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Effect of Jatropha Curcas Oil on the Thermorheological Properties of Asphalt Binder Modified with Recycled HDPE

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Effect of Jatropha Curcas Oil on the Thermorheological Properties of Asphalt Binder Modified with Recycled HDPE

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Abstract: The application of bio-oils in asphalt and polymer-modified asphalt (PMA), has recently received considerable attention as a pivotal method for enhancing the high-temperature performance of asphalt mixtures while maintaining good binder's workability. In this study, *Jatropha curcas* oil (JCO) was selected and evaluated as an PMA modifier. JCO-rHDPE-modified bio-asphalt was prepared with different JCO contents: 1, 3, and 5 wt.%. Physical tests (penetration, softening point, and ductility), rheological tests (dynamic viscosity and rolling thin-film oven test–RTFOT), and thermogravimetric analysis (TGA) were employed to evaluate the effect of JCO on the rheological, aging, and thermal properties of unmodified and HDPE-modified asphalt. The addition of JCO was effective in reducing the age hardening of asphalt binders due to an increase in penetration and ductility and a decrease in the softening point, and penetration index values. Aged asphalt binder with a combination of JCO and rHDPE has improved resistance to thermo-oxidative aging, exhibiting lower oxidation and volatilization after RTFOT. TGA indicated that the addition of JCO and rHDPE increases the thermal stability of modified binders by delaying the initial decomposition temperature of neat asphalt by 10°C. The incorporation of JCO leads to a decrease in the viscosity of both virgin and rHDPE-modified asphalt. Thus, JCO-rHDPE-modified asphalt has better workability as well as potentially reduced fuel consumption and harmful emissions at pavement service temperatures.

Keywords: Asphalt, *Jatropha Curcas* Oil, HDPE, Rheological Properties, Thermal Properties

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Introduction

Roads, are one of the most important assets of a country, they provide easy access to basic social amenities. Road extension has increased by approximately 12 million kilometers globally and construction of new surface roads is expected to reach 25 million kilometers by the year 2050 [1]. A growing demand for asphalt in road engineering and declining crude oil reserves around the world have impacted large-scale highway construction and maintenance [2]. Therefore, it is important to seek alternative binders to reduce the use of petroleum asphalt [3].

A good method for reducing fresh petroleum asphalt use is to apply polymers as binder modifiers [1]. Polymer modifiers reportedly possess the capacity to improve the properties of bitumen and thus the overall properties of hot mix asphalt (HMA) used in flexible pavement works [4]. Incorporating polymers into asphalt has many advantages that include, but are not limited to, enhanced fatigue resistance, improved thermal stress cracking, decreased temperature susceptibility, and reduced rutting [5]. Despite these improvements, the polymer loads level usually added to an asphalt matrix is limited (3 to 7 wt.%) [6]. This is because the use of high molecular mass polymers can produce thermodynamically unstable modified bitumen, and phase separation readily occurs during its storage at higher temperatures [7]. Moreover, the process of mixing polymer-modified asphalt binders (PMA) requires high shear and processing temperatures (170°C -180°C) to overcome the viscosity differences between bitumen and polymer and achieve adequate polymer dispersion, significantly impacting the technical properties and costs of the process [5].

To solve this issue, some authors attempted to mix the polymer-modified asphalt with bio-oil [8]. Several vegetable oils have been used as raw materials for flexible pavement applications including waste cooking oil (WCO), soybean oil, rapeseed, linseed, Jatropha curcas, mustard oil, corn oils, palm oil, coconut oil, sunflower oil, tung oil, and palm kernel oils [1,5]. JCO is a non-edible oil that cannot be used for nutritional purposes and does not compete with the food chain. It is thus considered more sustainable for pavement applications than any other food-based crop thanks to the presence of anti-nutritional factors, such as phorbol esters [5]. Ahmad et al. [9] investigated the feasibility of utilizing JCO as a bio-based agent. Their results derived from the positive penetration index (PI) results, which indicate good resistance to low-temperature cracking and storage stability and a higher softening point, showing that JCO was capable of rejuvenating and recycling aged bituminous mixtures as well as reducing construction and maintenance costs. It could also improve workability and the resistance to crack at low temperatures. To the best of our knowledge, no research on the incorporation of JCO in polymer-modified asphalt has been carried out. In this study, polymer bio-asphalt (PBA) binders were produced by modifying the base bitumen with recycled HDPE and JCO with enhanced engineering and thermal properties that can also be a sustainable way to avoid flexible pavements.

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Materials and Methods

Materials

A 50/70 penetration grade base asphalt binder from Puma Energy Mozambique was used. The rHDPE was obtained from the mechanical shredding of HDPE plastic bottles. They were washed and dried to remove residual material before extrusion and pelletizing. JCO seeds were collected in the Administrative Post of Sabié, Moamba District, Maputo, Mozambique (26° 02' 36'' S, 32° 19' 36'' E). The air-dried seeds were cracked, and the kernels were finely ground using mortar and pestle and stored at -14°C in screw-capped 15 mL polypropylene vials. The Soxhlet method was used to extract JCO oil, according to Shivani et al. [10], with slight modifications.

Sample Preparation

The preparation of the specimens was based on Langa et al. [11]. First, the base binder was heated up to 170 ± 5°C and the JCO was added. The binder was then mixed, using an IKA® EUROSTAR 20 high-speed shear emulsifying machine, for 15 min at a rotation speed of 500 rpm. Lastly, rHDPE was added and mixed for 45 min at a constant rotation speed of 4 000 rpm. The modified asphalts considered in this study are asphalt modified by (i) 5 wt.% HDPE (AH5); 5 wt.% JCO (AJ5); 5 wt.% HDPE and 1 wt.% JCO (AH5J1); 5 wt.% HDPE and 3 wt.% JCO (AH5J3); 5 wt.% HDPE, and 5 wt.% JCO (AH5J5).

Experimental Procedures

The physico-chemical properties of JCO were determined by a titration method, following the American Oil Chemists Society (AOCS) test procedure. Hence, the acid value (AV) and free fatty acid (FFA) were determined following AOCS Te 2a-64 standard method; the iodine value – AOCS Cd 1-25; and the saponification value (SV) – AOCS Cd 3c-91. The conventional rheological properties were measured by penetration (ASTM-D5), softening point (ASTM-D36), ductility at 25°C (ASTM-D113), and rotational viscosity at 165°C (ASTM-D4402). The short-term aging (RTFOT) experiment was conducted according to ASTM D2872 and evaluated through various aging indexes including mass change (%ΔW), ductility retention (DR), and viscosity aging index (VAI). Thermogravimetric analysis (TGA) was performed using a TA instrument, model STA 6000 TGA/DSC, where 15 ± 1 mg of the sample was heated in aluminum pans from 25°C to 600°C, with a heating rate of 10°C/min under N_2 atmosphere, with a flow rate of 100 mL/min.

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Results and Discussion

Physicochemical Properties of JCO

This study obtained a high extraction yield of JCO (54.35 wt.%). The JCO showed FFA, AV, SV, and iodine values (IV) of 1.63%, 3.25 ± 0.51 mg(KOH)/g, 181.21 ± 8.48 mg KOH/g, and 121.45 ± 3.17 g/100 g, respectively. The JCO extraction yield obtained in this study is within the yield in the works by Zimila et al. [12] (57.9 ± 3.6 wt.%). Previous studies show that FFA content in JCO from different countries varies from 0.4 to 2.3%, and according to Zhang et al. [13], AV in the range of 0.40 to 3.50 mg(KOH)/g are preferable with regard to the high-temperature rheology of asphalt binder. Ideal SV values for asphalt modification are between 177 to 187 mg(KOH)/g. Lower FFA values are required for asphalt modification as FFA are more prone to oxidation. On the other hand, the JCO obtained has good potential to reduce the viscosity of the polymer composite in line with the report from Mumtaz et al. [14], who suggested that low FFA improves lower kinematic viscosity.

Rheological Properties of Asphalt Binders

Table 1 shows that the addition of 5 wt.% rHDPE decreased the penetration value of virgin asphalt (VA) from 54 to 20 dmm and increased the softening point by 36% (from 47 to 64°C). On the other hand, the addition of 5 wt.% JCO to VA binder increased the penetration value by 28%, from 54 to 69 dmm, and the softening point decreased from 47 to 42°C. As for penetration, the addition of 5 wt.% rHDPE decreased the ductility of VA binder and 5 wt.% JCO increased the VA ductility. In ternary composites binders, the increase in JCO loads from 1 to 5 wt.% increased penetration and ductility and steadily decreased the softening point of HDPE-modified asphalt by 7, 20, and 52%. The change in asphalt consistency as a function of temperature was studied through the penetration index (PI). Lesueur [15] states that the typical range for paving-grade asphalts is -2 to +2.0, and for blown asphalt from +2 to +8. All prepared asphalt binders, except AJ5 and AH5J5, were within the range of the conventional paving asphalt binder. The results obtained showed that the addition of rHDPE leads to binder stiffness [15]. This increase in asphalt binder stiffness can be explained mainly by the formation of the polymeric network in the asphalt matrix, with absorption of the light fractions of the asphalt (maltenes) causing greater internal strength, a beneficial factor that increases binder resistance to permanent deformation at high temperatures [16]. Previous research reported that the addition of bio-oils increases penetration and softening point. These observations can be explained by the decrease in the ratio of asphaltenes to maltenes as a result of the increase in the ratio of lower molecular mass oily medium [17].

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Table 1. Asphalt classification for the paving purpose.

Binders	Viscosity at 165˚C, mPa.s		Ductility at 25˚C, cm		%			Penetration, dmm	Softening point, °C	PI
	Before RTFOT	After RTFOT	Before RTFOT	After RTFOT	Mass change	VAI	DR			
Virgin 50/70	77	91	>100.00	>100	0.077	18.18	-	54.00	47.00	-1.8
AH5	297	351	24.63	21.63	0.029	18.18	87.82	20.00	64.00	-0.2
AJ5	57	73	>100.00	>100	0.070	28.07	-	69.00	42.00	-2.7
AH5J1	261	310.5	26.4	23.47	-0.047	18.97	88.90	25.00	58.00	-0.9
AH5J3	252.5	290	29.63	26.67	-0.040	14.85	90.01	26.00	54.00	-1.6
AH5J5	230	285.5	37.66	34.55	0.035	24.13	91.74	31.00	48.00	-2.6

Table 1 shows that the AH5 binder has the highest viscosity value (297 mPa.s). This increase in viscosity might be explained by higher binder stiffness [15]. High viscosity reduces binder workability, causes non-uniform binder coating with aggregates, and requires higher temperatures for mixing and compaction stages [18]. The HDPE-modified asphalt binder viscosity decreased steadily by adding JCO from 1 to 5 wt.%. The observed viscosity reduction may be explained by the high unsaturated component content in JCO (JCO has a high iodine value). Hence, the JCO balances the chemical composition of the asphalt matrix, enhancing the activity of the molecules in the asphalt binder, and increases the intermolecular distance, or weakens the intermolecular forces [17].

Table 1 shows that VA, AH5, and AJ5 asphalt binders gained mass after aging (oxidation reactions). However, ternary binders registered a mass loss (evaporation of volatile components), except for the AH5J5 binder, which gained mass. All binders comply with the acceptable range of ±0.5% recommended by European standard EN 12607-1 for 50/70 asphalt binders. The aging proprieties of binders was also evaluated through VAI and DR. According to Galooyak et al. [19], lower VAI and higher DR values mean greater aging resistance. The results showed that VA and AH5 binders displayed the same VAI value (18.2%), while AJ5 binder presented a higher VAI value (28.1%). The AH5J3 binder had the lowest VAI value. In the ternary composite, the addition of JCO steadily increase the DR. These results demonstrate that, after aging, addition of HDPE and JCO decreases the viscosity and improves the resistance to thermal-oxidative aging of asphalt binder. This might occur because, during aging, naphthene aromatics are partially converted into polar aromatics, and the polar aromatics are converted into asphaltenes, causing an increase in asphaltene content [17].

Thermal Analysis

Figure 1 shows the TGA and DTG thermograms for asphalt, HDPE-modified asphalt, JCO-modified asphalt, and HDPE-JCO-modified asphalts. These thermograms illustrate that in non-oxidative

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(N_2 atmosphere) conditions, VA thermal decomposition occurs in a single stage. This observation corroborated those found by Tamele et al. [20]. The TGA results show that the initial and final decomposition temperatures for virgin asphalt were registered at 373 and 504°C, respectively, with a maximum degradation temperature of 448°C. According to Tamele et al. [20], below 400°C, the asphalt thermal decomposition can be attributed to the cracking of maltenes fractions, such as saturated and aromatic compounds. Above 400°C, decomposition of asphaltenes fractions and the formation of a coke residue occurs [20].

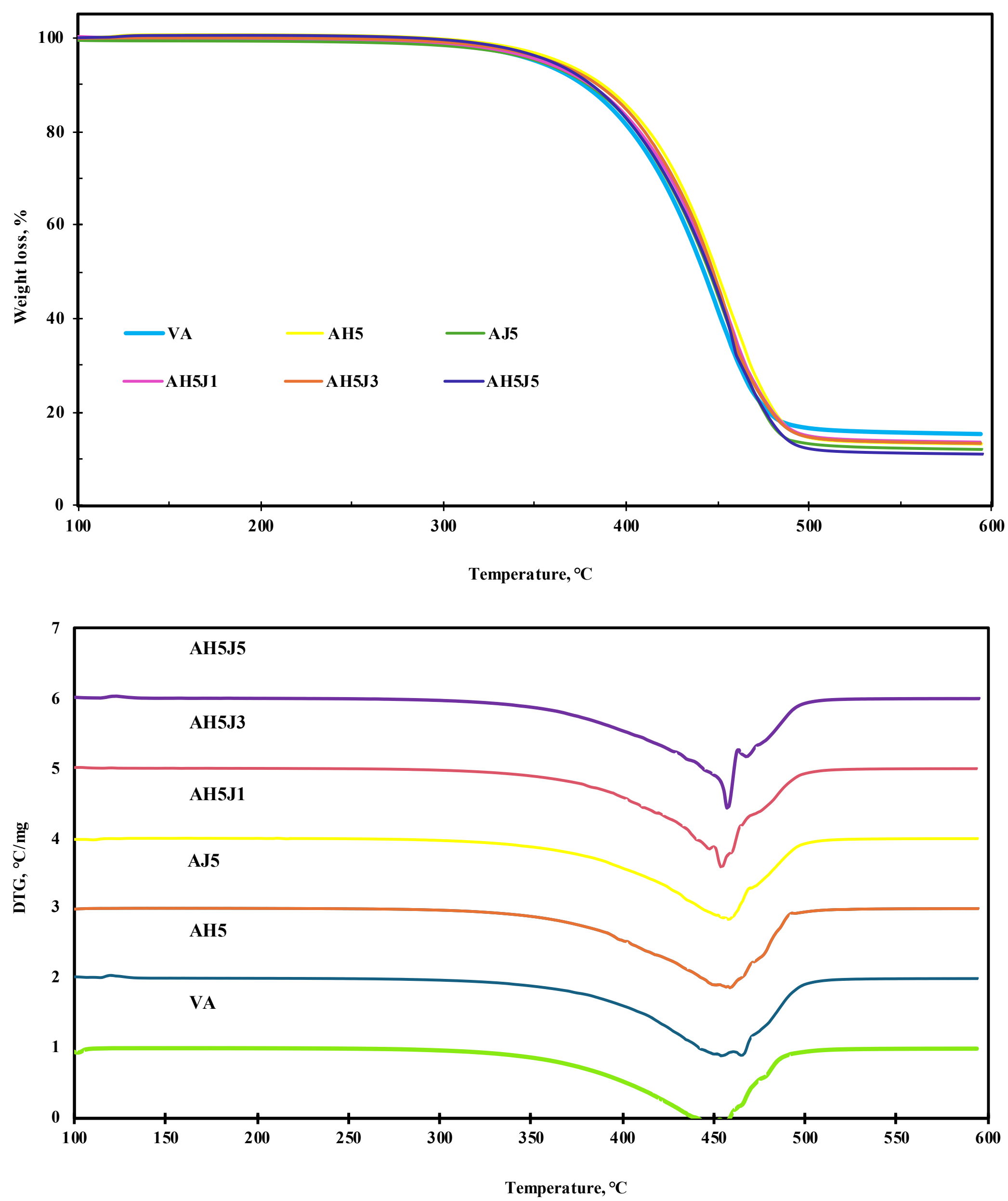

Figure 1. TGA thermograms of asphalt binders. (a) TG-curves; (b) DTG-curves.

The TGA-curves (Figure 1[a]) show that modified binders displayed a similar decomposition pattern to that of neat asphalt binder. However, in DTG curves (Figure 1[b]) of modified binders, there is a superimposition of two decomposition events, in agreement with results from [21]. For the first and more pronounced event, the overlapped peaks in the DTG-curves are due to the occurrence of polymer chains degradation [22], decomposition of cellulosic materials, and lignin compounds of JCO and evaporation of the maltene fraction of asphalt [11]. It can also be seen that the maximum decomposition temperature has been significantly improved. Thus, the incorporation of HDPE and JCO to the binder reduces its susceptibility to thermal decomposition, as specifically demonstrated by the AH5J3 sample. The shift to high observed temperatures could be a consequence of the interactions between the polar compounds of the HDPE and JCO with the asphalt polar fractions, which create forces that prevent the thermal rupture of bonds at relatively lower temperatures. The combination of JCO and HDPE to modify asphalt binders makes it more thermally resistant and consequently more stable to heating.

Conclusions

This study researched the feasibility of JCO as a bio-based modifier agent for unmodified asphalt and HDPE-modified asphalt. Based on this work, JCO was found to be effective in reducing age-hardening of asphalt. Specifically, the experimental data obtained showed that the addition of 1, 3, and 5 wt.% JCO can counteract the stiffening effect of the HDPE-modified asphalt, due to a noticeable increase in penetration and ductility, and a decrease in the softening point and PI values. The addition of 5 wt.% HDPE increases PI value while the addition of JCO reduces the PI value. At higher temperatures, the addition of JCO leads to a decrease in the viscosity of both VA and rHDPE-modified asphalt. Therefore, the addition of JCO to rHDPE-modified asphalt improves binder workability, reducing fuel consumption. At pavement service temperatures, the presence of rHDPE enhances the stability of the asphalt pavement. The interaction of JCO and HDPE is responsible for promoting significant improvements in asphalt binder thermos-oxidative aging resistance and preventing binder failures during the processing, storage, mixing, and compaction stages by exhibiting higher ductility retention, lower mass gain/loss, and lower viscosity aging ratio. The simultaneous incorporation of HDPE and JCO delays the initial decomposition temperature, especially when 3 wt.% JCO is used, which restricts decomposition by 10°C. Thus, it is recommended that the JCO content be kept at less than 3 wt.% for better bio-binder performance.

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