A Study of Rubber-REOB Extender to Produce Sustainable Modified Bitumens

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Abstract: Thanks to greater attention to the environment and the depletion of non-renewable resources, the sustainability and the circular economy have become crucial topics. The current trend of pavement engineering is to reduce the use of standard bitumen by replacing it with more sustainable materials such as industrial residues and by-products. In this regard, the present study aims to characterize innovative extended bitumen using recycled materials. Due to promising preliminary results as bitumen modifiers, the powdered rubber from end-of-life tires and the re-refined engine oil bottom (REOB) have been investigated as feasible components of bitumen extenders. Nevertheless, several variables strongly affect the performance of the resulting binder, which cannot be neglected. Hence, this research focuses on the rubber–REOB interaction in order to evaluate their optimum ratio, which may maximize the use and advantages of both recycled materials as suitable partial replacements for bitumen. Various rubber–REOB ratios were considered and investigated by means of low and high frequency nuclear magnetic resonance (NMR) spectrometers and scanning electron microscope (SEM).

Keywords: powdered rubber; re-refined engine oil bottom; bitumen extender; NMR analysis; SEM analysis; bitumen

1. Introduction

The production and construction of road pavements need a substantial amount of energy and non-renewable materials. Therefore, the use of recycled materials and/or by-products seems to be necessary to create a more sustainable future for asphalt mixtures. The recycled materials and by-products that come from construction and demolition waste or urban and industrial waste can be introduced in asphalt mixes as recycled aggregates (e.g., RAP, steel slag, ceramics) instead of only using mineral aggregates [1]; on the other hand, waste polymers and oils can be used at the binder level as additives or modifiers of bitumen. Since the binder has a significant effect on asphalt mixture performances, the modification of bituminous binders has become the mainstream of research in recent decades [2].

Practical experiences and research have shown that rubber from end-of-life tires (ELTs) may be successfully used as bitumen modifiers to improve the binder response over a wide range of temperatures [3]. Without neglecting the several parameters that influence the physico-chemical properties of modified binders such as type, quantity, and characteristics of constituent materials, some studies have highlighted the feasible replacement for styrene-butadiene-styrene (SBS) polymers with recycled rubber [4,5]. The rubberized binder shows good resistance to permanent deformations that turns into a high rutting resistance, which has been evaluated by the use of dynamic shear
rheometer (DSR) device [4,6]. Although, the SBS modified binder has the best resistance to crack, the binder that contains rubber shows the best anti-fatigue response [4]. In addition, based on rheological data, both virgin and waste polymers can decrease the brittleness of modified binders at intermediate temperature, and reduce the resulting stiffness at low temperatures [7]. However, the use of rubber has a disadvantageous aspect which is the overall increase in binder viscosity. This feature is important for pumpability and workability of modified binder [8]. The new candidates to improve low temperature properties and reduce the viscosity of the rubberized binders are oils that can have various origins (i.e., petroleum or bio-based oils, waste or refined used oils) [9]. Previous studies have highlighted the mitigation effect of oil when added to a modified binder regardless of its nature [10–12]. The oil modification alters the rheological and thermal behavior of bitumen, which has been observed through dynamic shear rheometer (DSR) and bending beam rheometer (BBR) analysis [9]. The introduction of oil leads to a decrease in the stiffness of binders, sometimes with adverse effects at high service temperature if overdosed. In detail, the study of [13] regarding the use of re-refined engine oil bottom (REOB) revealed that a limited concentration of the oil unaffected the thermal cracking performance of binders at low temperature and their fatigue cracking resistance at intermediate temperature. However, by increasing the concentration of REOB up to 15%, the binder strength and strain tolerance at intermediate temperature could be significantly influenced. Moreover, a large amount of oil may jeopardize the thermal cracking performance of binders [13]. Another study observed that blending standard bitumen with REOB at a rate of 9% did not compromise asphalt mixture stiffness and ageing [14]. On the other hand, a non-similar ageing susceptibility of fluxed and standard bitumens has been demonstrated, and the different binder responses were attributed to the composition of the various oils [9]. Therefore, the influence of oil has to be investigated deeply to minimize the related risks considering the maximum level that can be used and the variability of oil residues. Both wastes, ELTs and REOB, are engineering materials that represent a resource for further civil engineering applications. The compound of rubber particles and oil may represent a sustainable extender that is able to replace a certain quantity of standard bitumen without compromising the performances of the resulting binder, since they can mitigate their each other drawbacks.

As previously mentioned, the effect of rubber and oil modifications is strictly dependent on the constituent materials [9,15]. As a consequence, the complete characterization of modified binders requires the investigation of the components’ interactions themselves. The rubberized binder is produced with the so-called wet process, during which the rubber particles are thoroughly mixed with bitumen to obtain a ductile and elastic modified bitumen. The interaction of components is made up of two simultaneous phenomena: the partial digestion of the rubber particles into the bituminous matrix and the absorption of the aromatic fraction available in this latter within the rubber itself [16,17]. The absorption of the aromatic fraction from the bitumen into the rubber’s polymer chains is a physical interaction mainly controlled by the rubber particles’ shape and size that causes the rubber to swell and soften [18]. Therefore, during the reaction there is a simultaneous reduction in the oily fraction and the expansion of rubber particles forming a gel-like surface coating [16]. In this form, the particles of rubber are still visible (granular-like appearance) in the composite binder, even if the distance between the particles themselves decreases. If curing is carried out at an excessive temperature and/or for a too long period, the degradation phenomenon becomes prevalent and the rubber particles are totally digested in the bitumen [3].

Based on the promising results obtained so far, the present research pushes for a greater use of recycled materials in bituminous binders with the aim of using rubber and REOB as substitutes for bitumen, and not only as bitumen modifiers. The final objective of this study is the definition of a proper rubber-REOB compound that can replace the 25% by weight of standard bitumen obtaining an extended bitumen. Since the oil used is a petroleum-based material mainly constituted of oily fractions, it was assumed that rubber particles might absorb REOB as they absorb bitumen; this assumption has been used to define the optimum weight proportion of products to produce the extenders. Hence, to maximize the presence of both recycled materials, their interaction was investigated and various
extenders have been produced. Finally, the feasibility of using the selected extenders was evaluated by mixing them with a standard neat bitumen and assessing the rheological responses of the resulting extended bitumens.

2. Materials and Methods

In this study, two recycled materials (i.e., the powdered rubber from ELTs and the re-refined engine oil bottom (REOB)) were used to produce bitumen extenders that were able to replace a specific amount of petroleum bitumen obtaining extended bitumens.

The 50/70 penetration grade bitumen (B-50/70) was used as the reference material and base constituent of the extended bitumen. The powdered rubber (R) was produced from the trituration processes at an ambient temperature of waste tires from cars and trucks after the separation phase of textile and metallic parts of the tires themselves. The maximum dimension of rubber particles was 0.40 mm, while the density was 1.01 g/cm³. The Italian consortium, Ecopneus Scpa, to promote the recycle and the reuse of waste tires, provided the material. The REOB is the by-product of a vacuum tower in a re-refinery plant of exhausted engine oil supplied by Itelyum Srl. This research used and compared two recycled oils (hereinafter called O1 and O2, or Ox if both or one of them were considered alternatively) that were produced in two distinct refinery plants of the same company. Both REOBs had a density approximately equal to 1.00 g/cm³.

Five mixes were prepared per each REOB (i.e., O1 and O2) by varying the mass of each recycled materials. In particular, the considered R-REOB ratios were:

1. R:Ox = 3:1
2. R:Ox = 2:1
3. R:Ox = 1:1
4. R:Ox = 1:2
5. R:Ox = 1:3

All extenders were prepared by mixing the pre-heated materials. The first step consisted of warming up both materials at 130 °C in the oven; the Ox for at least 1 h 30', while R for 15'. Then, the Ox was added to the R portion and the recycled materials were mixed by the use of a propeller mixer at a rate of about 600 ÷ 650 rpm for 15'. The mixing phase was performed at a temperature equal to 130 °C. In order to keep the blend at a constant temperature during the mixing process, the container was immersed in a glycerine bath, which was continuously warmed up by a heating plate.

The resulting blends underwent nuclear magnetic resonance (NMR) and scanning electron microscopy (SEM) analysis to establish the optimum R–REOB ratio, which has been considered as the maximum amount of REOB that can be absorbed by R. The optimal proportion aims to maximize the use of both recycled materials. The spectroscopic analysis was carried out by two NMR instruments that operated at two different proton frequencies: a low resolution NMR (L-NMR) at 15 MHz and high resolution NMR (H-NMR) at 300 MHz [19]. The L-NMR is a homemade instrument, which has been used to perform relaxation experiments at ambient temperature; while, the H-NMR is a Bruker Avance 300 (Germany) that allowed the analysis of diffusion. Thanks to the software Mathematica, the collected data were post-processed and the spin–spin relaxation time (T₂) of all extenders were determined by fitting with an exponential equation. This relaxation time is concerned with the exchange of energy among spins without being affected by the surrounding environment [20]. The H-NMR spectra and diffusion properties of all samples were evaluated at the production temperature of 130 °C. The specimens do not need any specific conditioning before performing the tests. The scanning electron microscope (SEM, JEOL JXA-8230, Japan) allowed the investigation of the R–REOB blends’ morphological structure. The tests were run in vacuum mode on the pre-conditioned samples, which were sputter coated with a thin film of graphite. Various magnifications were considered to collect the images of all specimens.
Thanks to the definition of the optima R–REOB ratios (that is 1:1 and 1:2), the extenders were used to produce four extended bitumens replacing 25% by the total weight of the binder, and their rheological response was investigated. The list of constituents of the four extended bitumens and their percentages are reported in Table 1. The conditions of the extenders’ production have been defined in preliminary studies that have taken into consideration the optimal mixing temperature. The production of extended bitumens requires the pre-heating of constituents before mixing them. Both materials (i.e., optima extenders and bitumen) were warmed up at 160 °C, the R–REOB blends for more than 1 h and bitumen for more than 1 h 30’. They were mixed by the use of a propeller mixer at a constant rate of 800 rpm for 1 h. During the mixing phase, the materials were kept warm by the use of a heating plate.

| Extended Bitumen | Percentage of Constituent Materials |
|------------------|-------------------------------------|
|                  |          B   |           R   | O1/O2   |
| BRO1_1:1        | 75.0      | 12.5       | 12.5    |
| BRO2_1:1        | 75.0      | 12.5       | 12.5    |
| BRO1_1:2        | 75.0      | 8.3        | 16.7    |
| BRO2_1:2        | 75.0      | 8.3        | 16.7    |

The rheological analyses were carried out using a dynamic shear rheometer (DSR, Anton Paar MCR 302, Austria). This instrument has been used to investigate the extended bitumens’ behavior over a wide range of frequencies and temperatures thanks to the amplitude sweep and frequency sweep tests. The amplitude sweep test allows the definition of the linear visco-elastic (LVE) range of each extended bitumen, which is one of the input data to perform the frequency sweep test. During the amplitude sweep test, all samples were subjected to a variable strain that increased in a logarithmic manner from 0.1% to 15%, while the frequency was constant and equal to 1.59 Hz. The test was carried out at three temperatures (10, 30, and 60 °C) to define the most restrictive non-destructive deformation range. Thereafter, the extended bitumens underwent the frequency sweep test. Each specimen was subjected to the corresponding maximum deformation (LVE range) applied at different angular frequencies that logarithmically increased from 0.1 Hz to 10 Hz. The tests were performed at six temperatures: 10, 20, 30, 40, 50, and 60 °C. Following the standard EN 14770, the rheological analysis was carried out using the plate–plate configuration; plates with a diameter of 8 mm and a gap equal to 2 mm were chosen to perform all tests.

3. Results and Discussion

3.1. Nuclear Magnetic Resonance Measurements—T2 Relaxation Time and Diffusion Coefficient

The basic of spectroscopic analysis is the evaluation of the nuclei behavior that underwent an inhomogeneous external field, which perturbs the equilibrium in a steady uniform magnetic field. In fact, at equilibrium, nuclei are distributed among the energy levels according to the Boltzmann distribution with a specific net magnetization vector, but this state can be disrupted by the absorption of radio-frequency energy such as that caused by a NMR instrument [21]. After the removal of the disruption field, the nuclear spin system returns to its equilibrium state and the transverse component of the magnetization vector exponentially decays. The time constant T2 characterizes the signal decay, which is called spin–spin relaxation time because it is related to the exchange of energy between spins via flip-flop mechanisms [22]. Usually, the collected signal decay is an envelope of multi-exponential attenuation since the relaxation time varies in the sample due to the heterogeneity or surface relaxation differences [23].

In this study, the relaxation time T2 of pure oils and extenders was evaluated by the use of the L-NMR device [24]. The trend of spin–spin relaxation time and the resulting T2 value of both pure
oils and extenders are reported in Figure 1 and Table 2, respectively. In general, a short $T_2$ time corresponds to more rigid supra-molecular particles; while, higher $T_2$ times refer to low intra-molecular interactions [25]. The pure oils show the highest relaxation time over the corresponding extenders made with themselves, and it means a lower intra-molecular interactions of Ox. The introduction of rubber particles into Ox leads to a decrease in the $T_2$ values. The oil absorption by the rubber limits the mobility of the oil’s molecules, therefore the $T_2$ relaxation times, which reflects a more rapid relaxation decay. This trend is more evident in the extenders made with O1, which means a higher compatibility between the rubber and O1 than the R-O2 compounds. The relaxation time of the O1-extenders was reduced from 5.39×$10^{-3}$ s for O1 to about 4.00×$10^{-3}$ s for those extenders with an R content up to 50% by total weight. Then, more changes in the $T_2$ value can be observed in samples with a higher quantity of R than O1. In fact, their curves almost overlapped each other. On the other hand, the samples of R:O2 = 1:3 and R:O2 = 1:2 and pure O2 had similar $T_2$, as shown by the overlapping curves (see Figure 1). The amount of R in these two extenders does not seem to affect their relaxation time more than the reference one of pure O2. When the quantity of R is equal or higher than 50%, the reduction in $T_2$ values can be observed. Based on the collected data, the R-REOB ratios 1:1 and 1:2 represent the latest ratios after which some changes occurred in the relaxation time. Therefore, these two R-REOB proportions were defined as optimal.

![Figure 1](image)

**Figure 1.** Trend of spin–spin relaxation time of oils and extenders: (a) O1 and O1-R blends; (b) O2 and O2-R blends.

| Samples       | Relaxation Time $T_2$ [s] |
|---------------|--------------------------|
|               | O1                       | O2                       |
| Ox            | 5.39×$10^{-3}$           | 6.49×$10^{-3}$           |
| R:Ox = 3:1    | 2.71×$10^{-3}$           | 3.59×$10^{-3}$           |
| R:Ox = 2:1    | 3.00×$10^{-3}$           | 3.69×$10^{-3}$           |
| R:Ox = 1:1    | 4.22×$10^{-3}$           | 4.90×$10^{-3}$           |
| R:Ox = 1:2    | 4.21×$10^{-3}$           | 6.33×$10^{-3}$           |
| R:Ox = 1:3    | 4.07×$10^{-3}$           | 6.38×$10^{-3}$           |

The NMR measurements with the self-diffusion H-NMR probe allowed the evaluation of the self-diffusion coefficient (D) of oil into the extenders. The present measurements provide information...
concerning the molecular dynamics and spatial dimensions of the particles and cavities in order to establish the particles’ mobility and the microstructures of the samples [26]. The NMR spectra were obtained from Free Induction Decay by means of the Fourier transform. Path widths equal to $\pi/2$ and 16 scans were used to perform all of the NMR tests. The self-diffusion coefficient was determined directly by the use of a standard pulsed gradient stimulated echo (PGStE) sequence with a mono-exponential fitting [27]. The self-diffusion coefficient can be ascribed to the average diffusion phenomena of oil onto (external) and into (internal) the R particles. The self-diffusion coefficients of the extenders are shown in Figure 2. In theory, the self-diffusion coefficients should decrease with the addition of R because it reduces the particles’ mobility. In fact, the extenders at ratios equal to 2:1 and 3:1 showed low values of the self-diffusion coefficient for both O1 and O2 samples. The oil self-diffusion coefficient jumped at the ratio of 1:1. Hence, the behavior was in agreement with the higher mobility of the oil when the maximum absorption was reached.

![Figure 2. Self-diffusion coefficients (D) of the bitumen extenders.](image)

3.2. Scanning Electron Microscopy Analysis—Morphological Structure

The R and extenders underwent SEM analysis to evaluate their morphological structures. The images of the samples are shown in Figure 3. The increasing amount of oil in the samples is clearly visible moving from Figure 3a, that is, rubber particles without any oil, to Figure 3j,k, which contain a triple quantity of Ox than R. The sequence of images shows how the rubber may first absorb Ox; then, the amount of oil became high and started covering the R particles. Since the optimum R–REOB ratio is defined as the maximum amount of oil that can be absorbed by R, the extenders R:Ox = 1:1 and R:Ox = 1:2 can be identified as the optimal. The visual investigation of the morphological structures of samples confirmed the results obtained from spectroscopic analysis.
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Figure 3. Rubber and extenders images acquired by scanning electron microscope with a magnitude of about 150x. (a) R; (b) R:O1 = 3:1; (c) R:O2 = 3:1; (d) R:O1 = 2:1; (e) R:O2 = 2:1; (f) R:O1 = 1:1; (g) R:O2 = 1:1; (h) R:O1 = 1:2; (i) R:O2 = 1:2; (j) R:O1 = 1:3; (k) R:O2 = 1:3.

3.3. Dynamic Shear Rheometer Investigation—Rheological Behavior

The rheological responses of extended bitumens were investigated and compared with the behavior of the reference material in order to verify the possibility of using the extenders as a replacement for neat bitumen. Hence, we checked that the extended bitumens did not show performance degradations at the binder level. At first, the amplitude sweep test was carried out to define the linear viscoelastic (LVE) range of neat and extended bitumens, and the most restrictive ranges were defined at 10°C. The limits of samples non-destructive deformation that corresponded to the 95% of initial storage modulus were:

1. \( \gamma \text{ BRO1}_1:1 = 1.61\% \)
2. \( \gamma \text{ BRO2}_1:1 = 1.51\% \)
3. \( \gamma \text{ BRO1}_1:2 = 1.46\% \)
4. \( \gamma \text{ BRO2}_1:1 = 1.14\% \)
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5. \( \gamma_{B-50/70} = 1.61\% \)

The \( B-50/70 \) and \( BRO1_{1:1} \) had the same LVE limit; it seems that the substitution of standard bitumen with the compound O1-R in the proportion 1:1 does not weaken the resulting binder while the same extender made with O2 reduced the LVE limit of the binder, leading it to withstand a lower deformation until structural changes occur. Regarding the effect of different R–REOB ratios, double the amount of REOB than R into the extender strongly influences the response of binders, and the results confirmed the more detrimental effect of O2 than O1.

The complex shear modulus (\( G^* \)) and phase angle (\( \delta \)) master curves obtained from the frequency sweep tests are shown in Figure 4. Concerning the complex shear modulus master curves, all extended bitumens showed a stiffness reduction with respect to \( B-50/70 \) at high frequencies that corresponded to low temperatures. Lower values of \( G^* \) may turn into a greater thermal cracking resistance, which may be related to the addition of REOB. At intermediate conditions, the \( G^* \) values of extended bitumens were still lower than \( B-50/70 \); however, the differences between the binders decreased. By decreasing the frequencies, an inverted trend could be observed in the \( G^* \) master curves. About all of the extended bitumens showed a greater complex modulus than neat bitumen at low frequencies or high temperatures; only the \( BRO1_{1:1} \) sample had a similar response of \( B-50/70 \) and their master curves overlapped. The higher values of \( G^* \) at low frequencies means that almost all extended bitumens can better withstand permanent deformations. This improvement may be ascribed to the presence of R; as a matter of fact, the binders made with R–REOB ratio equal to 1:1 had a greater stiffness than those made with a ratio 1:2 over all tested frequencies. Nevertheless, the samples \( BRO1_{1:1} \) and \( BRO1_{1:2} \) showed the opposite behavior at low frequencies/high temperature, which could be related to the production and/or test issues (e.g., non-well homogenization of components or the sample is not representative).

On the other hand, the phase angle master curves of the extended bitumens showed lower values than that of neat bitumen, especially at low frequencies or high temperature. The introduction of R particles improves the elastic response of all bituminous binders. Moreover, the addition of a polymer (i.e., R) leads to changes in the shape of the binders’ phase angle master curves. The curves of the extended binders showed two different slopes, while the curve of the neat bitumen was continuous.
This research aimed to define suitable bitumen extenders by the use of rubber from ELTs and REOB maximizing the quantity of both recycled materials used. Furthermore, the feasibility of using these materials as bitumen extenders, replacing 25% by weight of bitumen itself, has been studied.

Thanks to the NMR and SEM measurements, the optimum proportion of the two recycled materials was determined; both spectroscopic and imaging investigations confirmed the ratios R:Ox = 1:1 and R:Ox = 1:2 as the optimal to maximize the quantities of both recycled materials. Hence, the NMR and SEM measurements were found to be useful to study the R–REOB interactions.

The rheological results of extended bitumens by means of DSR are promising. The partial substitution of standard bitumen by the use of R–REOB blends can improve the performance of binders at low temperature; most probably the addition of REOB, which is a softening agent, leads to an enhancement of their thermal cracking resistance. The extended bitumens have acquired a greater elasticity at all tested conditions, which can be related to the introduction of rubber. In addition, the waste polymers may improve the binder responses at high temperature; however, one extended bitumen did not show greater resistance to permanent deformation.

Due to the variability of the components used and the complexity of interactions that takes place between constituent materials, further studies are necessary to fully understand the effect of each added product and ensure good performances of the resulting extended bitumen. Furthermore, other materials can be used as constituents of the bituminous binders, which should be investigated.

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