


Article

Effects of Titanate Coupling Agent on Engineering Properties of Asphalt Binders and Mixtures Incorporating LLDPE-CaCO₃ Pellet

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Received: 31 May 2018; Accepted: 21 June 2018; Published: 24 June 2018



Abstract: This study was initiated to evaluate the performance of asphalt binders and mixtures incorporating linear low-density polyethylene- calcium carbonate (LLDPE-CaCO₃) pellet, either with or without titanate coupling agent. The detailed manufacturing process of modifier pellets was displayed. The coupling agent was used to enhance the cross-linking between materials by means of winding up covalent bonds or molecule chains, thus improving the performance of composites. In the preparation of modified bitumen, the preheated asphalt binder was mixed with the modifiers using a high shear mixer at 5000 rpm rotational speed for 45 min. Experimental works were conducted to evaluate the performance of asphalt binders in terms of volatile loss, viscosity, rutting potential, and low temperature cracking. Meanwhile, the asphalt mixtures were tested using the flow number test and tensile strength ratio (TSR) test. The addition of LLDPE-CaCO₃ modifiers and coupling agent does not significantly affect the volatile loss of modified asphalt binders. The addition of modifiers and coupling agent has significantly improved the resistance to permanent deformation of asphalt binders. Even though, the addition of LLDPE-CaCO₃ modifier and coupling agent remarkably increased the mixture stiffness that contributed to lower rutting potential, the resistance to low temperature cracking of asphalt binder was not adversely affected. The combination of 1% coupling agent with 3% PECC is optimum dosage for asphalt binder to have satisfactory performance in resistance to moisture damage and rutting.

Keywords: asphalt modification; coupling agent; rheological behavior; plastic; calcium carbonate powder

1. Introduction

Over decades, a wide range of modification at macro, meso-, micro- and nano-scales have been conducted to improve the performance of asphalt pavement [1]. This is essential to design durable,

safe and efficient asphalt pavement that can function efficiently across a wide range of temperatures and distresses. Polymer modified binders have got increasing use on improving the resistance to thermal cracking and permanent deformation, as well as reducing the fatigue cracking potential of asphalt pavement [2,3]. Brown et al. [4] mentioned that an ideal asphalt condition should exhibit both: (a) Relatively high stiffness at high temperature to prevent rutting and shoving and; (b) great adhesion between asphalt binder and aggregates matrices in the presence of water to reduce moisture induced damage, for example stripping. Additionally, Chen et al. [5] mentioned that the asphalt is continuously exposed to a wide range of climates, loading rate and time, but it does not have essential engineering properties to sustain those situations, where the binder is soft under hot summer days and brittle in the freezing condition.

Various types of polymer have been used to chemically or mechanically improve the properties of asphalt binder, which can be classified into three different categories: elastomer, plastomer and reactive polymers [4,6,7]. The application of polymers in the asphalt pavement has been growing rapidly since the early 1970s. Based on previous studies, modifications of asphalt binder using polymer materials can significantly improve the properties of asphalt material, such as reducing the temperature susceptibility, providing better rheological characteristics, as well as enhancing the material durability [3,8,9]. Polyethylene (PE) and polyethylene-based copolymers (new or recycled) has been used to modify the performance of asphalt binder and mixture over many years [2,10]. The PE and polypropylene (PP) are categorized as plastomers which can bring a high rigidity to the material and improve the resistance to permanent deformation under traffic load [11,12]. A study was performed by Habib et al. [13] to evaluate the rheological properties and interaction of asphalt binder with different thermoplastics, such as high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and PP. Based on their study, the viscoelastic behavior of asphalt binder was significantly affected by the modifier concentration, bitumen grade and the temperature. In addition, based on the overall studies, the best results occurred when the polymer concentration was limited to 3%, which resulted from the thermodynamically stable structure condition. This had significantly improved the resistance to rutting, fatigue, and temperature susceptibility.

Limestone (CaCO_3) is an inert material which has been used as an additive in asphalt mixture for more than 100 years. However, the hydrated lime came into regular use only just in the 1980s. Several states including Georgia, Nevada, Texas, Virginia, and Utah used lime to solve the water susceptibility issue on asphalt pavement [14]. CaCO_3 is the most widely used filler in thermoplastics because of its low cost and superior mechanical properties. Much effort has been focused to increase mechanical properties such as tensile and flexural strength, impact resistance of CaCO_3 -filled PP, HDPE, LDPE, and LLDPE composites [15]. The term "lime" is used referring to either quicklime or hydrated lime which comes originally from limestone. Calcinations process of limestone dissociated the calcium from carbon dioxide, leaving calcium oxide. This is known as quicklime, it is then combined with water to form hydrated lime. In the asphalt industry, the lime generally refers to hydrated lime or calcium hydroxide [16]. The fineness and high surface area of hydrated lime contributes to a high speed of chemical reaction. Hydrated lime is the only form of lime which has been shown to be useful in controlling stripping. Many aggregates are quite acidic and the asphalt binder also contains acids, the ions present at the interface of both materials repelled each other electrically. The presence of lime could neutralize the acidic aggregates and asphalt binder, which provide opposite-charge ions to enhance adhesion [16]. Thus, lime in asphalt mixture is not only used as an anti-stripping agent, but it may improve mixture stiffness, reduce plasticity index when clays are present and reduce the oxidation rate [14,16].

Lu and Isacson [17] revealed that, even though the thermoplastic modifiers had improved the viscosity and stiffness of asphalt binder, it did not significantly help in terms of elastic behavior. The embrittlement makes asphalt susceptible to fracture, especially when subjected to high levels of stress [18]. The polymer should be homogeneously dispersed into asphalt to ensure proper adhesion of the asphalt binder. However, incompatibility between the binder and the polymer is sometimes

inevitable. As a result, it is difficult to establish the bond, either in terms of a physical or chemical manner [18,19]. Prior to gaining a better performance, an application of coupling agent in organic materials or treating inorganic fillers has been used. This enhances the materials cross-linking by means of winding up covalent bonds or molecule chains, thus improving the performance of composites [20,21]. It was found that a small amount of coupling agent could increase shear resistance in mechanical properties [20]. There are various types of coupling agents that have been used to improve the bonding of composite materials such as: Silane, zirconate, dicarboxylic anhydride, titanate and phosphate ester. However, the most important commercial coupling agents are formed by silane and titanate [22]. A titanate coupling agent has been used in enhancing the bonding in CaCO₃-thermoplastic composites [23]. A study conducted by Atikler et al. [15] showed that a silane coupling agent had significantly ameliorated the mechanical properties of the HDPE-fly ash composites. Sae-oui et al. [24] reported that excessive use of a silane coupling agent could cause a negative effect on certain properties such as modulus and hardness due to plasticizing effect. Additionally, Chen et al. [25] also concluded that too much of a titanate coupling agent resulted in polymer bridging, and reduced the phase boundary condition. It would also influence the economic aspect, whereby the excess of a coupling agent could increase the cost of production. Former studies [26–28] had recommended using the titanate-coupling agent in a range of 0.1 wt % to 0.5 wt % to attain the best performance based on the adhesion test.

Even though various types of polymers have been used to enhance the performance of asphalt composite, only a few of them are considered as satisfactory based on the performance and economic standpoints [29,30]. In this study, newly manufactured asphalt modifiers that comprised of LLDPE and CaCO₃ with or without titanate coupling agent was used to enhance the engineering properties of asphalt binder and asphalt mixture durability towards various distresses.

2. Materials and Methods

2.1. Materials

2.1.1. Asphalt Binder and Aggregate

The basic materials that used in this study were obtained from a local source in Hancock, Michigan. The PG 58-28 was used as a control binder. The aggregate gradation used was based on Michigan Department of Transportation (MDOT) specifications for Upper Peninsula region. The nominal maximum aggregate size of the gradation is 9.5 mm and the designed traffic level is less than three million equivalent single axles loads (ESALs) based on the Superpave asphalt mixture design procedure.

2.1.2. Coupling Agent

For this project the coupling agent Ken-React[®] CAPS[®] L[®] 12/L was used [31]. Ken-React[®] CAPS[®] L[®] 12/L is a neoalkoxy titanate, with a specific gravity of 0.95, and is in the form of an off-white/beige solid pellet. Ken-React[®] CAPS[®] L[®] 12/L was used as-received. Figure 1 shows the chemical structure of the Ken-React[®] LICA[®] 12 (20% Active Portion of CAPS[®] L[®] 12/L). The chemical name for Ken-React[®] CAPS[®] L[®] 12/L is titanium IV 2,2 (bis-2-propenolatomethyl) butanolato, tris(dioctyl) phosphate-O [32]. Figure 2 shows the appearance of coupling agent.

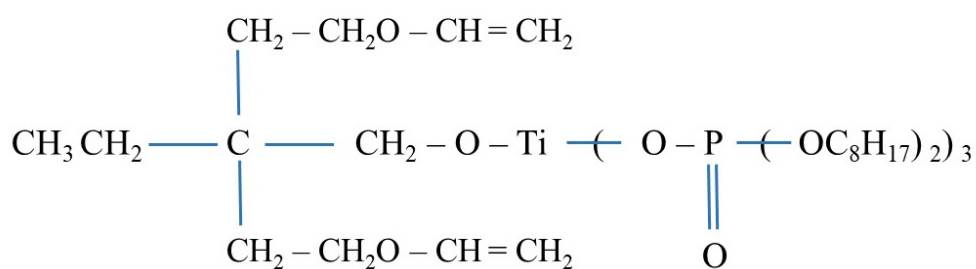


Figure 1. Chemical structure of Ken-React[®] LICA[®] 12 (20% active portion of CAPS[®] L[®] 12/L).

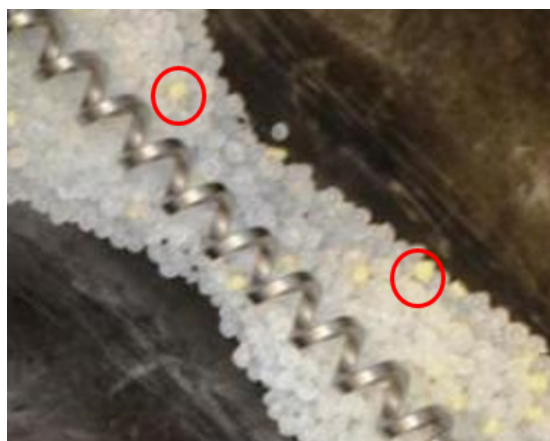


Figure 2. Titanate coupling agent (shown in red circle) mixed with LLDPE pellets.

2.1.3. Manufacturing Process of Modifier Pellets

A V-cone mixer was used operating at 24 rpm for four minutes to mix the Ken-React[®] CAPS[®] L[®] 12/L and LLDPE pellets. The modifier pellets were prepared using extrusion equipment in the Chemical Engineering Department at Michigan Technological University. An American Leistritz Extruder Corporation, model ZSE 27 has a 27 mm co-rotating intermeshing twin-screw extruder with ten heating zones, a length/diameter ratio of 40 and two stuffers was used to produce the modifier pellets. Two Schenck AccuRate gravimetric feeders were used to accurately control the amount of LLDPE, CaCO₃ and the coupling agent supplied into the extruder. Figure 3 illustrates the screw design that used during manufacturing of pellet modifiers [33]. The LLDPE and LLDPE/Ken-React[®] CAPS[®] L[®] 12/L coupling agent was added to zone 1. Meanwhile, CaCO₃ was added in Zone 5.

After passing through the extruder, the polymer strands (3 mm in diameter) enter a 3 m long water bath (Sterling Blower model WT-1008-10) and then a pelletizer (Accu-grind Conair Model 304) produced nominally 3 mm diameter by 3 mm long pellets. The final product of the manufacturing process is shown in Figure 4. After compounding, the pelletized composite resin was dried in an indirect heated dehumidifying oven (Bry Air RD-20) at 60 °C for 7 h. It was then stored in sealed moisture barrier bags prior to mixing with asphalt binder [34].

The extrusion conditions for different modifiers are shown in Table 1. Three different formulations were extruded. The first was called PECC, which contained 70 wt % LLDPE and 30 wt % CaCO₃. The second was called PECC-1CA, which contained 69.3 wt % LLDPE, 29.7 wt % CaCO₃, and 1 wt % Ken-React[®] CAPS[®] L[®] 12/L coupling agent. The third was called PECC-2CA, which contained 29.4 wt % CaCO₃, 68.6 wt % LLDPE, and 2 wt % Ken-React[®] CAPS[®] L[®] 12/L coupling agent.

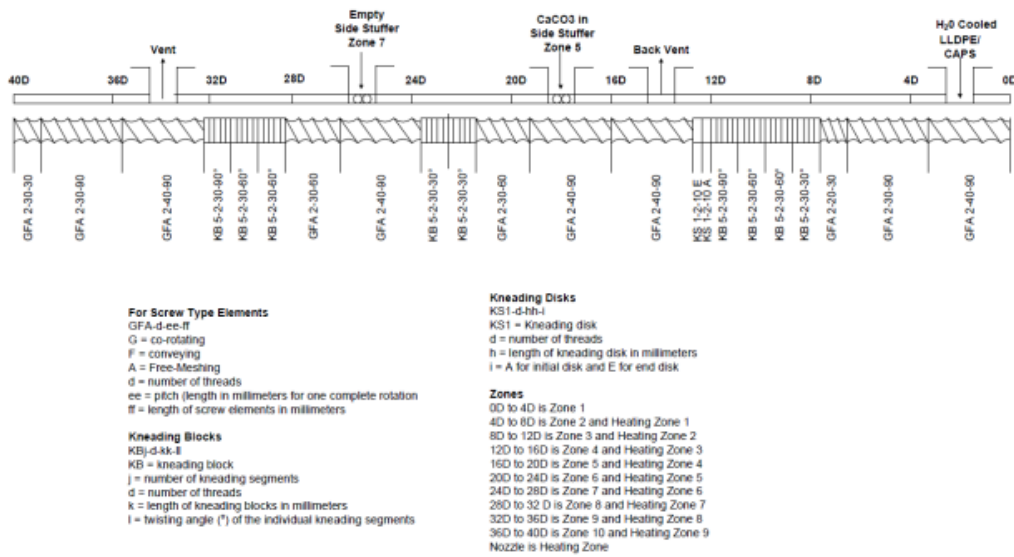


Figure 3. Extruder screw design.

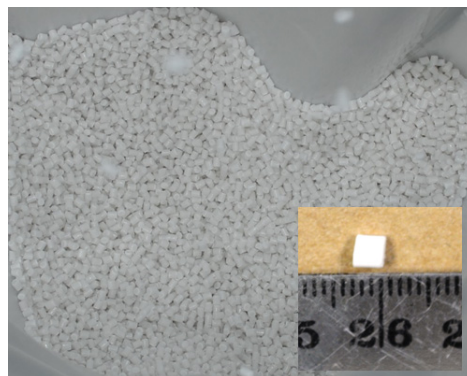


Figure 4. Final product of manufactured pellets.

Table 1. Extrusion conditions.

Material Number	PECC	PECC-1CA	PECC-2CA
Extrusion Date	March 12 2013	March 12 2013	March 12 2013
Extruder, rpm	250	250	250
Motor Amperage, %	27	27	27
Melt Temperature, °C	244	244	244
Melt Pressure, psig	80	80	80
#2 Feeder Setting, lb/h	6.0	6.0	6.0
Material in Feeder #2	CaCO ₃	CaCO ₃	CaCO ₃
#3 Feeder Setting, lb/h	14	14	14
Material in Feeder #3	LLDPE	LLDPE + CAPS	LLDPE + CAPS
Vacuum Port	1 atm	1 atm	1 atm
Zone 5 Side Stuffer Setting, rpm	300	300	300
Feeder at Zone 5	CaCO ₃	CaCO ₃	CaCO ₃
Zone 7 Side Stuffer setting, rpm	300	300	300
Feeder at Zone 7	none	none	none
Feed Section Temperature	H ₂ O Cooled	H ₂ O Cooled	H ₂ O Cooled
Zone 1 Temperature, °C	175	175	175
Zone 2 Temperature, °C	195	195	195
Zone 3 Temperature, °C	210	210	210

Table 1. Cont.

Material Number	PECC	PECC-1CA	PECC-2CA
Zone 4 Temperature, °C	220	215	215
Zone 5 Temperature, °C	220	220	215
Zone 6 Temperature, °C	220	220	215
Zone 7 Temperature, °C	220	220	215
Zone 8 Temperature, °C	220	220	215
Zone 9 Temperature, °C	220	220	215
Zone 10 Temperature, °C	220	220	220
Die Type and Gap	3 × 3 mm	3 × 3 mm	3 × 3 mm
Pelletizer Setting at 8/Bath	H ₂ O bath	H ₂ O bath	H ₂ O bath
Output Rate, lbs/h	20	20	20

Notes: (1) LLDPE and Ken-React® CAPS® L® 12/L mixed in V cone blender for 4 min at 24 rpm in 2 lb batches and then placed in Feeder 3. (2) Approximately 20 lbs of each extruded material was produced. (3) Feeder 3 helix: 0.5" open helix with end stub and 0.75" nozzle side discharge. (4) Feeder 3 Toshiba laptop feeder3_VectraA950RX0.5inopen0.75insidedischargejak.par. (5) Feeder 2 helix: 0.75" open helix with 0.75" ID polyliner. (6) Feeder 2 NEC laptop Thermocar file. (7) Extruder screw 5-14-05 design used from American Leistritz. Extruder screw cleaned in sand bath prior to use. (8) Purged with LLDPE at end of extrusion run to clean out extruder.

2.2. Methods

2.2.1. Preparation of Modified Asphalt Binder

The modified asphalt binders were prepared using a high shear mixer. The binder and modifiers were properly mixed to ensure the materials were evenly dispersed in asphalt binder. The temperature that used for the production of modified asphalt binder is at 170 °C. In the asphalt binder preparation process, about 500 g of asphalt binder PG 58-28 was poured into a one liter metal container. Then, an adequate amount of modifier was added to the same container and heated up in an oven for about two hours prior to the mixing process. After two hours of inducing the melting process, the binder and modifier were stirred using a high shear mixer at 5000 rpm rotational speed for 45 min. Based on literature review, LLDPE-related modifiers were used as asphalt modifiers in a range of 2% to 6% based on the weight of asphalt binder [11,13,35–38]. Based on the range, the amounts of modifier incorporated in the asphalt binder were decided at 3% and 5% based on the asphalt binder weight. At least three replicate specimens were used for all the asphalt binder and asphalt mixture tests.

2.2.2. Preparations of Asphalt Mixture Specimen

A bucket mixer was used to blend the aggregates and asphalt binder. The sample was compacted using a gyratory compactor at 86 gyrations. Prior to compaction, the mixture was heated in an oven for two hours to simulate the short-term aging condition that occurs during preparation of asphalt mixture in the field. The Superpave specifications [39–41] were referred during the preparation of asphalt mixture.

2.2.3. Asphalt Binder Test Method

The rolling thin film oven (RTFO) was used to quantify the volatiles lost (mass loss) during the short-term aging process of asphalt binder. Based on the Superpave Specification, the mass loss of asphalt binder should be less than 1 wt % to ensure the asphalt binder not to lose a significant number of volatiles over its life.

The rotational viscometer was used to determine the viscosity of asphalt binders at high temperature. During the sample preparation, about 10.5 g asphalt binder is required for each sample, and spindle #27 was used in this test. This test measures the required torque value to maintain a constant rotational speed (20 rpm) of a cylindrical spindle under a constant temperature. The results were recorded in centipoises (cP) at one-minute intervals for a total of three readings.

In this study, the multiple stress creep recovery (MSCR) was conducted by introducing the RTFO aged asphalt binder specimen to the repeated creep and recovery process at high temperature. The test has been conducted in accordance with AASHTO TP 70-13 at 58 °C, which is the high temperature grade of selected asphalt binder, PG 58-28. The 25 mm diameter with 1 mm thickness circular disk-shaped asphalt binder sample was used. Two stress levels were introduced to the sample, which were 0.1 kPa and 3.2 kPa at one second loading time and nine seconds recovery time while performing the test [42,43]. The test started with 0.1 kPa stress for ten cycles without time lags, and proceeded with 3.2 kPa stress under the same number of cycles. The new MSCR test, which is conducted based on AASHTO T 350-14, conducted 20 cycles 0.1 kPa stress loading and unloading. The MSCR test result may be different if conducted in accordance with AASHTON T 350 [44,45].

The bending beam rheometer (BBR) test was performed in accordance with AASHTO T 313; a simply supported beam of asphalt binder was subjected to a constant load of 980 mN for four minutes. The test was conducted at −12 °C, −18 °C and −24 °C to define the critical cracking temperature of control and modified binders.

2.2.4. Asphalt Mixture Test Method

The flow number test was referred to a dynamic creep or repeated load testing. Basically, a 0.1 s loading followed by a 0.9 s dwell (rest time) was applied to the specimen. Additionally, an effective temperature of 45 °C, often referred to as rutting temperature was used in this test [46,47]. Prior to the testing, the specimens were conditioned at 45 °C.

The tensile strength ratio (TSR) was used to evaluate the moisture susceptibility of asphalt mixture. The moisture susceptibility was evaluated by comparing the indirect tensile strength (ITS) of asphalt mixtures in dry and wet conditions. The ITS test was performed according to AASHTO T283. The specimens were tested at the room temperature and constant loading speed, 0.085 mm/s. The specimen was subjected to compression loads which act parallel to the vertical diameter plane.

3. Characterization of Asphalt Binder

3.1. Volatile Loss

At elevated temperature, the smaller molecules from asphalt binder are driven off, resulting in an increase of the asphalt's viscosity. The effects of heat and flowing air on a thin film of semi-solid asphaltic material are considered in this procedure. Figure 5 presents the mean mass loss values of each specimen tested using short-term aging protocol. Based on the test results, incorporation of modifiers and coupling agent do not significantly affect the volatile loss of modified asphalt binders compared to control binder PG 58-28.

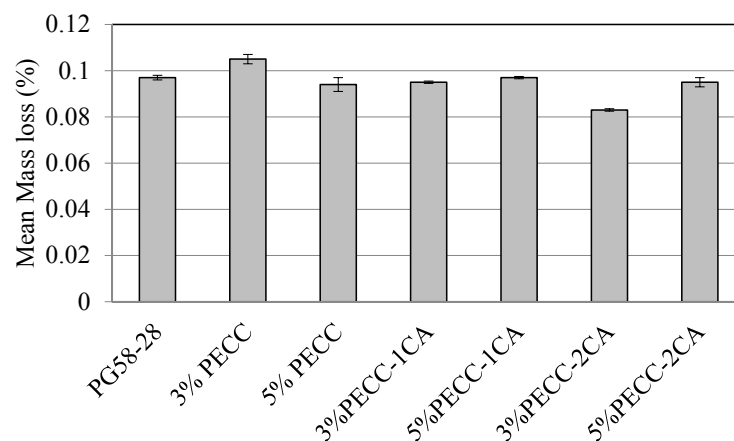


Figure 5. Mass loss test results of each asphalt binder.

3.2. Rotational Viscosity

Figures 6 and 7 show the results of asphalt binders modified using PECC and PECC-CA modifiers. Modified asphalt binders have higher viscosity value compared to the control asphalt binder. The addition of a titanate coupling agent has slightly increased the viscosity and consistency of asphalt binders, except for the specimen prepared using 3% PECC-1CA. The increments are ranging from 4% to 40% depending on the percentage of coupling agent and test temperature.

Hypothetically, the viscosity of asphalt binder could also be used as an early indicator of resistance to permanent deformation. Whereas, higher viscosity could sustain higher temperature before the binder flow or change its physical behavior. In the field, the melting temperature can be related to the atmospheric ambient temperature. In this study, the addition of modifiers and coupling agent has significantly improved the resistance to permanent deformation of asphalt binders.

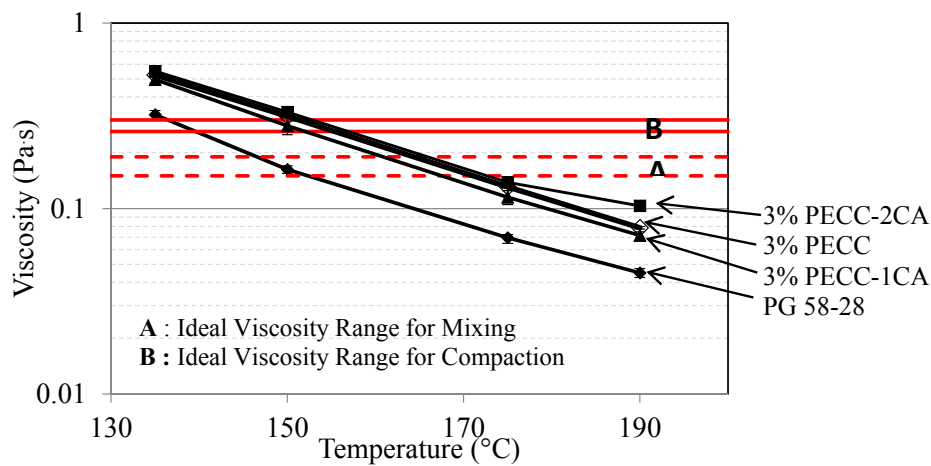


Figure 6. Modified Asphalt Binder Viscosity at Low Modifier Percentage.

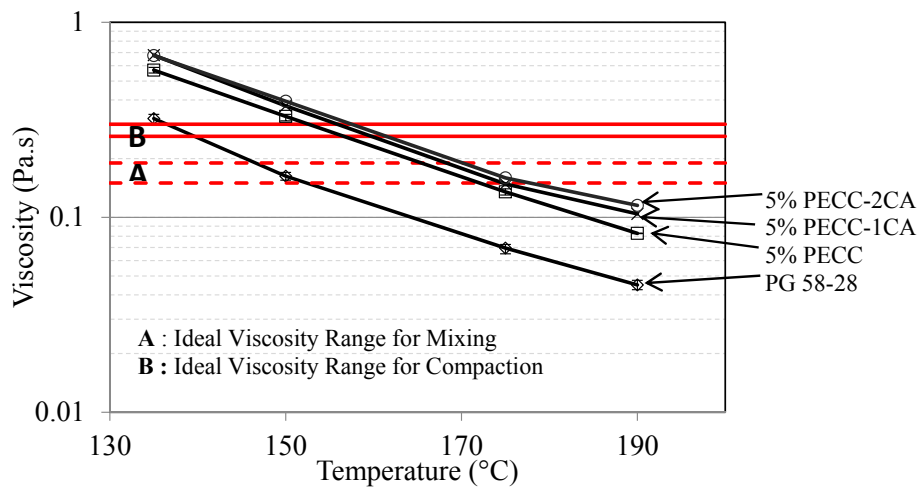


Figure 7. Modified asphalt binder viscosity at high modifier percentage.

3.3. Multiple Shear Creep Recovery

The DSR with $G^*/\sin \delta$ (AASHTO M320) is the typical parameter for rutting prediction of asphalt pavement. However, this method has been revised to provide a better prediction on the rutting performance of modified asphalt binder by MSCR. This method measures the permanent strain accumulated in the binder after designated cycles of shear loading and unloading. In which, lower permanent shear strain indicates higher rutting resistance of the pavement.

Subsequently, the rutting resistance of asphalt binder is characterized using non-recoverable compliance (J_{nr}) which is considered as the best approach to replace the current Superpave testing method, $G^*/\sin \delta$ ($\omega = 10 \text{ rad/s}$) [43,48]. Additionally, the percent recovery (R) is also determined in order to understand the high temperature viscoelastic deformation properties [43], where higher R value indicates a better resistance to rutting. Meanwhile, a lower J_{nr} value shows a better resistance to permanent deformation (rutting).

The mean recovery percentage ($n = 3$) of the tested asphalt binders are presented in Figures 8 and 9. Based on the non-recoverable compliance criteria, the results show that the modified binders have lower rutting potential as compared to the control binder, PG 58-28. Additions of newly manufactured pellets have significantly increased the resistance to permanent deformation by at least 27% greater than PG 58-28 binder. Asphalt binder modified using 5% PECC-1CA has shown the best performance, in terms of non-recoverable compliance criteria and percent recovery after continuously multiple loading action on the sample. Referring to the specimens prepared using 3% PECC-1CA and 3% PECC-2CA, application of 1% coupling agent in the PECC material represents better elastic response compared to 2% coupling agent, which is consistent to the J_{nr} analysis. Samples tested using lower stress levels have resulted in smaller non-recoverable compliance and superior in terms of percent recovery. This is clearly simulated the condition in the field, where heavy vehicles (e.g., lorries and trucks) cause more severe permanent deformation compared to other vehicles, as we can see the rut depths in the slow lane are typically more severe than the fast lane of a highway.

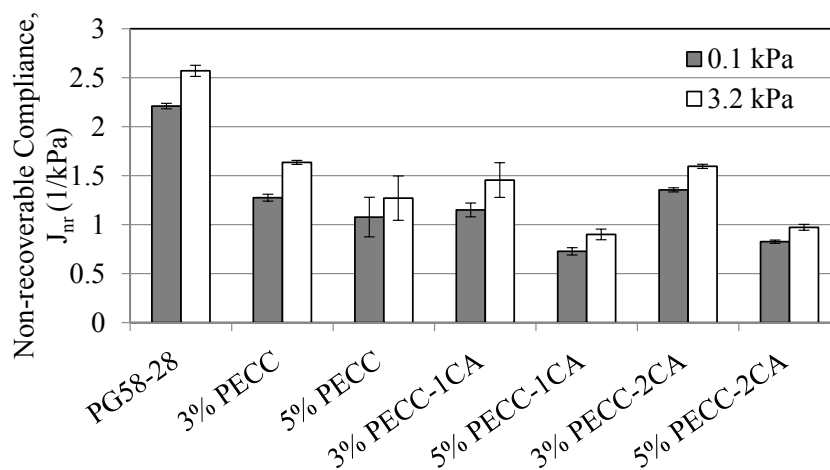


Figure 8. Non-recoverable compliance for evaluation of rutting potential.

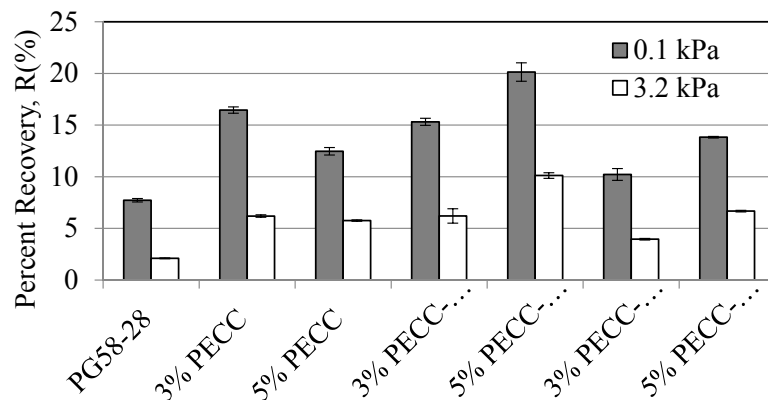


Figure 9. Recovery percentage of the tested asphalt binders.

Overall, without the presence of coupling agent, asphalt binder modified using 3% PECC has shown a better recovery percentage compared to 5% PECC sample. With the addition of coupling agent, a higher percentage could be adopted in the modification process of asphalt binder. However, the amount of coupling agent should be limited to 1% to avoid adverse effects on its resistance to rutting.

3.4. Low Temperature Cracking Using BBR Test

The BBR test was conducted to evaluate the low temperature stiffness and relaxation properties of asphalt binders, based on the function of load and duration. These parameters give an indication of an asphalt binder's ability to resist low temperature cracking.

The data was then analyzed to calculate the critical cracking temperatures (T_{cr}) of the asphalt binders based on the measured creep stiffness and m -values. Figure 10 shows the limiting low temperature or T_{cr} for each binder. Overall, all the modified asphalt binders have shown comparable performance in terms of resistance to low temperature cracking. It was found that incorporating 3% PECC-1CA modifier had contributed to the low temperature performance of the asphalt binder, where it could resist the thermal cracking at $-33.2\text{ }^{\circ}\text{C}$, compared to the control asphalt binder that may only resist the thermal cracking at temperature as low as $-30.5\text{ }^{\circ}\text{C}$.

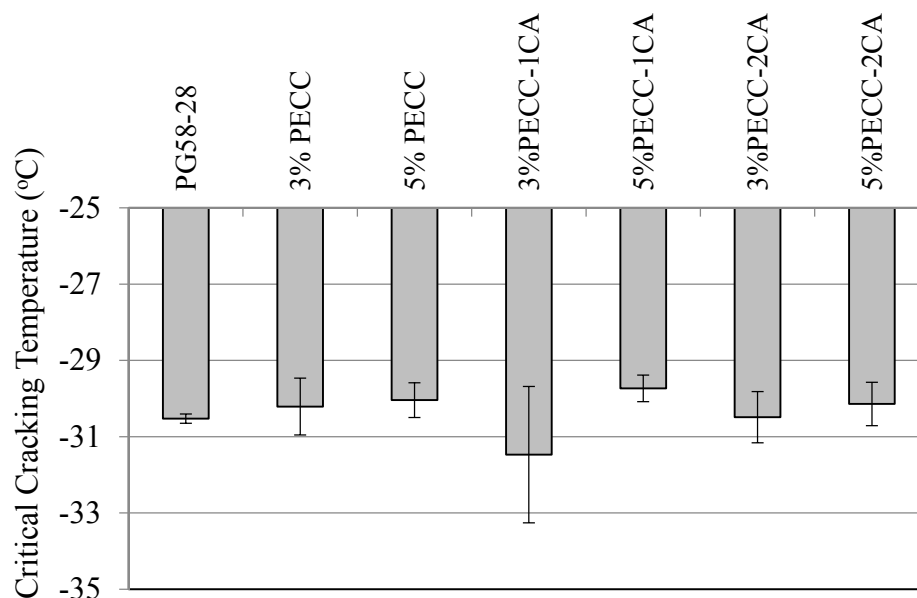


Figure 10. Critical cracking temperature of PECC-based asphalt binders compared to control specimen.

4. Performance of Asphalt Mixtures

4.1. Resistance to Permanent Deformation

Flow number test was conducted to evaluate the rutting resistance of asphalt pavement. The test was typically used to assess the resistance to permanent deformation for the past several years [49,50]. Faheem et al. [51] mentioned that flow number test has a strong correlation to the Traffic Force Index (TFI), which represents the densification loading by the traffic during its service life. It was also found that this test has a good correlation with the field rutting performance [52,53]. The test is performed by introducing repeated traffic loading (loading and unloading) on the cylindrical asphalt specimen and the permanent deformation is recorded as a function of load cycles at the minimum permanent strain rate.

Figure 11 shows the flow number test result. The specimens prepared using modified asphalt binders have significantly higher resistance to rutting compared to the control sample. Greater amount

of modifier has resulted in a higher flow number, which indicated a better resistance to rutting. The addition of coupling agent also has remarkably increased the mixture stiffness that contributes to lower rutting potential.

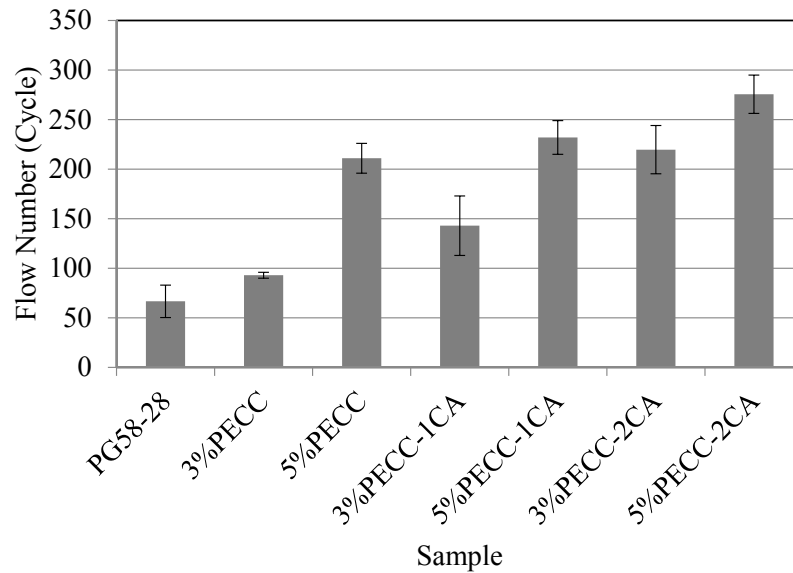


Figure 11. Flow number test results.

4.2. Moisture Susceptibility

Figure 12 shows the ITS values of tested samples. Overall, the addition of modifiers does not significantly alter the ITS of the sample in the dry condition, except 5% PECC-2CA. There are no significant effects of using different compositions of modifiers and the coupling agent in terms of indirect tensile strength results as indicated by the error bars presented. However, the modifiers help in enhancing the ITS values of the wet samples. The samples incorporated lower amount of modifiers (3%) have a better ITS value compared to sample prepared using 5% modifiers. Incorporating 1% and 2% coupling agents also do not have significant differences between them in term of wet samples' ITS values.

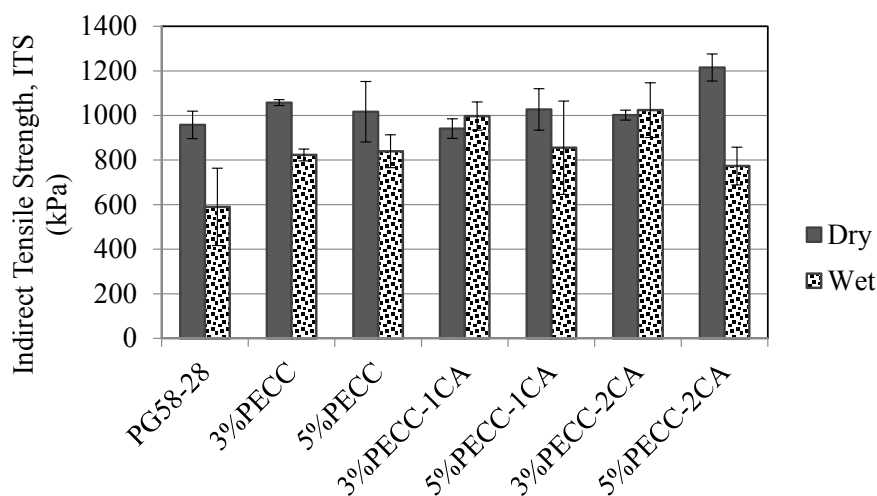


Figure 12. ITS test results.

Based on Figure 13, additions of modifiers have remarkably improved the TSR of modified asphalt mixtures compared to the control mixture, except specimen incorporating 5% PECC-2CA. Combination of 3% PECC and coupling agent at 1% and 2% has greatly enhanced the resistance to moisture damage of asphalt mixture. However, the combination of the coupling agent with 3% PECC is optimum for this study in order to avoid adverse due to moisture damage. The combination of 5% PECC and 2% coupling agent yield mixtures with worse moisture susceptibility characteristic as compared to other modified mixtures.

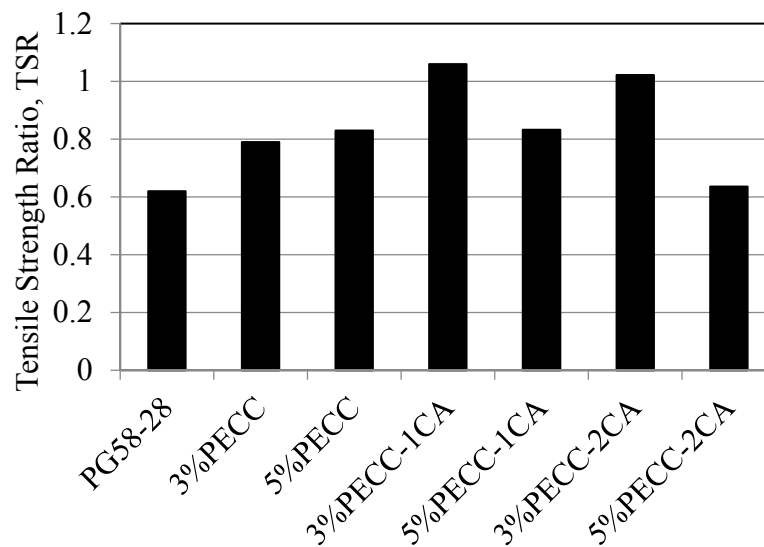


Figure 13. Moisture susceptibility of asphalt mixtures.

5. Conclusions

Based on the outcome of this study, several conclusions can be made as follows:

1. Addition of LLDPE-CaCO₃ modifiers and coupling agent do not significantly affect the volatile loss of modified asphalt binders.
2. Modified asphalt binders have higher viscosity value compared to the control asphalt binder. The addition of a titanate-coupling agent has slightly increased the viscosity and consistency of asphalt binders depending on the percentage of coupling agent and test temperature. The viscosity of asphalt binder could also be used as an early indicator of resistance to permanent deformation. The addition of modifiers and coupling agent has significantly improved the resistance to permanent deformation of asphalt binders.
3. With the addition of coupling agent, a higher percentage could be adopted in the modification process of asphalt binder. However, the amount of coupling agent should be limit to 1% to avoid adverse effects on its resistance to rutting.
4. Overall, all the modified asphalt binders have shown comparable performance in terms of resistance to low temperature cracking.
5. A greater amount of modifier has resulted in a higher flow number, which indicated a better resistance to rutting. The addition of coupling agent also has remarkably increased the mixture stiffness that contributes to lower rutting potential.
6. The modifiers help in enhancing the ITS values of the wet samples. The combination of the coupling agent with 3% PECC is optimum for this study to avoid adverse due to moisture damage.

Author Contributions: Mohd Rosli Mohd Hasan (Data curation, Writing- original draft, Methodology) Zhanping You (Supervision, Project administration, Writing- review & editing), Mohd Khairul Idham Mohd Satar (Formal analysis, Writing- review & editing), Muhammad Naquiddin Mohd Warid (Formal analysis, Writing- review &

editing), Nurul Hidayah Mohd Kamaruddin (Formal analysis, Writing- review & editing), Dongdong Ge (Formal analysis, Writing- review & editing), Ran Zhang (Formal analysis, Writing- review & editing).

Acknowledgments: The authors grateful to express their appreciation to Kenrich Petrochemicals, Inc. (Bayonne, NJ, USA), Specialty Minerals Inc. (Bethlehem, PA, USA), Payne & Dolan Inc. (Waukesha, WI, USA), and Dow Chemical Company (Midland, MI, USA) for donating test materials. The authors would like to acknowledge the research assistantships to Mohd Rosli Mohd Hasan, Mohd Khairul Idham Mohd Satar, Muhammad Naqiuddin Mohd Warid, Nurul Hidayah Mohd Kamaruddin, Ran Zhang, and Dongdong Ge. The authors also want to acknowledge Julia A. King from Department of Chemical Engineering of Michigan Technological University for her significant contributions in materials preparation, test design, and paper revision. It is impossible for the authors to complete the work without her effort. Any opinions, findings and conclusions expressed in this paper are those of the authors' and do not necessarily reflect the views of the official views and policies of any institution or company.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. You, Z.; Mills-Beale, J.; Foley, J.M.; Roy, S.; Odegard, G.M.; Dai, Q.; Goh, S.W. Nanoclay-modified asphalt materials: Preparation and characterization. *Constr. Build. Mater.* **2011**, *25*, 1072–1078. [[CrossRef](#)]
2. Ge, D.; Yan, K.; You, Z.; Xu, H. Modification mechanism of asphalt binder with waste tire rubber and recycled polyethylene. *Constr. Build. Mater.* **2016**, *126*, 66–76. [[CrossRef](#)]
3. Diab, A.; You, Z. Small and large strain rheological characterizations of polymer-and crumb rubber-modified asphalt binders. *Constr. Build. Mater.* **2017**, *144*, 168–177. [[CrossRef](#)]
4. Brown, E.R.; Kandhal, P.S.; Roberts, F.L.; Kim, Y.R.; Lee, D.Y.; Kennedy, T.W. *Hot Mix Asphalt Materials, Mixture Design, and Construction*; NAPA Research and Education Foundation: Auburn, AL, USA, 2009.
5. Chen, J.-S.; Liao, M.-C.; Shiah, M.-S. Asphalt modified by styrene-butadiene-styrene triblock copolymer: Morphology and model. *J. Mater. Civ. Eng.* **2002**, *14*, 224–229. [[CrossRef](#)]
6. Polacco, G.; Stastna, J.; Biondi, D.; Zanzotto, L. Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 230–245. [[CrossRef](#)]
7. Kalantar, Z.N.; Karim, M.R.; Mahrez, A. A review of using waste and virgin polymer in pavement. *Constr. Build. Mater.* **2012**, *33*, 55–62. [[CrossRef](#)]
8. Munera, J.; Ossa, E. Polymer modified bitumen: Optimization and selection. *Mater. Des.* **2014**, *62*, 91–97. [[CrossRef](#)]
9. Jan, H.; Aman, M.Y.; Tawab, M.; Ali, K.; Ali, B. *Performance Evaluation of Hot Mix Asphalt Concrete by Using Polymeric Waste Polyethylene, Modeling, Simulation, and Optimization*; Springer: Newyork, NY, USA, 2018.
10. Nakhaei, M.; Naderi, K.; Nasrekani, A.A.; Timm, D.H. *Chemical, Rheological, and Moisture Resistance Properties of Warm Mix Asphalt Modified with Polyethylene-Wax and Ethylene-Bis-Stearamide Additives*; Sage: Washington, DC, USA, 2018.
11. Polacco, G.; Berlincioni, S.; Biondi, D.; Stastna, J.; Zanzotto, L. Asphalt modification with different polyethylene-based polymers. *Eur. Polym. J.* **2005**, *41*, 2831–2844. [[CrossRef](#)]
12. Stastna, J.; Zanzotto, L.; Vacin, O. Viscosity function in polymer-modified asphalts. *J. Colloid Interface Sci.* **2003**, *259*, 200–207. [[CrossRef](#)]
13. Habib, N.Z.; Kamaruddin, I.; Napiah, M.; Tan, I.M. Rheological properties of polyethylene and polypropylene modified bitumen. *Int. J. Civ. Environ. Eng.* **2011**, *3*, 96–100.
14. Little, D.N.; Epps, J.A. *The Benefits of Hydrated Lime in Hot Mix Asphalt*; National Lime Association: Arlington, VA, USA, 2001.
15. Atikler, U.; Basalp, D.; Tihminlioğlu, F. Mechanical and morphological properties of recycled high-density polyethylene, filled with calcium carbonate and fly ash. *J. Appl. Polym. Sci.* **2006**, *102*, 4460–4467. [[CrossRef](#)]
16. Silva, R.V.; de Brito, J.; Dhir, R.K. Tensile strength behaviour of recycled aggregate concrete. *Constr. Build. Mater.* **2015**, *83*, 108–118. [[CrossRef](#)]
17. Lu, X.; Isacson, U. Compatibility and storage stability of styrene-butadiene-styrene copolymer modified bitumens. *Mater. Struct.* **1997**, *30*, 618–626. [[CrossRef](#)]
18. Estevez, M. Use of coupling agents to stabilize asphalt–rubber–gravel composite to improve its mechanical properties. *J. Clean. Product.* **2009**, *17*, 1359–1362. [[CrossRef](#)]
19. Marzocchi, A.; Roberts, M.G.; Bolen, H.E.; Harrington, E.R. Chemically modified Asphalt Compositions. Patent US4301051A, 24 February 1978.

20. Hristov, V.; Vlachopoulos, J. Influence of coupling agents on melt flow behavior of natural fiber composites. *Macromol. Mater. Eng.* **2007**, *292*, 608–619. [[CrossRef](#)]
21. Yao, H.; You, Z.; Li, L.; Lee, C.H.; Wingard, D.; Yap, Y.K.; Shi, X.; Goh, S.W. Properties and chemical bonding of asphalt and asphalt mixtures modified with nanosilica. *J. Mater. Civ. Eng.* **2012**, *25*, 1619–1630. [[CrossRef](#)]
22. Martí-Ferrer, F.; Vilaplana, F.; Ribes-Greus, A.; Benedito-Borrás, A.; Sanz-Box, C. Flour rice husk as filler in block copolymer polypropylene: Effect of different coupling agents. *J. Appl. Polym. Sci.* **2006**, *99*, 1823–1831. [[CrossRef](#)]
23. Albano, C.; Gonzalez, J.; Ichazo, M.; Rosales, C.; de Navarro, C.U.; Parra, C. Mechanical and morphological behavior of polyolefin blends in the presence of CaCO₃. *Compos. Struct.* **2000**, *48*, 49–58. [[CrossRef](#)]
24. Sae-oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. Roles of silane coupling agents on properties of silica-filled polychloroprene. *Eur. Polym. J.* **2006**, *42*, 479–486. [[CrossRef](#)]
25. Chen, W.-S.; Chang, Y.-L.; Hsiang, H.-I.; Hsu, F.-C.; Yen, F.-S. Effects of titanate coupling agent on the dielectric properties of NiZn ferrite powders–epoxy resin coatings. *Ceram. Int.* **2011**, *37*, 2347–2352. [[CrossRef](#)]
26. Zhang, A.Q.; Wang, Y.M.; Zhuang, C.Y. Discussion the effect on improving granite bituminous mixture performance by adding coupling agent. *Appl. Mech. Mater.* **2012**, *204*, 4115–4118. [[CrossRef](#)]
27. Zhang, A.Q.; Li, J. Surface modification research for asphalt mixture filler. *Appl. Mech. Mater.* **2012**, *174*, 821–825.
28. Zhang, A.; Wang, Y.; Sun, S. Improving water stability of granite-asphalt interface by adding titanate ester coupling agent. *Int. Conf. Transp. Eng.* **2009**. [[CrossRef](#)]
29. Pinnavaia, T.J.; Beall, G.W. *Polymer-Clay Nanocomposites*; Wiley Online Library: Indianapolis, IN, USA, 2000.
30. Jahromi, S.G.; Khodaii, A. Effects of nanoclay on rheological properties of bitumen binder. *Constr. Build. Mater.* **2009**, *23*, 2894–2904. [[CrossRef](#)]
31. Sugeran, G.; Monte, S.J. Neoalkoxy Organo-Titanates and Organo-Zirconates Useful As Coupling and Polymer Processing Agents. U.S. Patent 4623738, 1986.
32. Kenrich Petrochemicals, Inc. *Product Data Sheet: Ken-React[®] CAPS[®] L[®] 12/L-Titanate Coupling Agent*; Kenrich Petrochemicals, Inc.: Bayonne, NJ, USA, 2011.
33. Krueger, Q.J.; King, J.A. Synergistic effects of carbon fillers on shielding effectiveness in conductive nylon 6, 6-and polycarbonate-based resins. *Adv. Polym. Technol.* **2003**, *22*, 96–111. [[CrossRef](#)]
34. Clingerman, M.L. *Development and Modelling of Electrically Conductive Composite Materials*; Michigan Technological University: Houghton, MI, USA, 2001.
35. Al-Abdul Wahhab, H.I. Effect of modifiers and additives on fatigue behavior of asphalt concrete mixes in the gulf. *Int. J. Pavement Res. Technol.* **2012**, *5*, 326–332.
36. Wahhab, H.A.-A.; Abaker, I. Performance modification of asphalt binders using thermoplastic polymers. *J. Eng. Res.* **2004**, *1*, 19–28. [[CrossRef](#)]
37. Fang, C.; Li, T.; Zhou, S.; Wang, X.; Heiliger, L. Study on the modification mechanism of asphalt with waste packaging polymer. *Transp. Dev. Innov. Best Pract.* **2008**. [[CrossRef](#)]
38. Yousefi, A.A. Rubber-polyethylene modified bitumens. *Iran. Polym. J.* **2004**, *13*, 101–112.
39. Asphalt Institute. *Superpave Performance Graded Asphalt Binder Specification and Testing*, 3rd ed.; Asphalt Institute: Lexington, KY, USA, 2003.
40. Asphalt Institute. *Superpave Performance Graded Asphalt Binder Specification and Testing*; Asphalt Institute: Lexington, KY, USA, 1995.
41. Asphalt Institute. *Superpave*; Asphalt Institute: Lexington, KY, USA, 1996.
42. Greene, J.; Choubane, B.; Chun, S. Evaluation of a heavy polymer modified binder through accelerated pavement testing. In Proceedings of the Transportation Research Board 92nd Annual Meeting, Washington, DC, USA, 13–17 January 2013.
43. Wang, C.; Zhang, J.X.; Song, P.P. Short-term ageing influence on the creep and recovery characteristics of asphalt binders. *Appl. Mech. Mater.* **2013**, *275*, 2045–2050. [[CrossRef](#)]
44. Behnood, A.; Olek, J. Rheological properties of asphalt binders modified with styrene-butadiene-styrene (SBS), ground tire rubber (GTR), or polyphosphoric acid (PPA). *Constr. Build. Mater.* **2017**, *151*, 464–478. [[CrossRef](#)]
45. Behnood, A.; Olek, J. Stress-dependent behavior and rutting resistance of modified asphalt binders: An MSCR approach. *Constr. Build. Mater.* **2017**, *157*, 635–646. [[CrossRef](#)]

46. Witczak, M.W.; Kaloush, K.; Pellinen, T.; El-Basyouny, M.; Quintus, H.V. Simple performance test for superpave mix design. In *National Cooperative Highway Research Program*; NCHRP Report 465; National Academy Press: Washington, DC, USA, 2002.
47. Carpenter, S.H.; Vavrik, W.R. Repeated triaxial testing during mix design for performance characterization. *Transp. Res. Rec.* **2001**, *1767*, 76–84. [[CrossRef](#)]
48. D'Angelo, J.A. The relationship of the MSCR test to rutting. *Road Mater. Pavement Des.* **2009**, *10*, 61–80. [[CrossRef](#)]
49. Zhou, F.; Scullion, T.; Sun, L. Verification and modeling of three-stage permanent deformation behavior of asphalt mixes. *Am. Soc. Civ. Eng.* **2004**. [[CrossRef](#)]
50. Monismith, C.L.; Ogawa, N.; Freeme, C.R. Permanent deformation characteristics of subgrade soils due to repeated loading. *Transp. Res. Rec.* **1975**, *537*, 1–17.
51. Faheem, A.F.; Bahia, H.U.; Ajideh, H. Estimating results of a proposed simple performance test for hot-mix asphalt from superpave gyratory compactor results. *Transp. Res. Rec.* **2005**, *1929*, 104–113. [[CrossRef](#)]
52. Witczak, M.W. Specification criteria for simple performance tests for rutting. In *National Cooperative Highway Research Program*; NCHRP Report 580; Transportation research board: Washington, DC, USA, 2007.
53. Dongre, R.; D'Angelo, J.; Copeland, A. Refinement of flow number as determined by asphalt mixture performance. *J. Transp. Res. Rec.* **2009**, *2*, 127–136. [[CrossRef](#)]



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