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## Recycled bio-sourced glycerol and diglycerol for asphalt release agents (ARA)

Peter Mikhailenko<sup>a,b,\*</sup>, Alexandra Bertron<sup>a</sup>, Gildas Nyame Mendendy Boussambe<sup>c</sup>, Romain Valentin<sup>c</sup>, Zéphirin Mouloungui<sup>c</sup> and Erick Ringot<sup>a,d,e</sup>

<sup>a</sup>Laboratoire Matériaux et Durabilité des Constructions (LMDC) – Génie Civil, Université Paul Sabatier, Toulouse, France; <sup>b</sup>Centre for Pavement and Transportation Technology (CPATT) – Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, Canada; <sup>c</sup>Laboratoire de Chimie Agroindustrielle (LCA) – Chimie Agro-Industrielle, INP-ENSIACET4, Toulouse, France; <sup>d</sup>LR Vision, Castanet-Tolosan, France; <sup>e</sup>Kemerid, Castanet-Tolosan, France

The objective of this study is to develop bio-sourced waste chemicals for use as asphalt release agents. Glycerol was extracted from bio-sourced waste and transformed by transesterification into the surfactants undecenoates of glycerol (MUG) and undecenoates of diglycerol (MUDG). They were composed of glycerol, monoglycerol, diglycerol, triglycerol, tetraglycerol and water. The formulations were mixed separately with water at quantities of 5–50%, along with acetone and commercial bio-sourced ARAs in order to observe the effects. The formulations were subjected to performance testing with the asphalt slide test, finding significant reduction in adhesion for a number of different formulations. The interaction of the formulations with bitumen was tested by the bitumen degradation test, which was combined with FTIR ATR analysis, finding that the formulations do not dissolve the bitumen, but rather were adsorbed by the bitumen. The effects on asphalt mix of the best performing formulation, MUG at 20% in water, was tested by indirect tensile strength, determining that the formulation was acceptable for use in the field.

**Keywords:** asphalt release agents; asphalt testing; bio-sourced; FTIR analysis; glycerol; undecylenic acid

### 1. Introduction

The growing health and environmental concerns brought on by the use of petroleum-based products in the construction industry have necessitated the development of safer alternatives. Infrastructure, especially the transportation sector, uses many petroleum products. These uses include fuel (Esteban, Riba, Baquero, Puig, & Rius, 2012), asphalt pavement construction, where petroleum products have traditionally constituted the binder for the mix as well as additives like rejuvenating agents (Romera et al., 2006), along with various agents used in the construction process including bitumen removers and asphalt release agents (ARAs) (Mikhailenko, Ringot, Bertron, & Escadeillas, 2016). At this time, with growing environmental and workplace health concerns (Acton, 2013; Mikhailenko & Baaj, 2017), there is a growing impetus to replace

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\*Corresponding author. Email: [petermikhailenko@gmail.com](mailto:petermikhailenko@gmail.com)

petroleum base agents with bio-sourced and biodegradable substitutes (Mikhailenko, Bertron, & Ringot, 2016).

ARAs are sprayed on surfaces used in asphalt construction such as truck beds, pavers, finishers and tools, in order to prevent bitumen from sticking to them (Scardina, 2007; Tang & Isacsson, 2006). For ARAs, the traditional agent – diesel fuel – has seen a significant reduction in use due to the danger of runoff to the environment surrounding the construction site and posing a hazard to worker health, which has necessitated the development of bio-sourced alternatives (Davies, 2005; Mahr, Okabe, & Ito, 2003; Zaki & Troxler, 2013). These ARAs are said to function as substrates, creating a barrier between the asphalt and the surface of application.

While these agents have been shown to be less harmful than diesel to user health and the environment, they have been found at times to be less effective than diesel in reducing the adhesion of bitumen to surfaces (Tang, 2008). ARAs that have been based on organic C18 esters are seeing wide use in France as bio-sourced alternatives (Mikhailenko, 2015). While the damage to the asphalt that they can have been shown to be less than that for diesel, the results have been varied, with some agents causing significant bitumen degradation (Mikhailenko, Bertron, et al. 2016).

Prior to this study, the authors (Mikhailenko, Ringot, et al., 2016) developed test methods – based on the US ARA standards in (“NTPEP Evaluation of Asphalt Release Agents,” 2014) – in order to quantify the performance and potential damage to asphalt of ARAs. The asphalt slide test (AST) was developed to determine the best performing ARA by sliding hot asphalt down a plate with the ARA applied. The safety consisted was tested by indirect-tensile strength (ITS), which consisted of an asphalt cylinder in contact with the agent in ITS as well as the bitumen degradation test (BDT), which consisted of submerging a bitumen sample in the agent. Using this testing program, two types of mechanisms for ARAs were highlighted: (i) the softening of the bitumen between the mixture and metal and (ii) the formation of a substrate (barrier) layer between the bitumen and metal. The substrate or barrier ARAs were determined to be preferable due to (i) causing less damage to the asphalt, (ii) the reduction in the need to clean the surface of the truck bed or tools and (iii) the possibility of using a single agent application for multiple occasions (Mikhailenko, Bertron, et al., 2016).

Glycerol as a bio-sourced compound has been used in several industrial chemicals (Leoneti, Aragão-Leoneti, & de Oliveira, 2012), including ARAs (Artamendi, Allen, Ward, & Phillips, 2012; Dituro, Lockwood, Dotson, & Fang, 2002; Lockwood, Dituro, Dotson, & Fang, 1999; Zanzotto, Vacin, & Stastna, 2003), although the performance of these ARAs has not been verified. The advantages of glycerol-based agents are their biodegradability, water retention and surfactant properties (Leoneti et al., 2012). Additionally, glycerol is often available as a secondary waste product of industrial processes such as biofuel production (Ma & Hanna, 1999), being a by-product to the main product of production. Therefore, the use of glycerol in industrial products can also contribute towards bio-waste reduction.

The objective of this paper is to develop glycerol-based formulations and test their performance for use as barrier-type ARAs. The development consists of: (i) formulation of glycerol-based compounds, (ii) fabrication of ARA candidate formulations by mixing the compounds with water and other substances, (iii) investigation of the chemical interaction of the formulations with the bitumen (iv) determination of the performance of the formulations as ARAs followed by their optimization in terms of the water content. The testing of ARA performance was done by the AST. The testing of the damage to asphalt of the ARAs consisted of ITS and BDT. The chemical analysis was conducted by Fourier Transformed Infrared Spectrometry (FTIR).

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Bitumen

The bitumen used for testing and in the asphalt was Total 35/50 as classified by EN 12591, indicating a penetration (ASTM D5-EN 1426) value of between 3.5 and 5.0 mm.

#### 2.1.2. Asphalt mix

The asphalt mixes (BBSG 0-10 classe 3 by NF EN 13108-1) were manufactured in accordance with EN 12697-35 + A1 with Total 35/50 bitumen and limestone/silica aggregates. The aggregates consisted of coarse aggregates, fine aggregates and limestone filler that were graded in accordance with EN 13108-2.

#### 2.1.3. ARA candidate formulations

Glycerol can be extracted from biological waste sources, which can include biological waste from the production of corn, rapeseed and duck fat or from agricultural waste in the process of biodiesel production (transesterification reaction). This produces biodiesel with glycerol being a by-product. Diglycerol is then produced from the etherification of glycerol using a catalyst (Charles, Clacens, Pouilloux, & Barrault, 2003; Martin & Richter, 2011). These two bio-based molecules were synthesised with undecylenic acid by direct esterification reaction as a kind of solvo-surfactants. All of molecules were characterised by CPG (Gaurat et al., 2016; Nyame Mendendy, Boussambe, Valentin, & Mouloungui, 2015). Figure 1 shows the synthesis route to obtain the MUG and MUDG families. On the industrial scale, the processes would occur at a chemical plant.

Glycerol undecenoates (MUG) and diglycerol undecenoates (MUDG) are glycerol-based and diglycerol-based compounds, respectively, prepared by reacting glycerol (C11) and diglycerol (DiC11) with undecylenic acid that transforms into a solution of three by-products with surfactant properties (Figure 2).

The by-products for the transformation of glycerol are glycerol monoundecenoate (G MonoC11), glycerol diundecenoate (G DiC11), glycerol triundecenoate (G TriC11) and

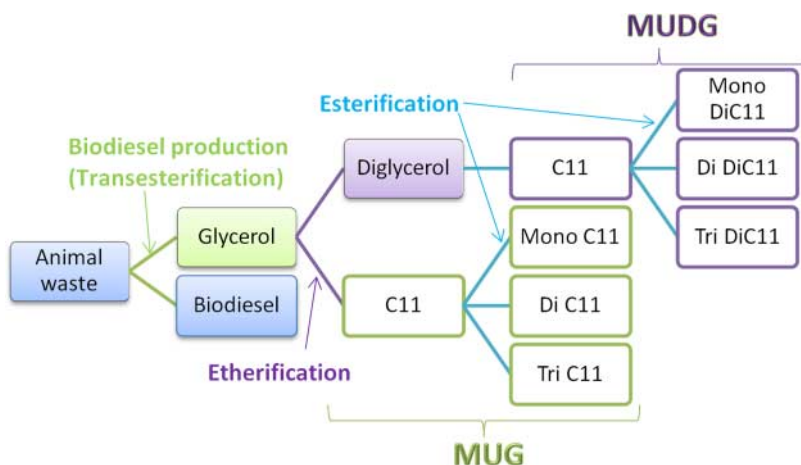


Figure 1. Chemical transformations involved in the production of MUG and MUDG.

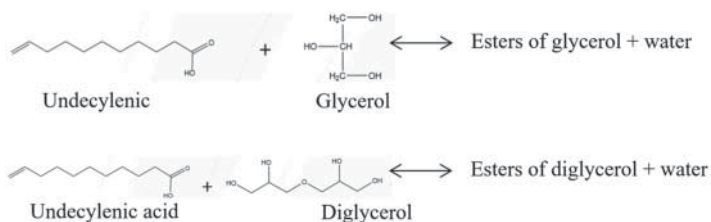


Figure 2. Esterification reactions of glycerol and diglycerol with undecylenic acid.

Table 1. Composition of glycerol-based formulations (Nyame Mendendy Boussambe, 2015).

Compound	MUG (Glycerol undecenoates)	Compound	MUDG (Diglycerol undecenoates)
C11	6.9%	C11	6.4%
G MonoC11	66.0%	DiG MonoC11	64.2%
G DiC11	26.0%	DiG DiC11	24.9%
G TriC11	0.9%	DiG TriC11	4.4%

Table 2. Chemical structure for MUG and MUDG components (Nyame Mendendy Boussambe, 2015).

Compound	Branch	Chemical structure
MUG	Glycerol MonoC11	
	Glycerol DiC11	
	Glycerol TriC11	
MUDG	Diglycerol MonoC11	
	Diglycerol DiC11	
	Diglycerol TriC11	

residual undecylenic acid (C11). For the transformation of diglycerol, the by-products consisted of diglycerol monoundecenoate (DiG MonoC11), diglycerol diundecenoate (DiG DiC11) and triundecenoate (DiG TriC11) along with residual undecylenic acid (Table 1). The structure of the by-products is described in Table 2.

MUG is a white semisolid at room temperature while MUDG is a yellow liquid. The melting point for MUG is 40–45°C. In addition to the base compounds, MUG and MUDG contained approximately 20 and 25% water, respectively, after production.

## **2.2. Performance as ARA by AST**

The ARA Performance Evaluation Apparatus (ARA-PEA) was developed for the performance of ARAs in reducing the adhesion between bitumen and construction materials as described in Mikhailenko, Ringot, et al. (2016). The AST involves spraying an ARA over an area of  $21 \times 40$  cm on a horizontal steel plate, so that the ARA is as evenly distributed as possible at around  $65 \pm 10$  mL/m<sup>2</sup>. This is followed by placing  $1200 \pm 10$  g of hot asphalt mix ( $150 \pm 10^\circ\text{C}$ ) on the surface of the plate, so that is spread out as evenly as possible. The plate is maintained horizontal, and a sheet of wax paper is placed on top of the asphalt mix to prevent sticking, followed by a wooden board ( $21 \times 40$  cm, 883 g). On top of the board, a load of 20 kg is placed creating a distributed pressure on the asphalt mix of 2.5 kPa. This simulates the transportation of the asphalt mix where there is a pressure on the asphalt mix in contact with the truck bed from the asphalt mix resting on top. The plate rests horizontally for 30 min, after which it is placed on the ARA-PEA, which heats the plate at 60°C and immediately inclined at 45°, simulating the discharge of the asphalt mix from the truck. The plate is heated underneath to simulate the heat on the truck bed due to the effect of having hot asphalt on it for an extended period of time (Mikhailenko, Ringot, et al., 2016). With the application of an ARA, the asphalt mix falls off the plate, and from this action, the following data can be taken for judging the performance of the ARA:

- The retention time that it takes the mixture to slide down after the plate is inclined.
- The residual mass of asphalt residue left on the plate;
- The nature of the asphalt residue left on the plate by image analysis;

The retention time for the asphalt mix has a high variability due to all of the variables that are present in the process, including the difficulty in applying the ARA evenly over the surface of the plate. The ARAs have varied viscosities, with the lower viscosity agents (such as diesel) spreading more evenly on the plate, so it is important not to have the viscosity too high so that the agents can be easily applied.

The residual mass is the more reliable indicator of ARA performance. It would correspond to either: (i) to the mass of residual bitumen that would need to be cleaned off the surface of the truck bed, with higher mass increasing required workload in the case of a dissolving ARA or (ii) a significant mass of ARA remains on the truck bed and can be left for the next asphalt load, increasing time between ARA application and reducing the required quantity of product in the case of a barrier or substrate ARA. With the image analysis being able to tell is if the mass includes residual bitumen (Mikhailenko, Bertron, et al., 2016). Two to four tests were conducted for each agent, depending on the variability of the first two tests.

## **2.3. Effects of agents on asphalt mix**

The propensity of the ARA to degrade bitumen and asphalt, as well as the nature of these interactions, needed to be evaluated before they could be determined to be suitable for road construction.

### 2.3.1. BDT with FTIR–ATR analysis

The degradation of bitumen directly by the ARA is determined by the BDT, previously developed in Mikhailenko, Ringot, et al. (2016). The samples (1–2 for each agent) were prepared by pouring  $10 \pm 1$  g of hot bitumen, heated at  $160 \pm 5^\circ\text{C}$  for 2 h, into circular silicon moulds. This produced “cone with flat top” shaped samples, with the dimensions:  $\text{Ø}37 \pm 0.5$  mm top,  $\text{Ø}31 \pm 0.5$  mm bottom and  $h = 10 \pm 0.5$  mm. The samples were left to cool for  $8 \pm 4$  h, after which they are demoulded and weighed to the nearest 0.01 g. The samples were placed into 150 mL graduated glass beakers of known mass, and the agent was poured over it so that the bitumen sample was completely (approximately 18 g of product, depending on its density). The sample was left for 24 h at a temperature of  $20 \pm 1^\circ\text{C}$ , after which, the solution was collected for FTIR analysis, with the bitumen sample now sticking to the bottom of the beaker. The sides of the beaker above the bitumen sample were wiped with a cloth and the remains of the samples are weighed to the nearest 0.01 g. The bitumen degradation (BD%) is taken as the difference between the mass of the bitumen sample before ( $B_B$ ) and after ( $B_A$ ) the test as shown in Equation (1).

$$\text{BD}\% = 100\% \times (B_B - B_A)/B_B. \quad (1)$$

The liquid collected from the beaker was subject to FTIR – Attenuated Total Reflectance (ATR) with a PerkinElmer Spotlight 400. The liquid left in the beaker is mixed and sampled with a pipette. Around 0.1–0.4 mL of the liquid was poured with the pipette on a Germanium crystal so that it was completely covered, and an analysis was effectuated 16 times with a  $4\text{ cm}^{-1}$  resolution with a range of  $4000\text{--}600\text{ cm}^{-1}$  for each agent. The objective of the test was to gain more information on the severity and the nature of the chemical modification of the bitumen by the ARA. The spectra of the original ARA were compared with the spectra for the solution after the BDT test. This, in turn, was compared with the spectrum for the bitumen.

### 2.3.2. Measuring the reduction in resistance in ITS of asphalt mix in contact with the agents

The effects of ARA on the mixture was observed by resistance in ITS as developed previously. The mixture was heated so that it was at  $150 \pm 10^\circ\text{C}$  before compaction and placed in the mould. The asphalt mix was compacted by a piston pressed (pre-heated to  $150 \pm 10^\circ\text{C}$ ) on the asphalt mix through a compressor and maintained for 3 min at a constant pressure of 2.5 MPa in order to attain a 4–8% voids content in accordance with NF P 98-150-1 for this mixture. The samples produced were  $\text{Ø}100$  mm pills, with a height of  $62 \pm 2$  mm and a plain surface on either side. The ARA was applied at 1 mL in the centre of the sample by a graduated pipette just before compaction of the asphalt mix.

The resistance was measured by ITS, which placed the cylindrical sample on its tangential side and proceeded to load it from the top uniaxially creating tension forces in the middle of the sample. The samples were tested seven days after the application of the ARA and the loading rate is kept at 1.27 mm/min. The tensile strength  $T$  can be derived from the maximum rupture force  $P$ , the thickness of the sample  $t$ , and the diameter of the sample  $d$ , as shown in Equation (2).

$$T = \frac{2P}{\pi dt}. \quad (2)$$

The degradation of the asphalt mix by the ARA from indirect tensile loading is taken as the reduction in resistance (RR%). The reduction of resistance represents the difference between the maximum resistance in tensile strength ( $T_{\text{ARA}}$ ) of the samples treated with an ARA and the



control ( $T_C$ ) samples as described in Equation (3) (Mikhailenko, Ringot, et al., 2016). Three samples were tested for each agent.

$$RR\% = 100\% \times (T_C - T_{ARA})/T_C. \quad (3)$$

### 3. Results

#### 3.1. Performance as ARA

The MUG compound was mixed with water at additions of 5%, 10%, 15%, 20%, 30% and 50% for testing with in AST. The MUG was also mixed with acetone at 10% in order to observe the effects of MUG mixed with a highly volatile compound. Additionally, it was mixed with ARA 1 – an ester-based commercial ARA observed in a previous study (Mikhailenko, Bertron, et al., 2016) – in order to observe the combined effects of the two types of agents. The images of the plates after the test are shown in Figure 3 while the residual mass and time to beginning of slide results are shown in Table 3.

For the formulations with water, the MUG was able to create a barrier between the plate and the asphalt – as with the commercial barrier-type agent (ARA 4) tested in Mikhailenko, Bertron, et al. (2016), as can be seen from no bitumen being present on the plate. In the case of MUG 5 H 95, where the MUG was too diluted, and so was not able to form a barrier between the bitumen and the plate. While having longer times to beginning of slide (15–325 s) than for AST than C18 ester-based ARAs tested in Mikhailenko, Bertron et al. (2016), the MUG compositions had much lower residual masses (0.08–1.41 g/m<sup>2</sup>).

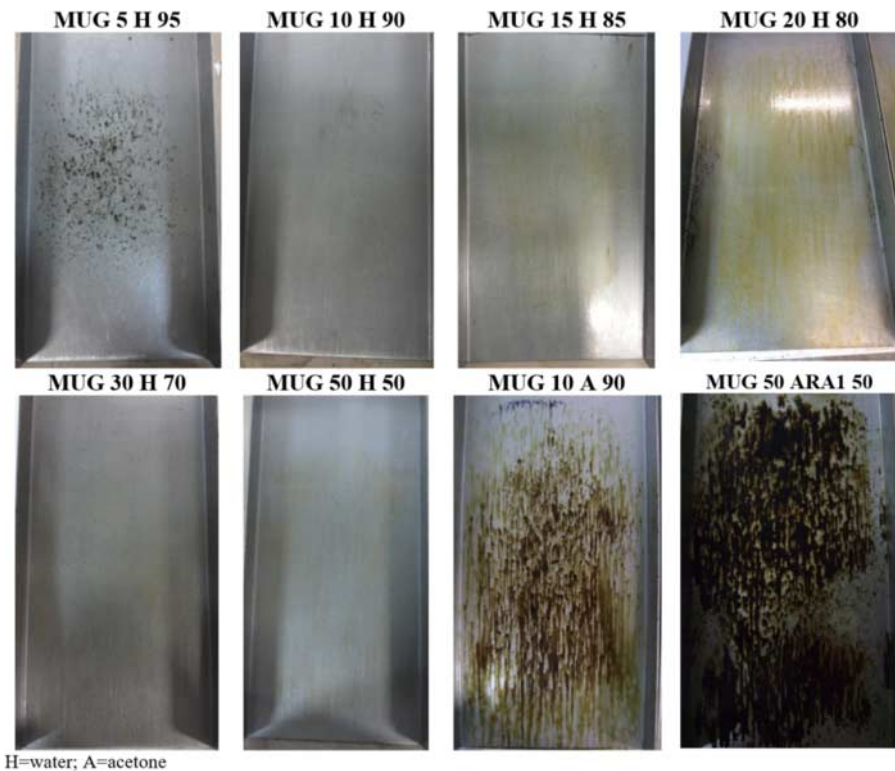


Figure 3. Images of plates after AST for MUG-based formulations.

Table 3. Results of AST for MUG-based formulations.

Formulation	Residual mass (g/m <sup>2</sup> )	Std Dev $\sigma$	Time to beginning of slide (s)	Std Dev $\sigma$
MUG 5 H 95	0.08	<i>0.07</i>	325.0	<i>63.6</i>
MUG 10 H 90	0.12	<i>0.07</i>	73.3	<i>23.2</i>
MUG 15 H 85	0.57	<i>0.26</i>	30.3	<i>31.0</i>
MUG 20 H 80	0.86	<i>0.15</i>	15.7	<i>3.8</i>
MUG 30 H 70	0.86	<i>0.24</i>	50.5	<i>26.2</i>
MUG 50 H 50	1.41	<i>0.15</i>	24.5	<i>2.1</i>
MUG 10 A 90	2.22	<i>0.19</i>	16.5	<i>17.7</i>
MUG 50 ARA1 50	4.83	<i>0.17</i>	11.3	<i>9.0</i>

Note: H: water; A: acetone. Italic values represent the standard deviation in the results.

It should be noted that the residual mass increased as the proportion of MUG increased, while the time to beginning of slide decreased. As discussed in the previous section, the residual mass of substrate ARAs is actually a useful property as it allows longer times before an ARA would need to be re-applied to a surface. In terms of optimization of the formulations, MUG 20 H 80 had the lowest time to beginning of slide while having the second highest time to beginning of slide (15.7 s) among the MUG formulations.

For MUG 10 A 90 with acetone, the formulation evaporated too quickly for the agent to act as a barrier, lightly dissolving the bitumen it was in contact with. The residual mass was at 2.22 g/m<sup>2</sup> and the time to beginning of slide was 16.5 s.

MUG 50 ARA1 50 showed performance characteristic of both parent agents in the mixture. The residual mass was lower than for ARA 1 (4.83 g/m<sup>2</sup>) (Mikhailenko, Bertron, et al., 2016), while the time to beginning of slide was lower than for MUG 50 H 50 (11.3 s).

The MUDG compound was more fluid than MUG, and thereby produced more fluid formulations. While these formulations spread on the plate more easily, they were also more likely to evaporate. As with the MUG formulations, MUDG functioned as a substrate, with the residual mass increasing as the proportion of MUDG increased, while the time to beginning of slide decreasing. The images of the plates after the test are shown in Figure 4 while the residual mass and time to beginning of slide results are shown in Table 4.

For MUDG 5 H 95, the formulation mostly evaporated from the hot asphalt, and the asphalt stuck to the plate after inclination, as for a test without any agent. This was also an issue with MUDG 10 H 90 and MUDG 15 H 85, where part of the bitumen penetrated the agent leaving some residue on the plate. This small amount of bitumen residue corresponded with a high time to beginning of slide.

In general, the MUDG molecules with the same proportion of water, functioned as a diluted MUG formulation with a lower residual mass (0.07–0.61 g/m<sup>2</sup>) and a higher time to beginning of slide (24–535 s). The MUDG 50 H 50 had the lowest time to beginning of slide at 24 s among the MUDG–water formulations.

The sample where MUDG was mixed with acetone, MUDG 10 A 90, gave an interesting performance result, as it was able to perform better in time to beginning of slide than any of the MUDG–water formulations (11 s). Unlike MUG 10 A 90, the formulation was able to create a barrier between the plate and the asphalt that did not degrade the bitumen, qualifying it as a substrate ARA. Despite acetone being more volatile than water, the residual mass on the plate for MUDG 10 A 90 was higher (0.61 g/m<sup>2</sup>) than for the same content of MUDG with water. These are indications that there is a particular interaction between MUDG and acetone that does not occur with MUDG and water.

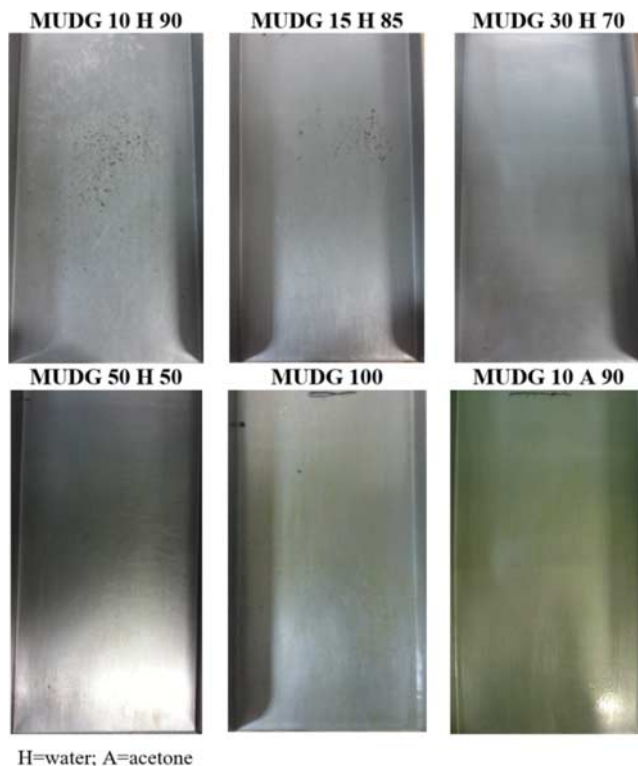


Figure 4. Images of plates after AST for MUDG-based formulations.

Table 4. Results of AST for MUDG-based formulations.

Formulation	Residual mass (g/m <sup>2</sup> )	Std dev $\sigma$	Time to beginning of slide (s)	Std dev $\sigma$
MUDG 5 H 95		DID NOT MOVE		
MUDG 10 H 90	0.07	0.05	535.3	161.9
MUDG 15 H 85	0.08	0.03	458.0	379.5
MUDG 20 H 80	0.10	0.10	260.0	183.8
MUDG 30 H 70	0.17	0.06	240.0	15.6
MUDG 50 H 50	0.61	0.09	24.0	15.9
MUDG 100	1.78	0.08	59.0	7.1
MUDG 10 A 90	0.64	0.00	11.0	1.4

H = water; A = acetone

### 3.2. Effects on asphalt mix and bitumen

#### 3.2.1. Interaction of formulations with bitumen

The MUG compound was tested in BDT after being mixed at 20% (MUG 20 H 80), 50% (MUG 50 H 50) with water, 50% (MUG50 A50) with acetone and 50% (MUG 50 ARA1 50) with ARA1. The MUDG compound was tested after being mixed at 20% (MUDG 20 H 80), 50% (MUDG 50 H 50) with water. MUG and MUDG had one or two tests per formulation (Table 5). The results show that all of the MUG and MUDG samples except for MUG 50 ARA1 did not degrade the bitumen, but were adsorbed by it, resulting in an increase in sample mass and negative values for bitumen degradation.

Table 5. BDT results for bio-sourced candidate formulations.

Formulation	% Bitumen degradation	CVAR%
MUG 20 H 80	-3.22**	*
MUG 50 H 50	-4.26**	7.21
MUDG 20 H 80	-4.05**	*
MUDG 50 H 50	-3.63**	*
MUG 50 A 50	-2.79**	0.88
MUG 50 ARA1 50	3.49	*
Acetone	-0.66**	*
H <sub>2</sub> O	-1.09**	*

Note: H: water; A: acetone.

<sup>a</sup>Only single test conducted.

<sup>b</sup>Bitumen sample gained mass.

The MUG and MUDG compounds were tested in FTIR–ATR analysis undiluted, and after being mixed at 20% in water (MUG 20 H 80 due to promising performance in AST of this formulation and MUDG 20 H 80 for comparison). The MUG 20 H 80 and MUDG 20 H 80 BDT solutions were analysed in FTIR–ATR as well.

The FTIR–ATR analysis of the MUG 20 H 80 and MUDG 20 H 80 formulations (Figure 5) found heavy indications of water as can be expected (due to both formulations being over 80% water) with a broad peak around  $3450\text{ cm}^{-1}$  corresponding to O–H stretching and a peak around  $1640\text{ cm}^{-1}$  corresponding to the H–O–H scissors (Mojet, Ebbesen, & Lefferts, 2010). The FTIR signatures of the two formulations were identical, likely them being of the same source and the overwhelming presence of water. The FTIR analysis of the BDT solution confirms that the MUG and MUDG formulations did not degrade the bitumen but were adsorbed by it, with the formulations and their BDT solutions showing no difference except for a peak around  $1060\text{ cm}^{-1}$  that is present in the MUG 20 H 80 and MUDG 20 H 80 formulations, but not the BDT solution.

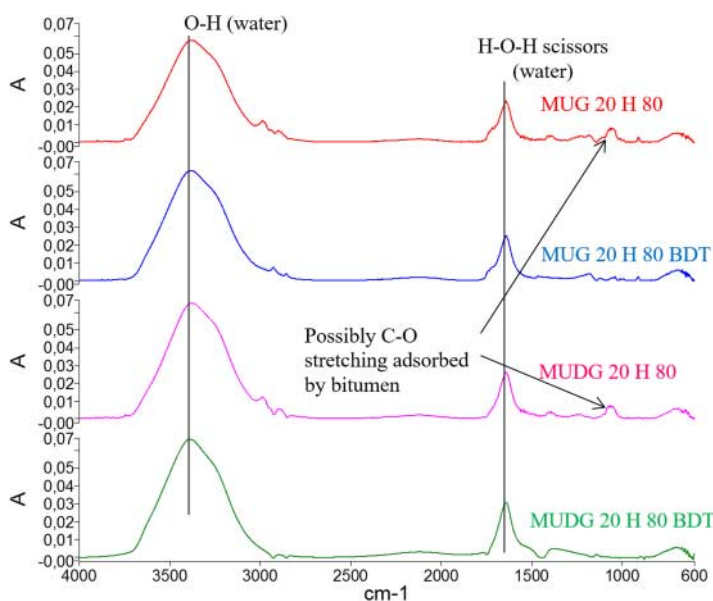


Figure 5. FTIR–ATR spectra MUG 20 H 80, MUG 20 H 80 BDT solution, MUDG 20 H 80 and MUDG 20 H 80 BDT solution.

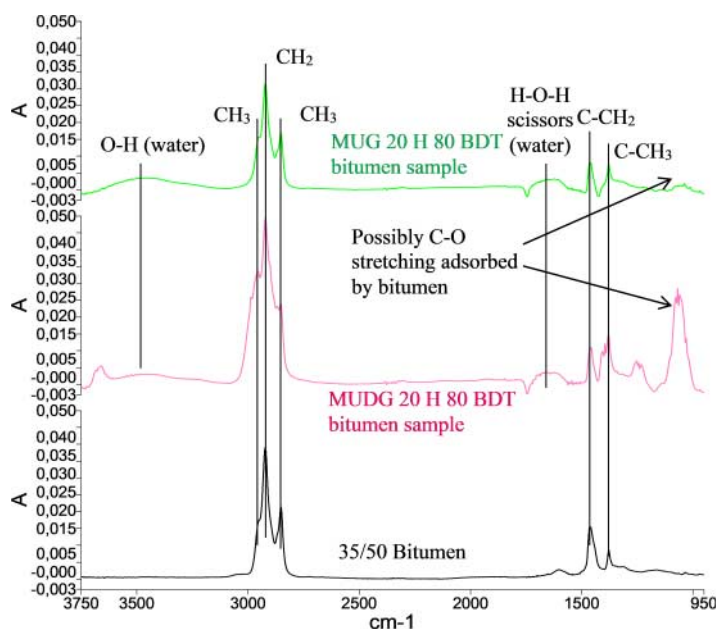


Figure 6. FTIR–ATR spectra ( $3750\text{--}950\text{ cm}^{-1}$ ) of bitumen sample after BDT with MUG 20 H 80, bitumen sample after BDT with MUDG 20 H 80 and 35/50 bitumen.

This peak possible corresponds to C–O stretching (Nakanishi, 1962) and could be an indication of some part of the formulations being adsorbed by the bitumen as with the commercial substrate ARA tested in Mikhailenko, Bertron, et al. (2016).

In order to determine if the bitumen was modified, an FTIR–ATR analysis was conducted on the bitumen sample after the BDT test of MUG 20 H 80 and MUDG 20 H 80 (Figure 6). The spectra for the BDT bitumen samples were modified relative to the bitumen by itself. The presence of water and possible C–O stretching around  $1060\text{ cm}^{-1}$  described previously were present in the bitumen samples. The peaks were more significant for the post-BDT MUDG 20 H 80 bitumen sample, likely due to the fact that MUDG is less viscous than MUG, and is thereby more easily adsorbed by the bitumen.

### 3.2.2. Reduction in resistance in ITS of asphalt in contact with ARAs

ITS testing for the damage by the ARA was conducted for the MUG 20 H 80 formulation, due to its superior performance in the AST compared to the other MUG and MUDG based formulations. The RR% was found to be 21.2% for the two samples tested with a standard deviation of 3.16%,

Table 6. Resistance reduction for ITS testing (MUG 20 H 80 and commercial comparisons).

Agent	% Resistance reduction	<i>Std Dev <math>\sigma</math></i>
ARA 2	21.8	<i>1.62</i>
ARA 4	11.3	<i>1.47</i>
MUG 20 H 80	21.2	<i>3.16</i>

Note: *Italic values represent the standard deviation in the results.*

making it more damaging to asphalt than ARA 4, and the same as ARA 2, the best performing substrate and ester C18-based commercial ARAs from a previous study (Mikhailenko, Bertron, et al., 2016), respectively (Table 6).

## 4. Discussion

### 4.1. Functioning of formulations as ARAs

The formulations based on MUG and MUDG were found to function as substrate barriers in their performance as ARAs. The residual mass from the asphalt slide testing for the MUG and MUDG formulations with water, did not contain bitumen residue (as shown with FTIR), with the exception of MUG 5 H 95, MUDG 5 H 95, MUDG 10 H 90 and MUDG 15 H 85, which had too low of an active product content to create barrier between the asphalt and the plate.

The MUG had a higher viscosity than MUDG (dynamic viscosity of 13 Pa\*s for MUG compared to 1 Pa\*s for MUDG), and so was more effective at lower concentrations, and so was more effective at lower concentrations. Additionally, MUG had a higher evaporation temperature before being mixed with water, indicating that the MUDG could have had a tendency to evaporate from the contact with the hot asphalt, especially with high proportions of water. The fact that MUG–water formulations functioned as substrates had higher residual mass and lower time to beginning of slide durations made them superior performing ARAs to MUDG–water formulations.

It was previously demonstrated that glycerol undecenoates and diglycerol undecenoates self-assemble vesicles and aggregates at low concentrations in water. With the increase in the concentration of these amphiphilic molecules, the self-assembling forms a lamellar phase (Nyame Mendendy Boussambe, Valentin, & Mouloungui, 2014; Nyame Mendendy Boussambe et al., 2017). It is this self-assembling lamellar phase which would be responsible for the creation of a bilayer on the steel surface when the formulation is applied. The surfactant formulations would create the barrier shown in Figure 7, where the hydrophilic heads of the formulations binding the water in the middle, between the steel plate and the lipophilic asphalt.

The MUDG was more adsorbed by the bitumen as shown by the BDT with –4% for MUDG 20 H 80 compared to –3% for MUG 20 H 80 test and the FTIR–ATR analysis of the bitumen

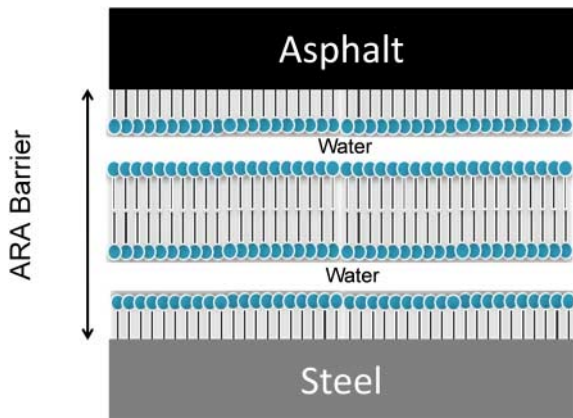


Figure 7. Hypothetical amphiphilic structure for MUG and MUDG formulations retaining water and functioning as barriers between the asphalt and the steel plate they are applied to.

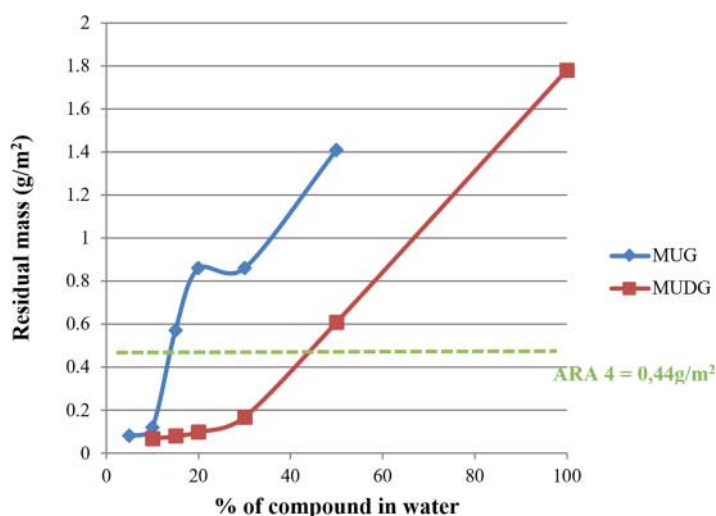


Figure 8. AST Performance of MUG and MUDG formulations with water in terms of residual mass compared to ARA 4.

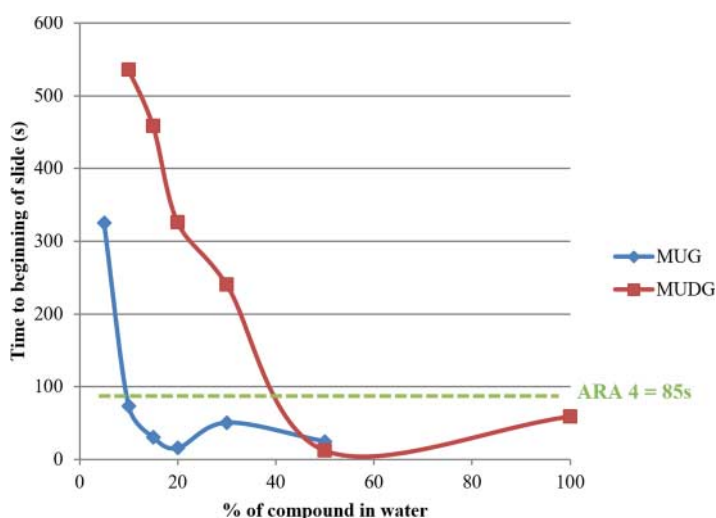


Figure 9. AST Performance of MUG and MUDG formulations with water in terms of time to beginning of slide compared to ARA 4.

samples after the BDT test. This resulted in less MUDG being available to form a barrier relative to MUG.

In terms of comparing the MUG and MUDG formulations with commercial agents, the only comparison from this study is ARA 4, the commercial substrate agent tested in Mikhailenko, Bertron, et al. (2016), which functions in the same way as MUG and MUDG, that is, as a substrate barrier.

A comparison of AST performance characteristics of the MUG and MUDG formulations with water relative to the commercial substrate is shown in Figures 8 and 9. A higher residual mass for substrate ARAs is preferable, due to the economic advantage of being able to go a longer time before having to re-apply the agent.



The residual mass for ARA 4 of 0.44 g/m<sup>2</sup> corresponded to a similar residual mass for MUG concentrated at 10–15% in water and MUDG concentrated at 30–50% in water. For time to beginning of slide, ARA 4 is comparable to MUG at 5% in water and MUDG at 30–50% in water. It should be noted as well that the results for the time to beginning of slide have higher standard deviations than residual mass, and that the residual mass is the more important and consistent indicator of ARA performance.

MUG and MUDG were mixed with acetone at 10%. While the MUG–acetone formulation lixiviated the bitumen on the plate, the MUDG–acetone formulation performed as a substrate. Additionally, the time of beginning of slide was lower for the MUDG 10 A 90 than for the MUG–acetone formulation or any formulation of MUDG and water. These results suggest an interaction between MUDG and acetone that is markedly different from the one between MUG and acetone. Nevertheless, it should be kept in mind that acetone is far more expensive than water, and this is not an economically feasible solution as is.

Based on this analysis, MUG 20 H 80 was selected as the optimum formulation for an ARA from this study. The ITS sample with MUG 20 H 80 was found to be 21% less resistant than the control, a result comparable to the least damaging C18-based ARA 2, but more than for ARA 4 (11%). This difference can be explained by the BDT result and FTIR–ATR analysis, as MUG 20 H 80 (–3.2%) was more adsorbed by the bitumen than ARA 4 (–1.8%). As it is shown that ARAs adsorbed into the bitumen reduce its resistance and therefore, it is in the interests of ARA development to reduce the adsorption of the agent by bitumen.

MUG 20 H 80 remains a strong ARA candidate, although the precise optimum content should be confirmed through field trials. If we take cost into consideration, MUG 15 H 85 may be the optimum candidate as it had a lower residual mass and similar time to beginning of slide to MUG 20 H 80. However, MUG 15 H 85 would be cheaper since water would be much less expensive than MUG.

## 5. Conclusions

The conclusions for the study of recycled bio-sourced glycerol as ARAs are as follows:

- Both MUG and MUDG mixed with water perform as substrate barrier ARAs. Both formulations do not dissolve bitumen in BDT, although a small amount of the formulations is absorbed. The formulations' amphiphilic structure entraps water, allowing them to perform as effective barriers.
- MUG–water formulations were found to be a more effective substrate barriers than the same formulations with MUDG. This was reflected in both a reduction in adhesion between the asphalt and the plate, as well as the higher residual mass of the agent, allowing for repeat use.
- The formulation of MUG 20 H 80 was determined to be the optimum formulation for use as an ARA, based on reducing asphalt adhesion to the applied surface and having a reasonable residual mass of the formulation, allowing for multiple asphalt loads on the same applied surface, where it performed better than the commercial substrate ARA. This formulation reduced the resistance of asphalt in ITS, but at a reasonable amount compared with commercial ester-based ARAs.

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## References

- Acton, Q. A. (2013). *Silicones – advances in research and application*. Atlanta, GA: Scholarly Editions.
- Artamendi, I., Allen, B., Ward, C., & Phillips, P. (2012). Differential thermal contraction of asphalt components. In A. Scarpas, N. Kringos, I. Al-Qadi, & L. A. (Eds.), *7th RILEM international conference on cracking in pavements* (pp. 953–962). Delft, Netherlands: Springer.
- Charles, G., Clacens, J.-M., Pouilloux, Y., & Barrault, J. (2003). Préparation de diglycérol et triglycérol par polymérisation directe du glycérol en présence de catalyseurs mésoporeux basiques. *Oléagineux, Corps Gras, Lipides*, 10(1), 74–82. doi:10.1051/ocl.2003.0074
- Davies, G. (2005). *U.S. Patent 6486249*. Washington, DC: U.S. Patent and Trademark Office.
- Dituro, M. A., Lockwood, F. E., Dotson, D. J., & Fang, J. (2002). *U.S. Patent 6486249*. Washington, DC: U.S. Patent and Trademark Office.
- Esteban, B., Riba, J.-R., Baquero, G., Puig, R., & Rius, A. (2012). Characterization of the surface tension of vegetable oils to be used as fuel in diesel engines. *Fuel*, 102(0), 231–238. doi:10.1016/j.fuel.2012.07.042
- Gaurat, F., Jackubowski, M., Nicolai, A., Barsi, P., Mikhailenko, P., Baurion, M., . . . Fabre, J.-F. (2016). *French patent 3035659*. Courbevoie: Institut national de la propriété industrielle.
- Leoneti, A. B., Aragão-Leoneti, V., & de Oliveira, S. V. W. B. (2012). Glycerol as a by-product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerol. *Renewable Energy*, 45, 138–145. doi:10.1016/j.renene.2012.02.032
- Lockwood, F., Dituro, M., Dotson, D., & Fang, J. (1999). *Patent WO1999054413*. Geneva: World Intellectual Property Organization.
- Ma, F., & Hanna, M. A. (1999). Biodiesel production: A review. *Bioresource Technology*, 70(1), 1–15. doi:10.1016/S0960-8524(99)00025-5
- Mahr, G., Okabe, T., & Ito, K. (2003). *U.S. Patent 6506444*. Washington, DC: U.S. Patent and Trademark Office.
- Martin, A., & Richter, M. (2011). Oligomerization of glycerol – a critical review. *European Journal of Lipid Science and Technology*, 113(1), 100–117. doi:10.1002/ejlt.201000386
- Mikhailenko, P. (2015). *Valorisation of by-products and products from agro-industry for the development of release and rejuvenating agents for bituminous materials (PhD Thesis)*. Université Paul Sabatier Toulouse III, Toulouse.
- Mikhailenko, P., & Baaj, H. (2017). *Survey of current asphalt binder extraction and recovery practices*. In 2017 Transportation Association of Canada Conference. St. John's, Canada.
- Mikhailenko, P., Bertron, A., & Ringot, E. (2016). Determination of the performance and damage to asphalt of bio-sourced asphalt release agents (ARAs) part II: Evaluation of biodegradable products for use as ARAs and bitumen removers (BRs). *Materials and Structures*, 49(4), 1419–1432. doi:10.1617/s11527-015-0663-x
- Mikhailenko, P., Ringot, E., Bertron, A., & Escadeillas, G. (2016). Determination of the performance and damage to asphalt of bio-sourced asphalt release agents (ARAs) part I: Developing test methods. *Materials and Structures*, 49(4), 1403–1418. doi:10.1617/s11527-015-0585-7
- Mojet, B. L., Ebbesen, S. D., & Lefferts, L. (2010). Light at the interface: The potential of attenuated total reflection infrared spectroscopy for understanding heterogeneous catalysis in water. *Chemical Society Reviews*, 39(12), 4643–4655. doi:10.1039/c0cs00014k
- Nakanishi, K. (1962). *Infrared absorption spectroscopy, practical*. San Francisco, CA: Holden-Day.
- NTPEP. (2014). Evaluation of asphalt release agents.
- Nyame Mendendy Boussambe, G. (2015). *Utilisation d'une composition comprenant un mono- ou di-alkylénate en C7-C15 de mono- à tétra- (trialkanol en C3-C6) comme auxiliaire de mise en œuvre de produits bitumineux et/ou de béton (PhD Thesis)*. Laboratoire de Chimie Agro-industrielle, INRA, Toulouse.
- Nyame Mendendy Boussambe, G., Valentin, R., Fabre, J.-F., Navailles, L., Nallet, F., Gaillard, C., & Mouloungui, Z. (2017). Self-assembling behavior of glycerol monoundecenoate in water. *Langmuir*, 33(13), 3223–3233. doi:10.1021/acs.langmuir.6b03584
- Nyame Mendendy Boussambe, G., Valentin, R., & Mouloungui, Z. (2014). *Self-assembling in water and on surfaces of biobased nano-objects of pure glycerol monoundecylenate and pure diglycerol monoundecylenate*. In 4th International Colloids Conference. Madrid.
- Nyame Mendendy Boussambe, G., Valentin, R., & Mouloungui, Z. (2015). Structural analysis of partial and total esters of glycerol undecenoates and diglycerol undecenoates. *Journal of the American Oil Chemists' Society*, 92(11–12), 1567–1577. doi:10.1007/s11746-015-2725-1

- Romera, R., Santamaría, A., Peña, J., Muñoz, M., Barral, M., García, E., & Jañez, V. (2006). Rheological aspects of the rejuvenation of aged bitumen. *Rheologica Acta*, 45(4), 474–478. doi:10.1007/s00397-005-0078-7
- Scardina, M. (2007). An introduction to asphalt release agent. *The Asphalt RAP*, 1(7), 1–4.
- Tang, B. (2008). *Applications of solid-phase microextraction to chemical characterization of materials used in road construction (PhD Thesis)*. Division of Highway Engineering, Royal Institute of Technology.
- Tang, B., & Isacson, U. (2006). Chemical characterization of oil-based asphalt release agents and their emissions. *Fuel*, 85(9), 1232–1241. doi:10.1016/j.fuel.2005.11.002
- Zaki, N. N., & Troxler, R. E. (2013). *U.S. Patent application 2013/0156962*. Washington, DC: U.S. Patent and Trademark Office.
- Zanzotto, L., Vacin, O. J., & Stastna, J. (2003). *Dynamic and transient testing of asphalt binder and paving mix*. Presented at Sixth International RILEM Symposium on Performance Testing and Evaluation of Bituminous Materials, Zurich, Switzerland. doi:10.1617/2912143772.005