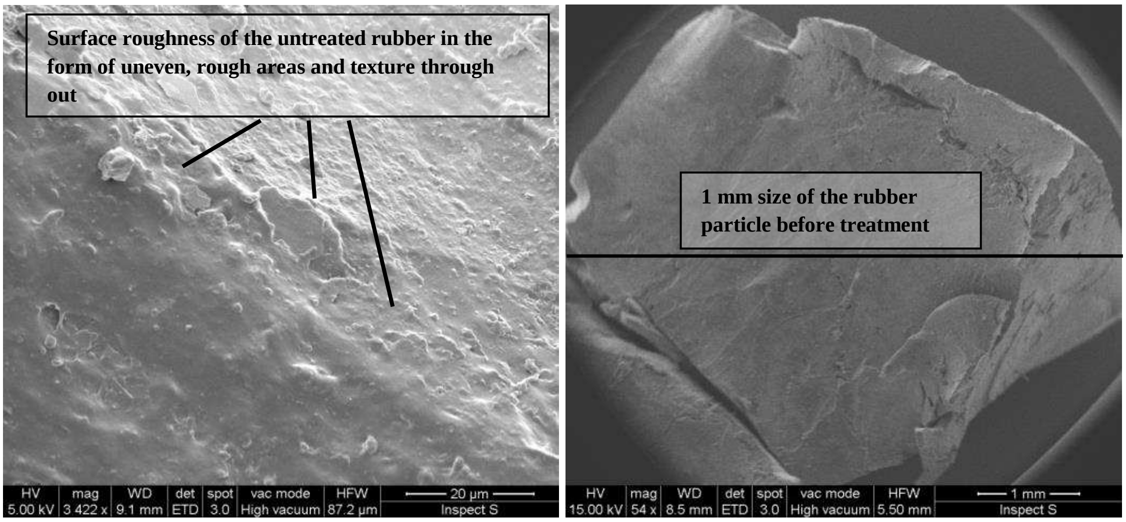
$$\varepsilon_r = \varepsilon' + j\varepsilon'' \tag{1}$$

Where ε' represents the energy stored by the material and ε'' represents any losses of the energy. Measuring the influence of the material on the s-parameters at discrete frequencies one can relate it to various material characteristics such as material composition, its type, concentration, size/size distribution, etc. in the sample under test [31].

3. RESULTS AND DISCUSSION

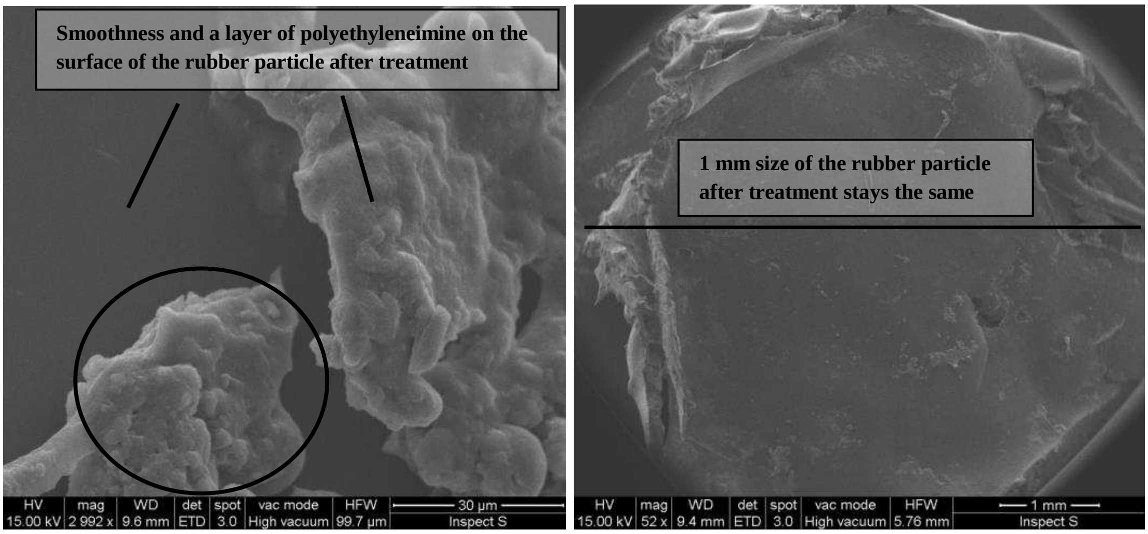
3.1. Scanning Electron Microscope (SEM) surface analysis

The results of the SEM analysis of the surface of the untreated and treated rubber samples is shown in Figure 3, 4 and 5 for comparison. The same particle size was chosen for a like-to-like comparison both in the case of untreated and treated rubber which was about 1 mm. The surface treatment for the SEM analysis was carried out as described in section 2.2.



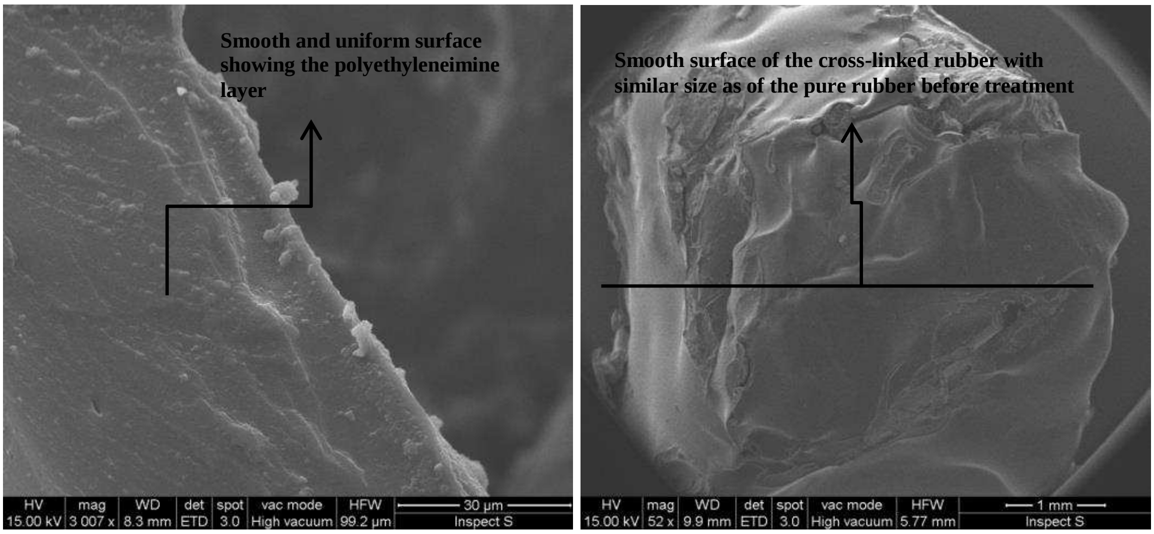
(a) (b)

Figure 3. (a) SEM analysis of the untreated crumb rubber surface at the magnification of 3422x (b) SEM analysis showing the particle size of the untreated rubber to be approximately 1 mm



(a) (b)

Figure 4. (a) SEM analysis of the 6% polyethyleneimine treated crumb rubber surface at the magnification of approximately 3000x (b) SEM analysis showing the particle size of the treated rubber to be approximately 1 mm



(a) (b)

Figure 5. (a) SEM analysis of the 9% polyethyleneimine treated crumb rubber surface at the magnification of approximately 3000x (b) SEM analysis showing the particle size of the treated rubber to be approximately 1 mm

The comparison of the two rubber samples in Figure 3 and 4 in terms of both their surface properties (appearance, texture, smoothness) and change in the size shows promising results and demonstrate the effectiveness of the treatment. Looking at the surface of the untreated rubber in Figure 3 (a) shows the surface being rough at approximately 3000x magnification. Comparing it with the treated rubber surface in Figure 4 (a) shows the smooth surface labelled, Figure 4(a), covered by the film of polyethyleneimine even after going through the harsh temperature conditions that resembles to the actual treatment and its interaction with bitumen. It is noticed in Figure 4(a) that some parts of the treated rubber has an excess of polyethyleneimine, an example of which is indicated and encircled in the Figure. This might be mitigated in the case of bitumen with further mixing to spread the layer uniformly. Figure 3(b) and 4(b) shows that size comparison before and after treatment of the similar size rubber sample. It can be observed that the particle sizes remain similar before and after treatment, hence demonstrating the least (which would be confirmed with the microwave analysis in section 3.2) as well as the durability and effectiveness of the treatment to reduce the absorption of light fractions into the rubber. Additional result of the treated rubber sample with higher percentage of polyethyleneimine is presented in Figure 5 to verify the existence and effectiveness of the coating. A better uniformity in the coating was achieved as shown in Figure 5(a) at approximately 3000x magnification compared to Figure 4(a). When comparing the treated surface, Figure 5(a), with the untreated rubber in Figure 3(a) it is noticed that the treated rubber surface has smoother appearance in comparison to the untreated rubber surface that shows rough surface and texture as in Figure 3(a). In terms of the change in the size of the sample after treatment, it can noticed in Figure 5(b) that the sample size of 1 mm doesn’t change in comparison to Figure 3(b), untreated rubber. This indicates the effectiveness of the cross-linking treatment to reduce the swelling of rubber particles.

3.2. Microwave analysis

The microwave cylindrical resonant cavity was utilised for the microwave analyses of the sample. It is a bespoke cavity resonator designed at the Radio Frequency and Microwave (RFM) group, Liverpool John Moores University to carry out the analysis of various materials such as carbon, silver products, polymers, etc. The technique is non-invasive and non-destructive. The resonant cavity is classed as a closed box short circuited at both ends. Both the electric and magnetic energy is stored within the cavity. These fields together form a standing wave at certain frequencies causing the resonance to occur inside the cavity. Because of this phenomena various modes may exist in the cavity, each of them with its own resonant frequency and a quality factor (Q) associated with it. For the cylindrical cavity, the fundamental modes are TE_{111} and TM_{010}. The TE (Transverse Electric) mode has a magnetic component in the direction of propagation whereas the TM (Transverse magnetic) mode has an electric component in the direction of propagation of wave. In this way, the power dissipated in the metallic walls of the cavity due to the applied electromagnetic wave (in the microwave frequency region) can be used to study the material under test based on its interaction with the material [32, 33]. The setup of the microwave spectroscopy system is shown in Figure 6.

Due to the response of the microwaves to the bitumen, the reflected power, S_{11}, described in the section 2.5 was considered for the analysis before and after the treatment. The signal represents the change in the dielectric properties of the bitumen samples based on its absorption into rubber, and any changes incurred as a result of the reduction in the light fractions percentage. After the range of experiments conducted it was found that the reflected power in the frequency range of 2.329-2.347 GHz was best suited to indicate the absorption of waste rubber for each sample and the effectiveness of the treatment through the resonant peaks obtained.

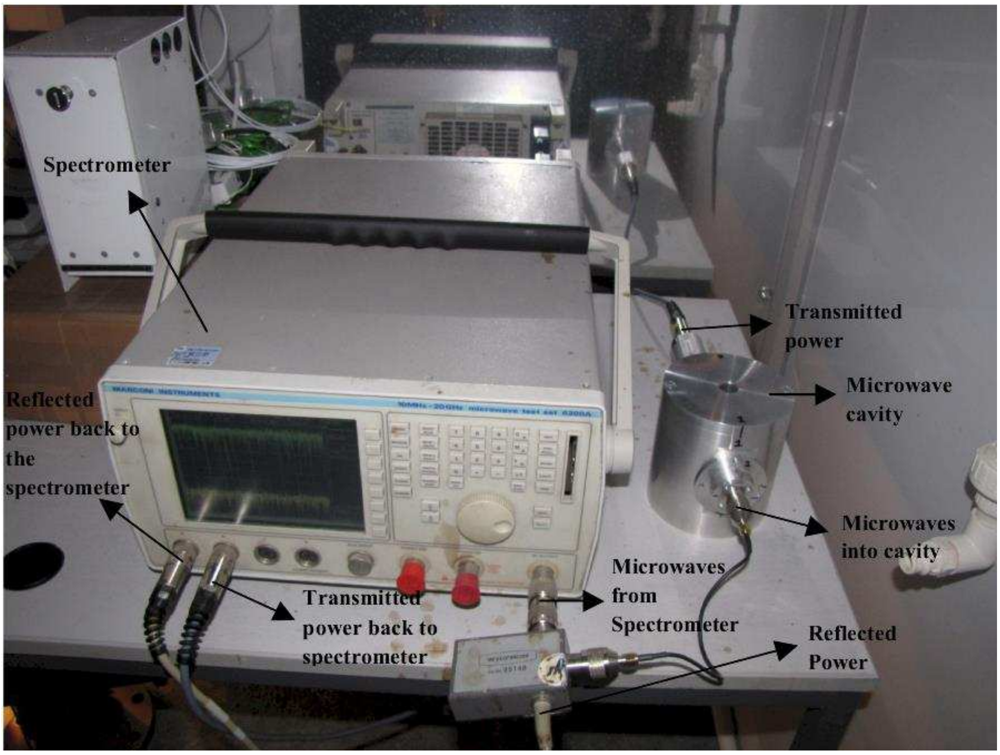


Figure 6. Non-invasive real-time cylindrical microwave cavity setup for the bitumen analysis

The microwave analysis results of four samples are presented in Figure 7. The samples analysed include:

- Bitumen sample, un-cured.
- Bitumen sample, cured for 6 hours to compare with the 6 hours cured bitumen extracted from the blend with treated rubber.
- Bitumen extracted from the blend containing pure/untreated rubber.
- Bitumen extracted from the blend containing the 10% (by weight) of the treated rubber oxidised with 0.1 mol/L of potassium dichromate ($K_2Cr_2O_7$), 0.5 mol/L of sulphuric acid (H_2SO_4) and water (H_2O) and cross-linked with 3% of polyethyleneimine.

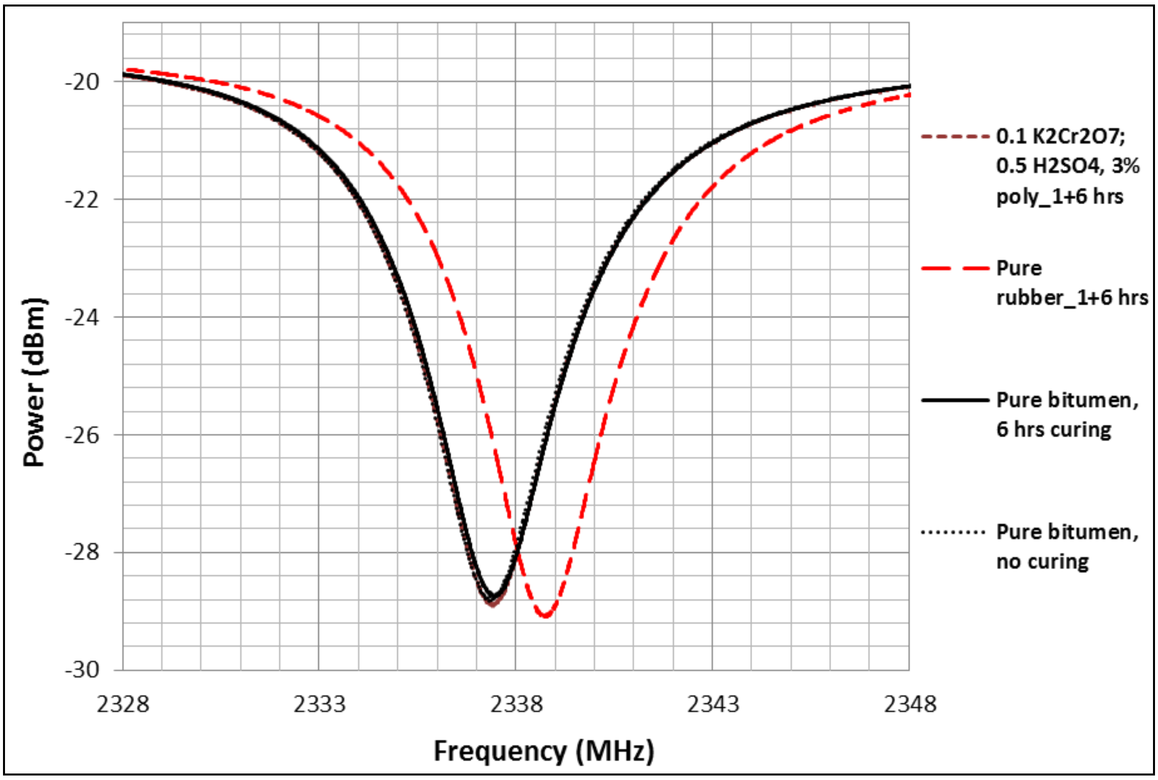


Figure 7: Effects of 1 hour mixing plus 6 hours curing using 3% polyethyleneimine treatment in the rubber-bitumen blend (10:100 ratio) containing rubber oxidised with 0.1 mol/L K2Cr2O7, 0.5 mol/L of H2SO4, and water

The resonant peak of the bitumen (cured and uncured) sample were detected at around 2.3374 GHz and 2.3373 GHz respectively. When these peaks were compared with the bitumen sample extracted from the blend containing the untreated rubber mixed for 1 hour and further cured for 6 hours, a shift to the right was observed with a resonant peak detected at the frequency of 2.3387 GHz. The shift was approximately 1.34 and 1.4441 MHz from the cured and uncured bitumen sample. This amount of shift (in MHz) is significant keeping in consideration the sensitivity of the instrument. This signifies that the bitumen has changed its properties due to its light fractions absorbed by the rubber. When the curve of the bitumen retrieved from the treated rubber bitumen blend was analysed the peak frequency was observed at 2.3373 which is an overlap on the uncured bitumen sample curve. Thus, the bitumen was exhibiting the dielectric properties similar to the pure bitumen and could be linked with the loss of light fraction in the bitumen. On this occasion, the results indicate minimal absorption of light fractions into the treated rubber.

To indicate the effectiveness of the chemical treatment, microwave analysis of a sample oxidised with 0.1 mol/L K2Cr2O7, 0.1 mol/L of H2SO4, and water followed by 3% polyethyleneimine is also presented in Figure 8.

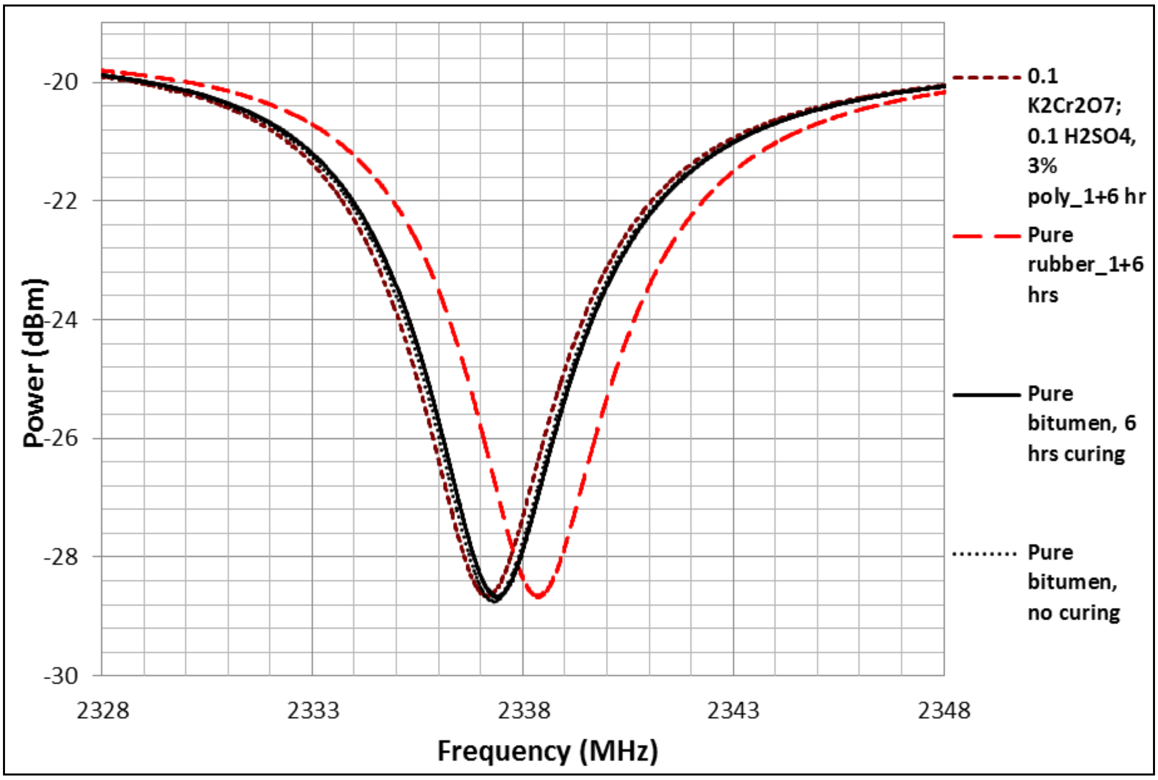


Figure 8: Effect of 1 hour mixing plus 6 hours curing and 3% polyethyleneimine on rubber-bitumen blend (10:100) containing rubber oxidised with 0.1 mol/L $K_2Cr_2O_7$, 0.1 mol/L of H_2SO_4, and water

The four samples presented in Figure 8 are:

- Pure bitumen sample, un-cured
- Bitumen sample, cured for 6 hours to compare it with the bitumen sample extracted from the cured blend with treated rubber.
- Bitumen sample extracted from the blend with pure/untreated rubber.
- Bitumen sample extracted from the blend containing 10% (by weight) of the treated rubber, oxidised with 0.1 mol/L $K_2Cr_2O_7$, 0.1 mol/L of H_2SO_4, and water and cross-linked with 3% of the polyethyleneimine.

It can be noticed from Figure 8 that the resonant frequencies of pure bitumen sample (cured and un-cured) are detected at around 2.33742 & 2.33732 GHz. In comparison, the curve of the bitumen sample retrieved from the pure/untreated rubber-bitumen blend shifted to the right showing the peak at approximately 2.33834 GHz, a difference of 0.92 and 1.02 MHz from the cured and un-cured sample respectively. It is a considerable shift when compared to the peak value of the bitumen sample retrieved from the blend with modified rubber. It has a peak at 2.33713 GHz, representing a shift of approximately 0.29 & 0.19 MHz to the left, a value closer to the cured and un-cured sample of the pure bitumen. Similar to the result in Figure 7, the peak value of the modified bitumen in Figure 8 indicates the dielectric properties of the modified bitumen sample close to the pure bitumen showing a reduction in the migration of light fractions into rubber. However, it is slightly towards the left in comparison to modified bitumen in Figure 7 indicating a slight change in the dielectric properties of the modified bitumen. Hence, the combination of treatment in Figure 7 was more effective in comparison to the treatment in Figure 8, i.e. 0.1 mol/L K2Cr2O7, 0.1 mol/L of H2SO4, and water followed by 3% polyethyleneimine in comparison with the later 0.1 mol/L K2Cr2O7, 0.5 mol/L of H2SO4, and water followed by 3% of polyethyleneimine. This shows that a higher molar concentration of H2SO4 was more effective.

3.3. Mechanical testing and results

3.3.1. Mix design

The mix design was selected based on the target application. The target applications included surfaces such as a light traffic areas, sports pitches, golf courses, walkways/pathways, etc. The available recipe of the mix designs in the British and European Standard for this kind of application includes a 6 mm medium graded surface course (MGSC) mix and a dense graded surface course mix. Since, the purpose was to modify the mix design and accommodate the waste rubber aggregates (along with their swelling properties) the MGSC mix design was selected for carrying out the mix designs and mechanical testing. A typical MGSC mix gradation target limit according to the PD6691 [34] is shown in Table 3.

Table 3. The target limit for the composition of Medium Graded Surface Course (MGSC) mix [34]

Mixture description	**AC 6 med surface**
Test sieve aperture size	**% by mass passing**
10	100
6.3	98
4	-
2	33-41
1	14-26
0.250	-
0.063	4-7

For the purpose of the laboratory based mix design of the samples, the mean value of the percentage of the respective size of the aggregates was selected for the new mix designs. The mix gradation chart for the target limit and composition is shown in Figure 9.

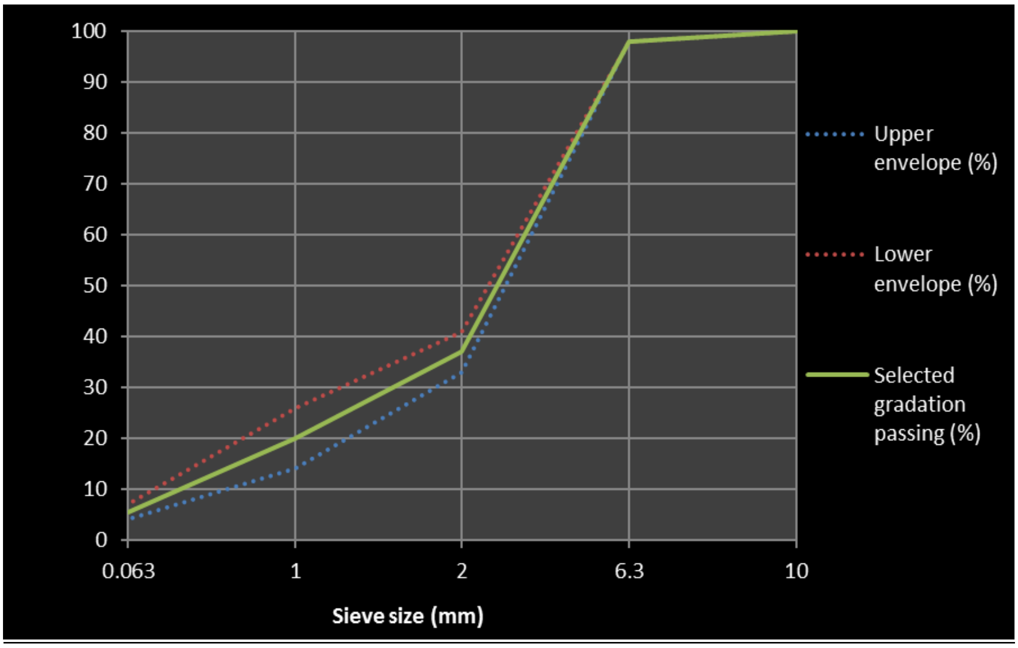


Figure 9: MGSC mix gradation chart for the target limit and compostion

3.3.2. Optimisation of the mix design and samples prepared

The mix design of the control and rubberised samples in terms of the amount of bitumen and rubber was optimised using the flow chart of Figure 10. The samples prepared were as follows:

- Control sample
- Sample with untreated rubber
- Sample with treated rubber using method 1 (TP1)
- Sample with treated rubber using method 2 (TP2)

Typically, the difference between the TP1 and TP2 treatment method was that in TP1 the rubber was first oxidised and then cross-linked in the rubber-bitumen blend mixed for 1 hour and cured for further 6 hours as stated in section 2.4. However, to examine the impact of a variation in the treatment method, in TP2 the oxidised rubber was first cross-linked using the polyethyleneimine and cured for 3 hours in the oven at 170-180°C. The rubber obtained was then used in the preparation of rubberised bituminous mix samples.

All the bituminous samples (control, untreated rubberised and treated rubberised) were prepared and compacted according to the British Standards [35, 36]. The samples prepared were tested using the Indirect Tensile Stiffness Modulus (ITSM), for the stiffness behaviour, and Repeated Load Axial Test (RLAT), to evaluate the resistance to permanent deformation. Ageing tests were also conducted on both the control and modified bituminous samples to examine the effect of ageing to simulate the theoretical service life from 6 hours to 10 years. Some of the samples prepared are presented in Figure 11.

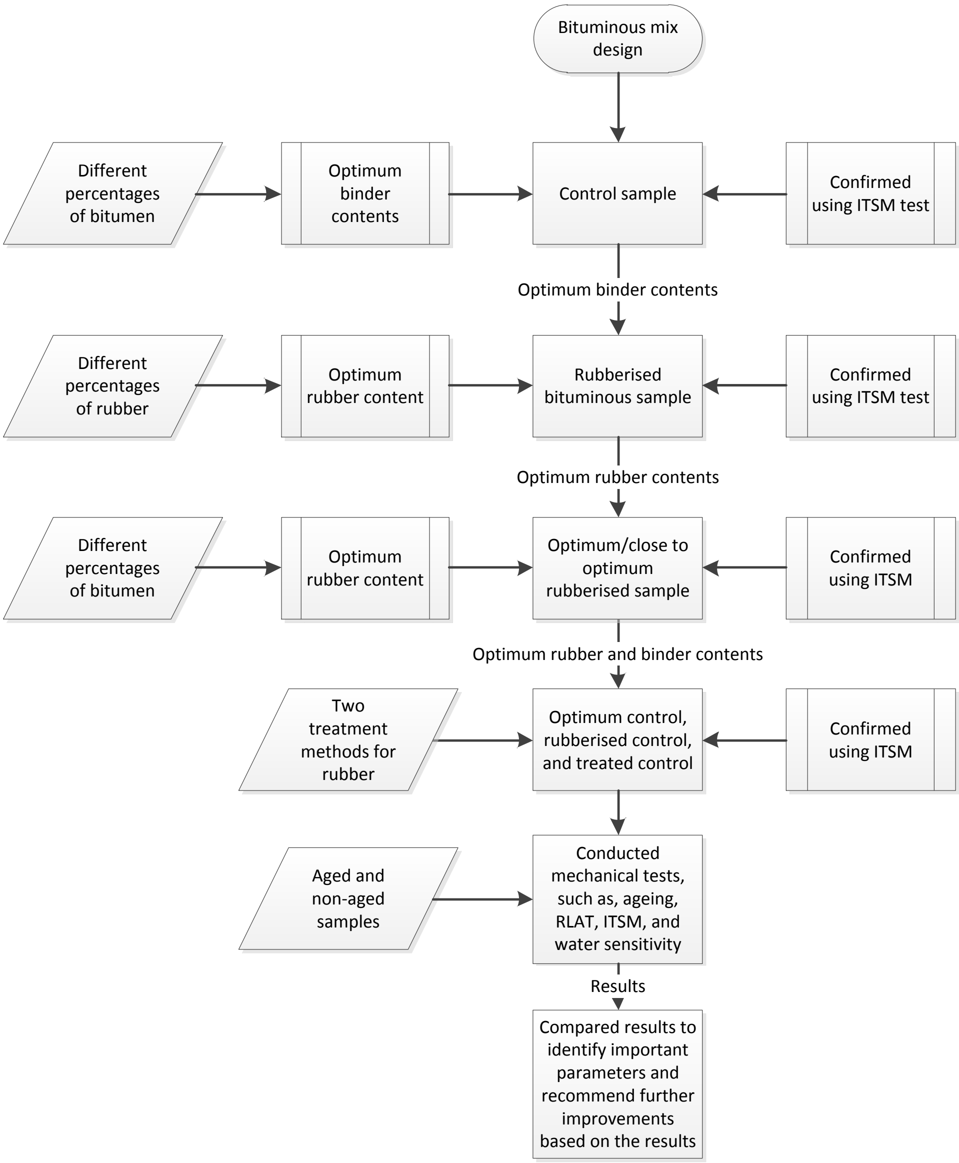


Figure 10: Schematic representation of the overall strategy to optimise the mix design

Figure 11: Subset of the bituminous mix samples preparaed (control and rubberised)

3.3.3. Indirect Tensile Stiffness Modulus (ITSM) test

The test conditions set for the ITSM test were the horizontal strain/deformation of 0.005% of the specimen diameter, the rise time of 124 ± 4 ms (equivalent to the frequency of 1.33 Hz), the specimen diameter of 100 mm, the specimen thickness between 30-70 mm, and the test temperature of 20°C. The stiffness results and comparison of various samples are presented in Figure 12.

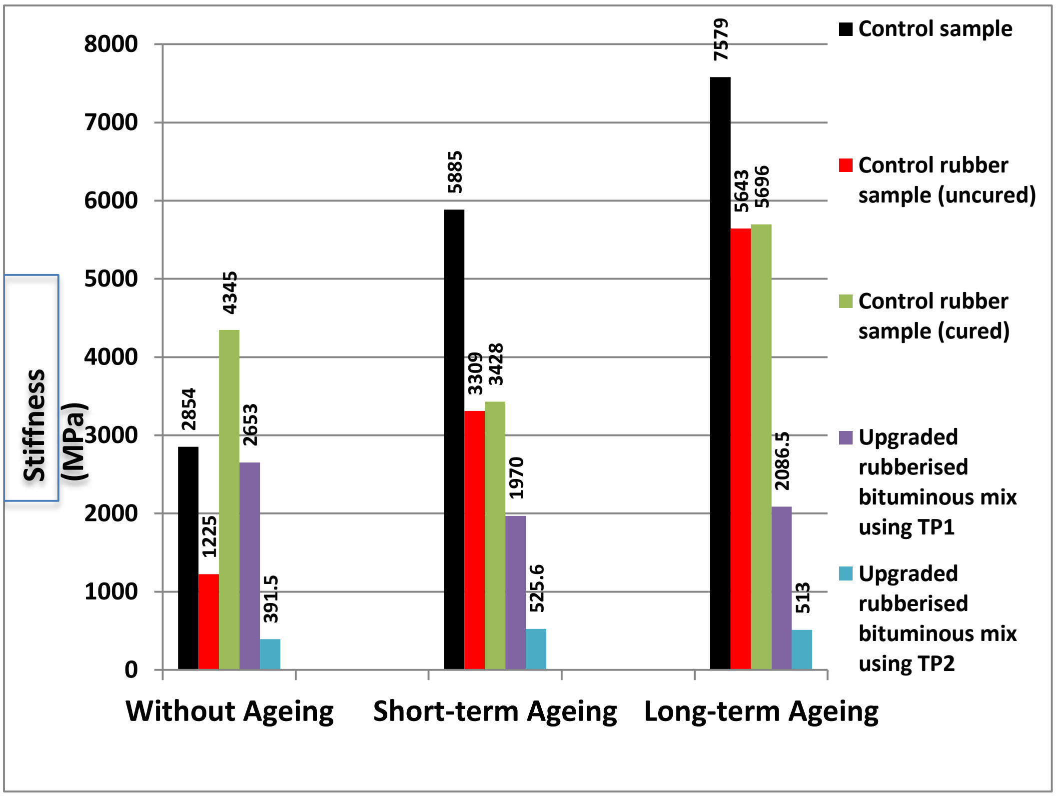


Figure 12: Stiffness Modulus of the control and rubberised bituminous samples (aged and unaged)

The results show that in the case of unaged samples the highest value of the stiffness was obtained for the untreated rubberised bituminous sample cured for 6 hours. The value of the stiffness of the TP1 treated rubberised bituminous mix has a value of 2653 MPa, comparable to the control sample of 2854 MPa. The stiffness values for the TP2 treated rubberised bituminous mix and the uncured control rubber sample has the lowest values. In comparison to the unaged samples, the short-term aged samples showed variation in the stiffness values of the samples. The highest value was obtained for the control sample followed by the cured untreated rubberised bituminous sample that was slightly higher than the uncured untreated rubberised sample (3309 MPa). The value of the TP1 treated rubberised bituminous sample dropped to 1970 MPa compared to its unaged version. However, it was still significantly higher than the TP2 treated rubberised bituminous sample. The last comparison was between the long term aged samples. Significantly higher values were obtained for the control and untreated rubberised bituminous samples (cured and uncured). However, the stiffness value of the TP1 treated rubberised bituminous sample increased (2086.5 MPa) with ageing showing improvement in its stiffness. In contrast the TP2 treated rubberised bituminous mix stiffness reduced further to 513 MPa. On repetition similar results were obtained. The results show that the stiffness value needs improvement in the case of lightly trafficked areas applications. However, the TP1 treated mix can be utilised for playground and footpath applications after changes in the mix design (such as the type of filler and percentage of waste rubber) to improve its performance. This will be verified in the proposed following study.

3.3.4. Repeated Load Axial (RLA) test

To study the resistance to permanent deformation of the newly developed rubberised bituminous mix, an RLA test was used. Again, the comparison was made among the control sample (no rubber), the control rubberised sample and treated rubberised sample (both aged and unaged state). The results are presented in Figure 13 and 14 for unaged and aged samples respectively.

By comparing Figure 13 and 14 it can be concluded that the deformation of all the samples decreased after ageing compared to the unaged samples. Improvement was observed in the results of the untreated rubberised sample (cured) whereby the axial strain reduced from 50,000 micro-strain to 14500 micro-strain for 3600 pulses. Also, significant improvement was observed in the RLA value of the TP1 treated rubberised bituminous sample with the axial strain reduced from 55,000 micro-strain to almost 40,000 micro-strain for 3,600 pulses. In contrast, for both the untreated rubberised bituminous sample (uncured) and TP2 treated rubberised bituminous sample, the failure occurred at 300 and 1300 pulses respectively, earlier than the completion of the load pulses

(Figure 13). Improvement was observed though in the case of uncured rubberised bituminous sample with an axial strain value of 52,000 micro-strain (Figure 14) compared to the failure that occurred at the value of 73,858 micro-strain following 2100 pulses (Figure 13).

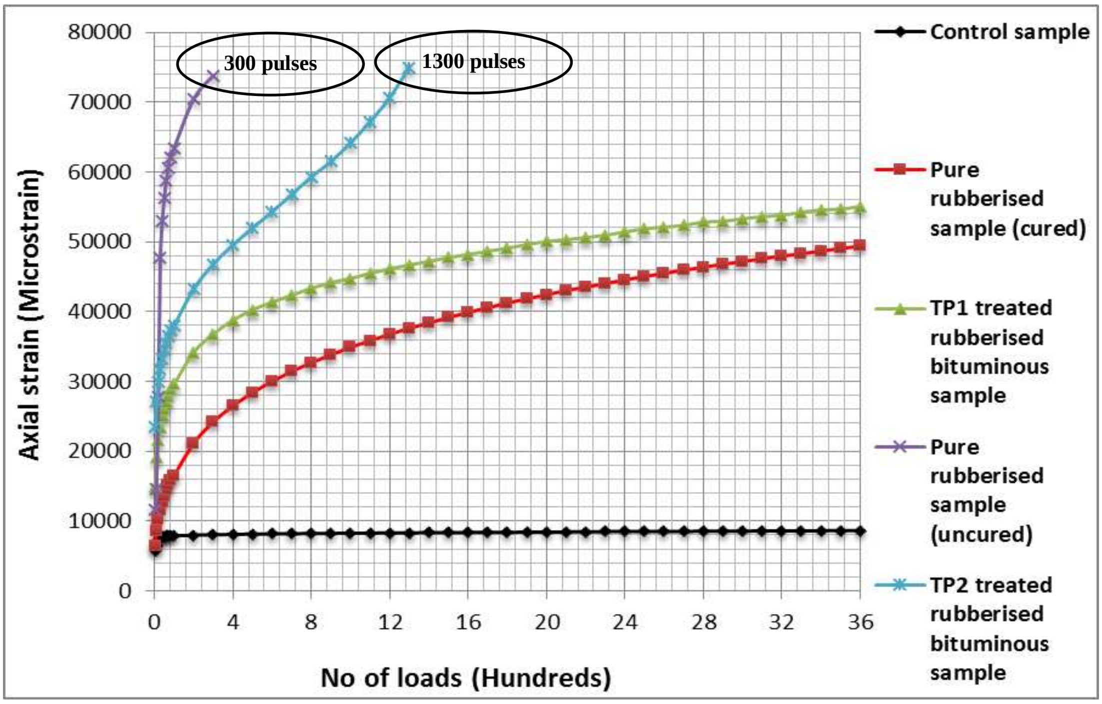


Figure 13: Repeated load axial test results of the unaged control and rubberised samples

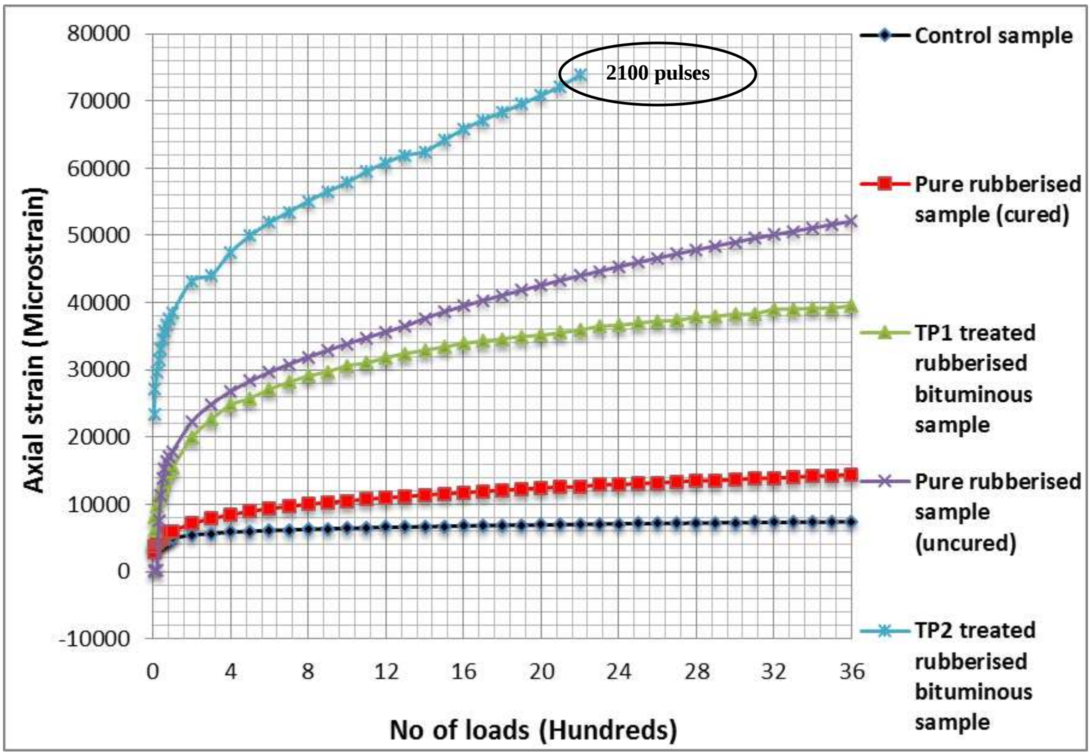


Figure 14: Repeated load axial test results of the aged control and rubberised samples

The results show that the TP1 treated rubberised need improvement in terms of the deformation properties for its application in the light traffic areas but may be suitable for the applications such as playgrounds, footpaths, etc. after minor amendments in the design. This could be achieved through the use of an alternative filler or by the inclusion of fibres into the mix and retested to see the improvement. It is therefore recommended that the future work should utilise fibres in the mix or replace the filler used with the mineral filler such as hydrated limestone. Literature [37-40] suggested that by replacing the ordinary filler from the aggregate source with the mineral filler such as white cement, ordinary Portland cement, hydrated limestone dust, ceramic waste dust, coal fly ash, etc. and adding fibres substantially improves the mechanical properties of the material which might be suitable for light traffic areas, etc. It would be interesting to have further laboratory trials and tests using these fillers with the TP1 treated waste rubber to monitor and analyse the impact of such addition.

4. CONCLUSIONS AND RECOMMENDATIONS

Tests were conducted to monitor and analyse two aspects of the current study. This included:

- The quality of the waste rubber surface treatment to reduce its absorption properties. The tests conducted were the SEM surface analysis of the rubber and Microwave spectroscopy analysis of the bitumen.
- Mechanical properties of the newly designed bituminous mixes by utilising the treated and untreated rubber and comparing it with the control samples through Stiffness modulus test and Repeated load axial test.

The following were the conclusions from the analysis and mechanical test results.

- The SEM analysis in Figure 4 & 5 of the surface treatment showed the existence of the film on the surface of the rubber particle. This indicates the durability of the thin film on the surface under harsh temperature conditions of mixing.
- The microwave spectroscopy analysis of various samples of bitumen such as the pure bitumen, bitumen out of the untreated rubber bitumen blend and bitumen from the treated rubber bitumen blend successfully showed the variation in the bitumen properties when the rubber was mixed with the bitumen. The microwave spectrum obtained for the bitumen from treated rubber bitumen blend showed

the properties close to the pure bitumen demonstrating the effectiveness of the treatment. This provided evidence of the reduction in the absorption properties of the rubber. Whereas, the bitumen from the untreated rubber bitumen blend had a shifted spectrum from the pure bitumen case showing the change in its properties due to the absorption of light fraction from bitumen into rubber.

- The mechanical test results indicates that the mix design need improvement in the following/future study to make it applicable for a range of applications. The results show that the material is only suitable for applications such as indoor and small play areas and possibly walkways and pathways.
- As mentioned in the last section, the mechanical behaviour of the mix can be studied in the subsequent studies to monitor any improvements by replacing the ordinary filler with mineral filler or by the addition of various types of fibres.
- Future work is required on the use of higher percentage of rubber than 10% to make the material more suitable for sensitive applications such as children’s playgrounds, sports track and pitches, etc. that require higher flexibility and softness of the surface with shock absorbing properties.
- Thorough mechanical testing is required to ensure the durability of the material with additional tests such as Head Injury Criterion (HIC), etc. to make it suitable for additional industrial applications such as children’s playground, sports pitches, tennis courts and turfs.
- Field trials along with the modifications in the mix design are also recommended for the newly devised TP1 treated rubberised mix to monitor it over a certain period of time and in a range if weather conditions.
- The results show that the treatment technique has the potential to reduce the absorption properties of the waste rubber and improve the bituminous mix mechanical properties with further modifications in the design. However, further studies with additional chemical treatments and testing is recommended to verify the claim. It would also be interesting to verify the reduction in absorption by analysing the bitumen samples through a suitable existing techniques such as FT-IR.

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REFERENCES

[1] WRAP and BSI. (2012), "PAS 107:2007; Specification for the manufacture and storage of size reduced tyre materials", Copyright © BSI, ISBN: 978-0-580-74112-8, pp. 1-38.

[2] Williams, P.T. (2005), "Waste treatment and disposal; Introduction", Chapter 1, © John Wiley & Sons Inc., ISBN 0-470-84913-4, pp. 1-62.

[3] Jacob, P., Kashyap, P., Suparat, T., and Visvanathan, C. (2014), "Dealing with emerging waste streams: used tyre assessment in Thailand using material flow analysis" Waste Management & Research, Vol. 32 (9), pp. 918-926.

[4] Hernández-Olivares, F., Witoszek-Schultz, B., Alonso-Fernández, M., and Benito-Moro, C. (2009), "Rubber-modified hot-mix asphalt pavement by dry process" International Journal of Pavement Engineering, Vol. 10, No. 4, pp. 277-288(12), Publisher: Taylor and Francis Ltd.

[5] Rahman, M.M., Airey, G.D., and Collop, A.C. (2005), "The mechanical properties of the dry process CRM asphalt mixtures following short-term and long-term ageing" 7th International Conference on the Bearing Capacity of Roads, Railways and Airfields, BCRA, Norway, Trondheim, Workshop 2, pp. W2-W15.

[6] Presti, D.L. (2013), "Recycled tyre rubber modified bitumens for road asphalt mixtures: A literature review" Construction and Building Materials, Volume 49, pp. 863-881.

[7] Airey, G.D., Rahman, M.M., and Collop, A.C. (2003), "Absorption of bitumen into crumb rubber using the basket drainage method" Source: International Journal of Pavement Engineering, Vol. 4, n 2, pp. 105-119.

[8] Cao, W. (2007), "Study on properties of recycled tire rubber modified asphalt mixtures using dry processes" Construction and Building Materials, Vol. 21, Issue 5, pp. 1011-1015.

[9] Al-Nageim, H. And Robinson, H. (2007), "Upgraded waste plastic and rubber aggregates for use in asphalt: A laboratory study" Asphalt professionals.

[10] Walsh, I.D. (2009), "The effect of crumb rubber in hot bitumen", LCMT 2009 8th Annual International Conference on Sustainable Aggregates, Pavement Engineering, & Asphalt Technology, 18th-19th February 2009, Liverpool, United Kingdom.

[11] Navarro, F.J., Partal, P., Martinez-Boza, F., and Gallegos, C. (2005), "Influence of crumb rubber concentration on the rheological behaviour of a crumb rubber modified bitumen" Energy & Fuels, ISSN: 0887-0624, 2005, Vol. 19, n 5, pp. 1984-1990.

[12] Palit, S.K., Reddy, K.S., and Pandey, B.B. (2004), "Laboratory evaluation of crumb rubber modified asphalt mixes", Source: Journal of Materials in Civil Engineering, Vol. 16, n. 1, pp. 45-53.

[13] Huang, Y., Bird, R.N., and Heidrich, O. (2007), "A review of the use of recycled solid waste materials in asphalt pavements" Resources, Conservation and Recycling, Vol. 52, Issue 1, pp. 58-73.

[14] ETRma (2011), "End of life tyres: A valuable resource with growing potential", Copyright ETRma, Published by: ETRma, pp. 1-22.

[15] Davies, R. and P. Heseltine, P. (2005), "An essential guide to BS EN 1176 and BS EN 1177; Children's playground equipment and surfacing", Published by: The Play Inspection Company, <http://www.wicksteed.co.uk/legislation.html> (Feb 10, 2016).

[16] Lee, S., Akisetty, C.K., and Amirkhanian, S.N. (2008), "The Effect of Crumb Rubber Modifier (CRM) on the performance properties of rubberized binders in HMA pavements" Construction and Building Materials, Vol. 22, Issue 7, pp. 1368-1376.

[17] Airey, G.D., Singleton, T.M., and Collop, A.C. (2002), "Properties of polymer modified bitumen after rubber-bitumen interaction" Journal of Materials in Civil Engineering, Vol. 14, No. 4, 344-354.

[18] Read, J. and Whiteoak, D. (2003), "The Shell Bitumen Handbook" Constitution, Structure and Rheology of Bitumen, 5th edition, ISBN: 0-7277-3220-X, Thomas Telford Publishing, London, pp. 31-34.

[19] Xiao, F., Amirkhanian, S.N., Shen, J., AND Putman, B. (2009), "Influences of crumb rubber size and type on Reclaimed Asphalt Pavement (RAP) mixtures" Construction and Building Materials, Vol. 23, Issue 2, pp. 1028-1034.

[20] Shakhnazarli, R.Z., Ishchenko, N.Ya., Nazaraliev, Kh.G., Mamedoy, B.A., and Guliey, A.M. (2009), "Polymer-bitumen compounds with crumb rubber, secondary Polyethylene, and Polyamide fiber waste", Source: Russian Journal of Applied Chemistry, Vol. 82, n. 7, pp. 1310-1313.

[21] Sharma, V. And Goyal, S. (2006), “Comparative study of natural fibres and crumb rubber modified stone matrix asphalt mixtures”, Source: Canadian Journal of Civil Engineering, Vol. 33: n. 10, pp. 134-139.

[22] Yildirim, Y. (2007), “Polymer modified asphalt binders”, Source: Construction and Building Materials, Vol. 21, Issue 1, pp. 66-72.

[23] Frantzis, P. (2003), “Development of crumb rubber reinforced bituminous binder under laboratory conditions”, Source: Journal of Material Science, Vol. 38, Issue 7, pp. 1397-1401.

[24] Yadollahi, G. And Mollahosseini, H.S. (2011), “Improving the performance of Crumb Rubber bitumen by means of Poly Phosphoric Acid (PPA) and Vestenamer additives”, Source: Construction and Building Materials, Vol. 25, Issue 7, pp. 3108-3116.

[25] Ateeq, M., Wylie, S., Al-Shamma’a, A. and Al-Nageim, H. (2012a), “Microwave spectroscopy: a potential technique to analyse bitumen dielectric and physical properties” Measurement Science and Technology, Volume 23, 13pp.

[26] Ateeq, M., Senouci, A., Al-Nageim, H., Al-Shamma’a, A. (2012b), “Microwave spectroscopy for the analysis of absorption properties of treated waste rubber aggregates” Journal of Hazardous, Toxic, and Radioactive Waste, Volume 16, No. 4, pp. 334-342.

[27] Agilent. (2004), “Microwave dielectric spectroscopy workshop: Measure the difference”, Copyright © Agilent technologies Inc., USA, pp. 1-42.

[28] Korostynska, O., Mason, A., Al-Shamma’a, A.I. (2013), “Flexible microwave sensors for real-time analysis of water contaminants” Journal of Electromagnetic Waves and Applications, Volume. 27, Issue. 16, pp. 2075-2089.

[29] Blakey, R., Korostynska, O., Mason, A., and Al-Shamma’a, A. (2012), “Real-time microwave based sensing method for vegetable oil type verification” Procedia Engineering, Volume. 47, pp. 623-626.

[30] Mason, A., Abdullah, B., Muradov, M., Korostynska, O., Al-Shamma’a, A.I., Bjarnadottir, S.G., Lunde, K., and Alvseike, O. (2016), “Theoretical basis and application for measuring pork loin drip loss using microwave spectroscopy” Sensors, Volume. 16, No. 2, p. 182.

[31] Mason, A., Korostynska, O., Ortoneda-Pedrola, M., Shaw, A., and Al-Shamma'a, A. (2013), “A resonant co-planar sensor at microwave frequencies for biomedical applications” Sensors and Actuators A: Physical, Volume. 202, pp. 170-175.

[32] Pozar, D.M. (2005), “Microwave Engineering” Microwave Resonators, 3rd edition, ISBN: 0-471-44878-8, John Wiley & Sons, 278-286.

[33] Pollack, G. and Stump, D. (2002), “Electromagnetism” Waveguides and Transmission Lines, ISBN: 0-8053-8567-3, Copyright © Pearson Education, 523-559.

[34] PD6691. (2015), “Guidance on the use of BS EN 13108, Bituminous mixtures – Material specifications” BSI Standard Publications, ISBN: 978 0 580 83074 7, © The British Standards Institution, pp. 1-88.

[35] BSEN12697-30. (2012), “Bituminous mixtures. Test methods for hot mix asphalt. Part 30: Specimen preparation by impact compactor” British Standard, ISBN 978 0 580 75767 9, © The British Standard Institution, pp. 1-25.

[36] BSEN12697-35. (2004), “Bituminous mixtures- Test methods for hot mix asphalt- Part 35: Laboratory mixing” British Standard, ISBN 978 0 580 59836 4, © The British Standard Institution, pp. 1-10.

[37] Aljassara, A.H., Metwali, S., and Ali, M.A. (2004), “Effect of filler types on marshall stability and retained strength of asphalt concretes” International Journal of Pavement Engineering, Volume 5, Issue 1, pp. 47-51.

[38] Muniandy, R. and Aburkaba, E. (2011), “The effect of type and particle size of industrial wastes filler on indirect tensile stiffness and fatigue performance of stone mastic asphalt mixtures” Australian Journal of Basic and Applied Sciences, Volume 11, Issue 5, pp. 297-308.

[39] Moghaddam, T.B., Karim, M.R., and Abdelaziz, M. (2011), “A review on fatigue and rutting performance of asphalt mixes” Scientific Research and Essays, Volume 6, No. 4, pp. 670-682.

[40] Silva, H.M.R.D. (2008), “Study on the use of bituminous mixtures modified with Acrylic fibres in road pavement overlays” First International Conference on Transportation Infrastructure, iSMARTi. Beijing, China.