This is the Pre-Published Version.
The Version of Record of this manuscript has been published and is available in HKIE Transactions, 07 Mar 2019 (Published online), http://www.hkie.org.hk/10.1080/1023697X.2018.1534617.

Eco-friendly Paving Materials Using Waste PET and Reclaimed Asphalt Pavement

Anand Sreeram
PhD Candidate
Department of Civil and Environmental Engineering
The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong
Tel: (852) 60535528
Email: anand.sreeram@connect.polyu.edu.hk

Zhen Leng*
Assistant Professor
Department of Civil and Environmental Engineering
The Hong Kong Polytechnic University
Hung Hong, Kowloon, Hong Kong
Tel: (852) 27666007
Email: zhen.leng@polyu.edu.hk
* Corresponding author

Rabindra Kumar Padhan
Post-Doctoral Researcher
Department of Civil and Environmental Engineering
The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong
Tel: (852) 69061790
Email: rabindra.k.padhan@polyu.edu.hk

Xin Qu
PhD Candidate
Institute of Highway Engineering
RWTH Aachen University
D52074, Aachen, Germany
Tel: (49) 2418025220
Email: qu@isac.rwth-aachen.de

Word Count: 3510

Eco-friendly paving materials using waste PET and reclaimed asphalt pavement

A. Sreeram [a], Z. Leng [a*], R.K Padhan [a], X. Qu [b]
[a] Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, [b] Institute of Road and Traffic Engineering, RWTH Aachen University, Aachen, Germany

Abstract

Waste polyethylene terephthalate (PET) and reclaimed asphalt pavement (RAP) represent two categories of waste materials that are currently enduring major recycling efforts around the world. This study proposes a method to incorporate PET based additives into asphalt mixtures containing RAP. Waste PET was chemically treated using an aminolysis process to synthesize PET based additives. The effect of the additives on asphalt binder was then characterized through molecular dynamic simulation (MDS) which indicated that the additives increase the intermolecular interaction within the asphalt binder molecules. Subsequently, binders modified with PET additives were used to prepare mixtures containing RAP at various percentages and tested through conventional rheological tests, such as Marshall Stability tests and Indirect Tensile Stiffness Modulus (ITSM) tests. Mixtures with 2% of PET additives and RAP showed improved stability and Marshall quotient values, demonstrating better resistance to permanent deformation. It was also observed that the PET additives have substantial effect to reduce the ageing effect of mixtures containing RAP, thereby improving the longevity and service life of pavement mixtures. Overall, the results indicated that the usage of such PET derived additives can have a significant positive effect in improving the performance of asphalt mixtures containing RAP and initiates a novel outlet in the disposal of these two globally relevant waste materials.

Keywords: PET, RAP, Chemical Recycling, Sustainability, Paving Materials

[*] Corresponding author. Email: zhen.leng@polyu.edu.hk

1. Introduction

Nowadays, the utilisation of reclaimed asphalt pavement (RAP) in pavement applications has become a routine strategy around the world to promote the eco-efficiency of roads [1]. Although many studies have proved the feasibility of producing robust mixtures containing RAP, there are still concerns regarding the durability and long-term performance of RAP mixtures [1]. As RAP contains stiffer binder which has undergone years of natural ageing through the service life of pavement, the incorporation of RAP in conventional hot mix asphalt (HMA) results in a potentially stiffer and more brittle mixture. While this extra stiffness might improve certain performance properties, such as rutting, it also introduces various concerns related to long term performance, such as moisture damage and fatigue cracking [2, 3]. To mitigate the extra stiffness on the various performance properties of mixtures, there has been considerable research regarding the use of various additives, such as polymers and rejuvenators in conjunction with RAP to provide a more reliable mixture performance [4]. The incorporation of polymers, such as styrene–butadiene–styrene (SBS), ethyl vinyl acetate (EVA), polyethylene (PE), and polyethylene terephthalate (PET) materials in asphalt pavement has been well examined and broadly recognized [5-7]. It has been established that such polymer modification notably improves the performance properties of mixtures, especially in relation to moisture damage and long-term performance [6]. Therefore, the usage of polymeric additives in RAP mixtures is a natural one to overcome its traditional deficiencies. The main aim of this study is to investigate the performance properties of RAP mixtures modified through the addition of waste PET based additives to improve its overall mixture performance, thereby simultaneously recycling two waste materials. It is expected that such collective use of waste materials in pavement applications will provide an efficient recycling outlet and minimise the pressure of disposal.

2. PET Recycling

PET is a common type of polyester used in manufacture of various types of packaging material such as plastic bottles and containers. A disproportionate amount of waste PET in relation to its production has been produced over the past decades due to widespread use. As a result, the recycling of PET has been widely promoted and shown an increasing trend in the past few years [8]. Particularly, plastic PET bottles pose a substantial challenge in disposal due to its superior resistance against environmental factors and cheaper price in comparison to other commonly used materials. PET recycling can be carried using both chemical and physical methods, although the former is preferred as it can eradicate the need for discarding in landfills. Chemical recycling also offers the possibility to produce industrially useful products to maximise the life cycle of PET based products [9]. Application of PET based additives in road pavement has been explored by prior studies and shown promising results in terms of performance properties [10, 11]. For example, some studies used a dry process wherein PET waste was added into the mixture as partial replacement for aggregate. It was reported that such modification enhanced the Marshall Stability and fatigue life but introduced other practical concerns such as phase separation and decrease in specific gravity [11]. Therefore, an application involving homogeneous mixing through a wet process seems to be more suitable for practical pavement applications [12]. Additives prepared through the aminolysis and glycolysis reactions of waste PET have been used to modify asphalt binders through a wet mixing process and shown to improve performance properties in relation to moisture damage, fatigue life and overall rheological performance [13]. From these studies, it seems that PET additives synthesised through an aminolysis process in particular has immense potential to improve performance of asphalt mixtures, including those with RAP constituents. In a preliminary work conducted by the authors, it was observed that amine-based PET additives improved the moisture damage and fatigue properties of RAP mixtures [14]. Nevertheless, the study primarily investigated the effect of PET additives in terms of asphalt binder performance. For field applications, it is critical to study the effect of such additives in terms of acceptable design criteria and mixture performance. In this study, an additive was synthesised through the polymeric degradation of waste PET by Triethylenetetramine (TETA) and used for asphalt binder modification. Subsequently, rheological tests were conducted for mixtures prepared with the binders at different percentages of RAP.

3. Materials and Experimental Program

3.1 Materials

Asphalt binder of penetration grade of 60/70, which is a common type of bitumen used locally in Hong Kong was used as the virgin binder in this study. The gradation of the mixtures is presented in Table 1. The coarse aggregates (greater than 5mm) and fine aggregates (smaller than 5mm) were local granite rocks. The RAP was obtained from wearing course milling and provided by the Hong Kong Highways Department. To synthesise the PET additive, waste plastic bottles were collected and cut into pieces of around 5cm by 5cm. The TETA used for the degradation of waste PET was of industrial grade obtained from Aldrich chemicals.

Table 1. Gradation of mixture

	Mixture Gradation	RAP gradation
Sieve Size (mm)	Pass ratio (%)	
14	100	100
10	85.0	94.1
5	58.0	87.8
2.36	38.0	70.0
1.18	26.0	50.2
0.6	17.9	32.7
0.3	11.0	19.2

0.15	3.4	9.7
0.075	3.0	3.4

3.2 Synthesis of PET Additive

The aminolysis of PET into benzamide derivatives was conducted using 30g of PET reacted with excess TETA in the presence of nitrogen gas under reflux at around 130^{o}C [7]. The PET degradation reaction was completed when the reactant solution turned homogeneous. The product was then crystallized in cold water and filtered out to obtain a yellow semi powder like solid. The process to produce PET additives from waste PET bottles is illustrated diagrammatically in Figure 1.

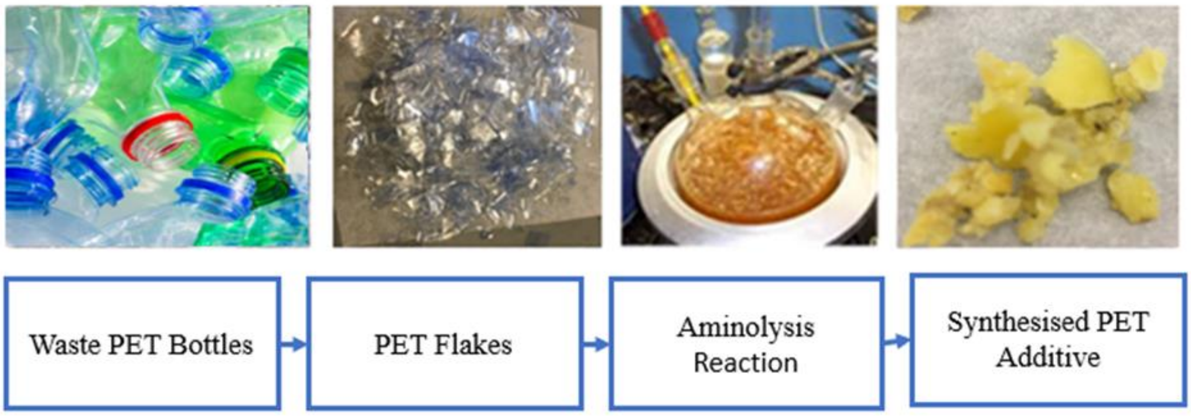


Figure 1. Synthesis of PET additives from waste PET bottles

3.2.1 Mechanism of Reaction

PET possesses a labile ester group in every repeating unit as presented in Figure 2. Such groups are susceptible to solvolysis reaction by polar species such as free amines present in TETA. These polar groups exist due to the electronegativity difference between nitrogen and oxygen giving rise to a lone pair of electrons. As represented by the reaction mechanism in Figure 3, the amine group of TETA reacts with the ester group of PET to form PET derived additives.

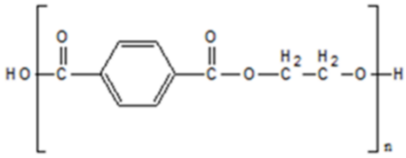


Figure 2. Structure of PET

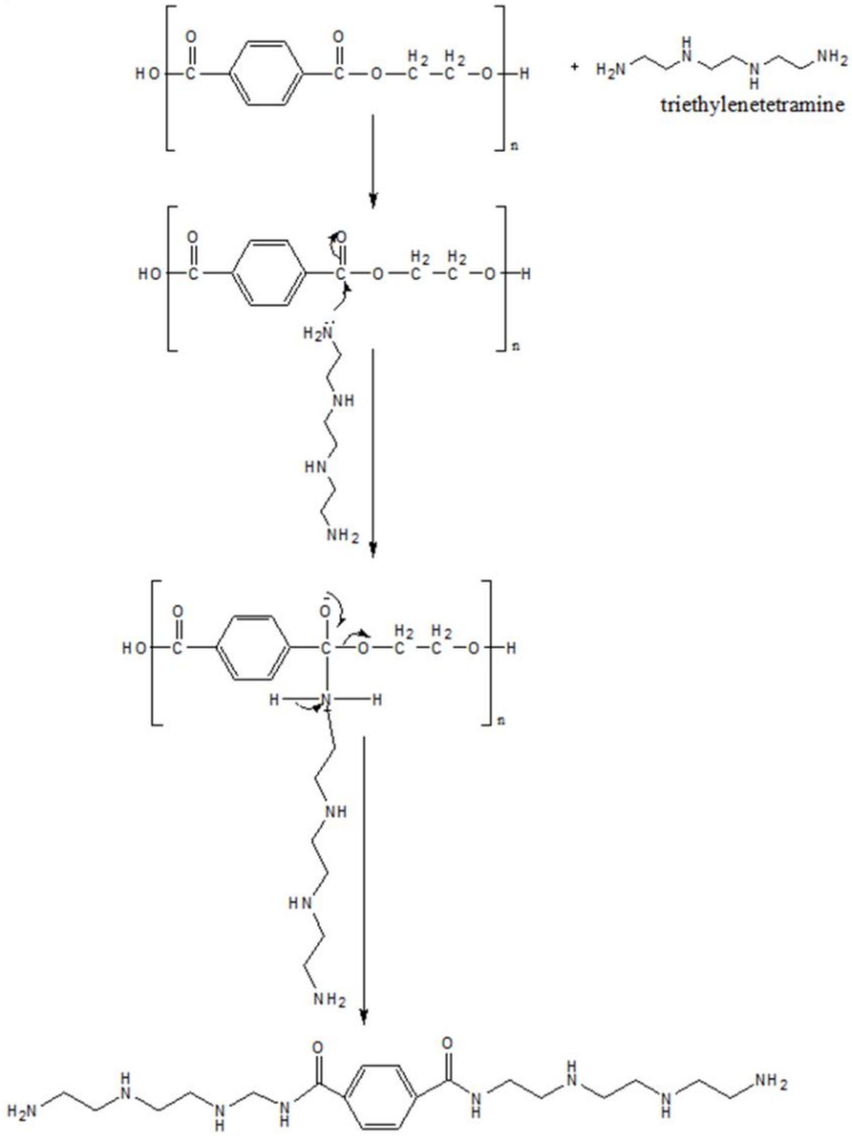


Figure 3. Reaction mechanism of aminolysis

3.2.2 Chemical Characterization of PET Additive

The crystallized product obtained from the aminolysis of waste PET was first characterized by Fourier-transform Infrared (FTIR) spectroscopy analysis as seen in Figure 4. The spectra of the additive were tested using Attenuated total reflectance (ATR). In ATR, evanescent light which is located in the region of contact between the sample specimen and a crystal of high refractive index is attenuated as a result of molecular vibrations. The spectra confirmed the PET degradation and showed the absorption peaks with wave numbers of 1503 cm^{-1}, 1540 cm^{-1} and 1630 cm^{-1} for the aromatic group and two amide groups, respectively. The additive was also then studied by Simultaneous Thermal Analysis presented in Figure 5. The major mass loss from the Thermogravimetric analysis (TGA) was seen to occur between the temperatures of 200^{o}C and 400^{o}C, corresponding to the loss of oxidative and nitrogenous species. Further, the Differential scanning calorimetry (DSC) analysis measured the heat flow into and out of the test sample as compared to a reference, and presents the sample heat capacity as well as endo-exothermic events with temperature changes. The mechanism of DSC test is described by the following equation:

$$\frac{dQ}{dT} = C\frac{dT}{dt} + f\,(t, T) \qquad (1)$$

Where,

$\frac{dQ}{dT}$= total heat flow

C= heat capacity of test sample

$\frac{dT}{dt}$= heating rate

f (t, T) = kinetic component, from the time dependence of crystallization, melting, or chemical reaction

From the analysis of the PET additive sample, two exothermic peaks representing the transition state to crystallinity were observed around 197^{o}C and 234^{o}C, respectively.

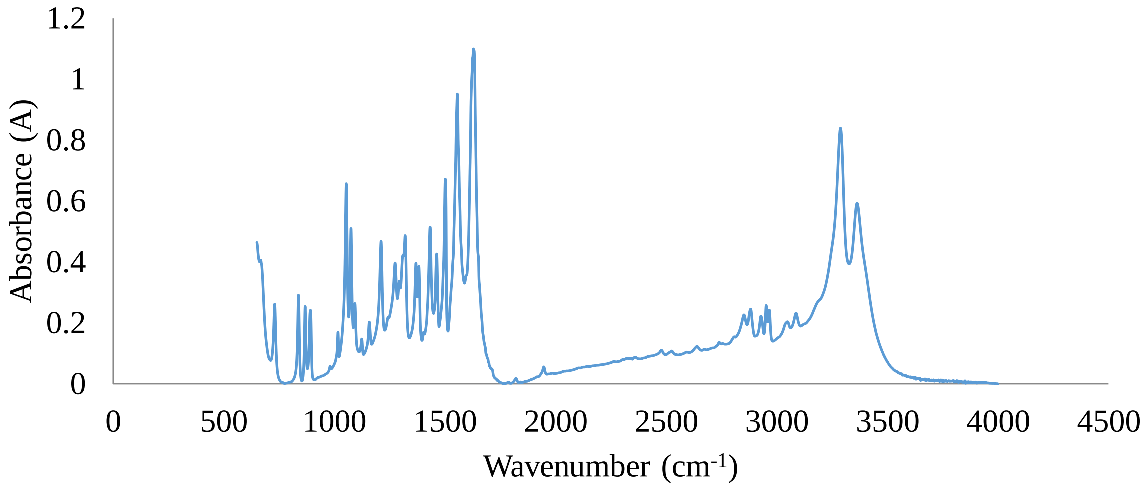


Figure 4. FTIR spectra of PET additive

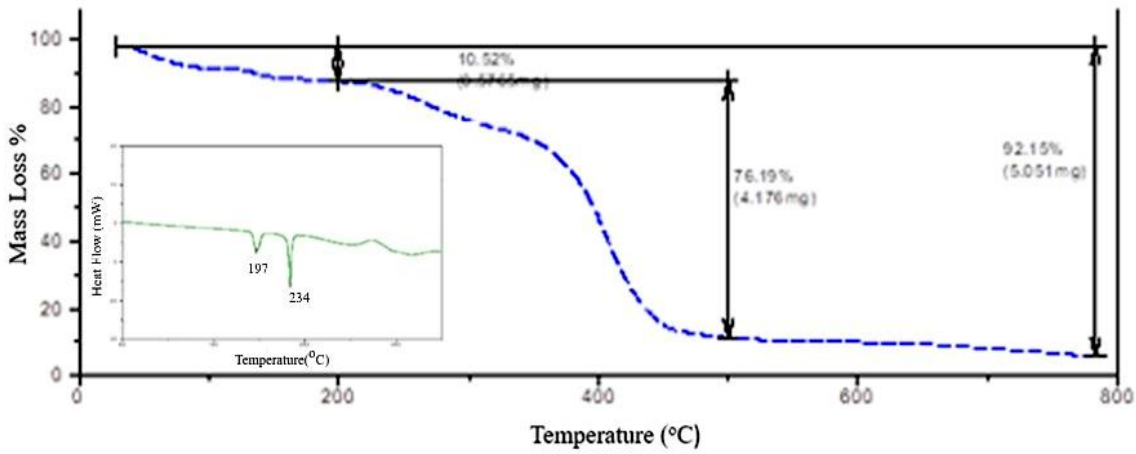
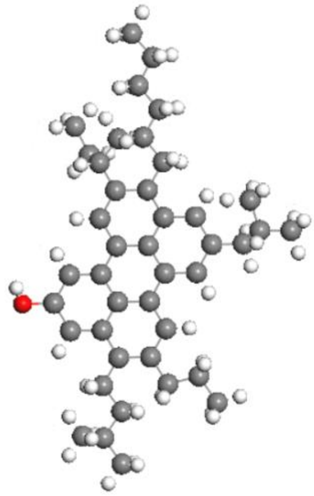


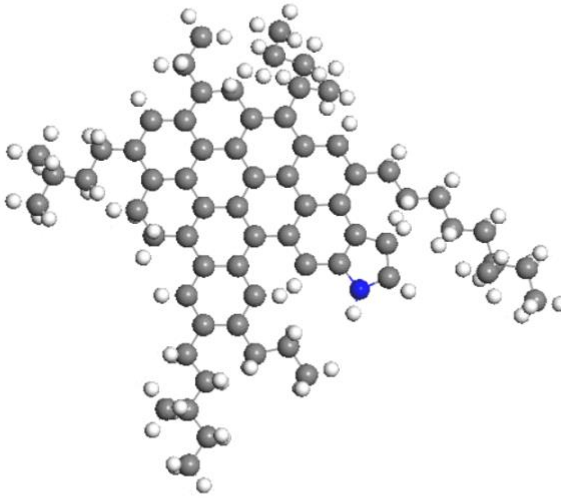
Figure 5. TGA/DSC analysis of PET additive

3.2.3 Molecular Dynamic Simulation

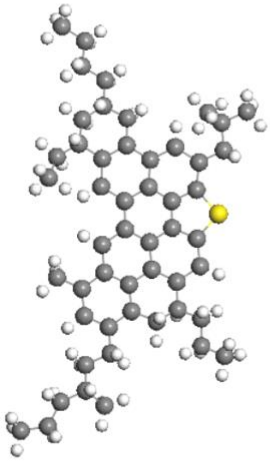
The effect of the PET additive on asphalt binder was evaluated by Molecular Dynamic Simulation (MDS) using Materials Studio software program. Firstly, in order to create the PET modified asphalt binder molecular model, a 12-component asphalt binder model was used to characterize the virgin asphalt binder. The equability of this asphalt binder was validated using element analysis and Hansen solubility [15]. The molecular structures of the 12 components and PET additive are shown in Figure 6.



Asphaltene-phenol



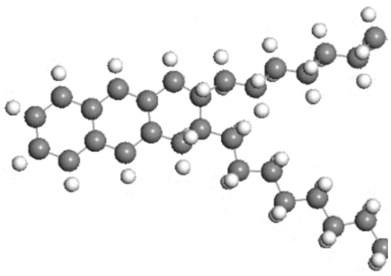
Asphaltene-pyrrole



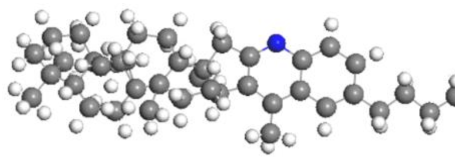
Asphaltene-thiophene

1

Perhydrophenanthrene-naphthalene



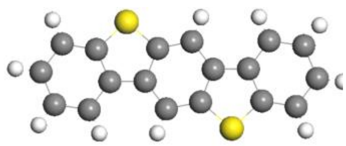
Dioctyl-cyclohexane-naphthalene



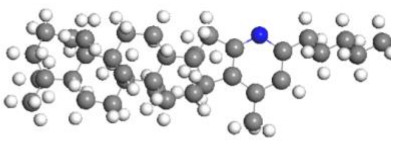
Quinolinohopane

2

Thioisorenieratane

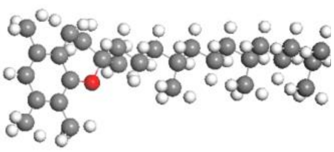


Trimethylbenzeneoxane

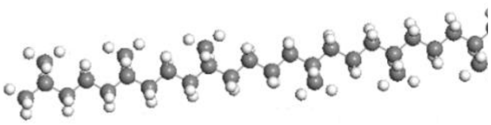


Pyridinohopane

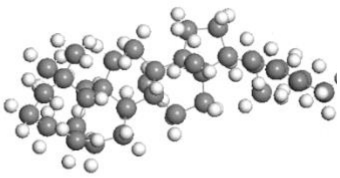
3



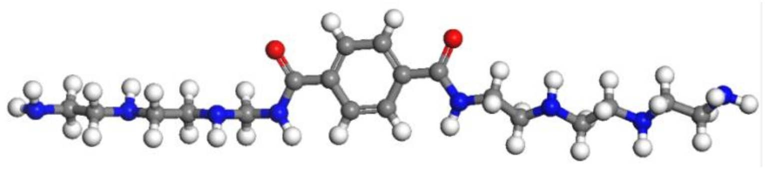
Benzobisbenzothiophen e



Squalane



Hopane



PET Additive

Figure 6. Structures of 12 components in asphalt binder and PET additive [16-26]

To investigate the influence of the PET additive on the properties of the asphalt binder, 2 PET and 4 PET molecules were added into the binder model to obtain the binders with 2% and 4% PET contents according to the molar mass of the 12 components of binder and PET additive.

3.2.3.1 Density

The densities of the binders were examined through MDS to estimate the bulk properties of the molecular models with a duration of 100ps under normal pressure and temperature conditions. The computation process took about 12 hours and the simulated density results are shown in Figure 7. It was observed that the density of binder increased with the addition of PET. 2% PET and 4% PET showed an increment of around 0.3% and 0.7% in density compared to the original binder.

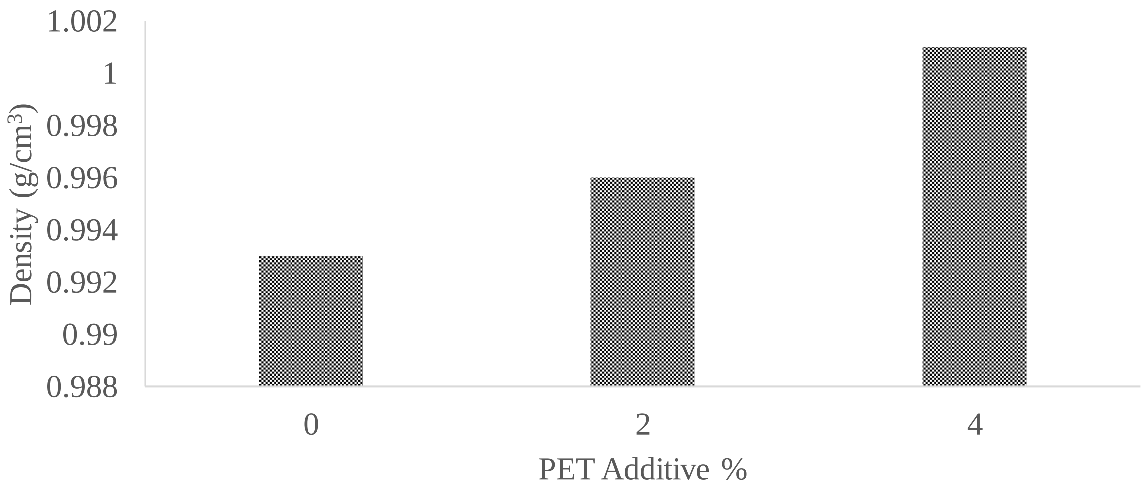


Figure 7. Density results of binders with different PET contents

3.2.3.2 Cohesion Energy Density

The cohesive energy density (CED) is a property that can be used to assess the internal intermolecular interaction inside an asphalt binder molecule model and represents mutual attraction between the molecules of the same material. It has been confirmed from past studies that mechanical properties such as complex modulus has a relationship with the CED value [27]. The CED results of the asphalt binder with PET additive and virgin binder are shown in Figure 8. It was observed that the CED values of PET modified binders were around 25% larger than that of the virgin binder, indicating that the addition of PET increases the intermolecular interaction. Therefore, it is likely that such PET based additives can increase the micro-mechanical properties of conventional asphalt binder.

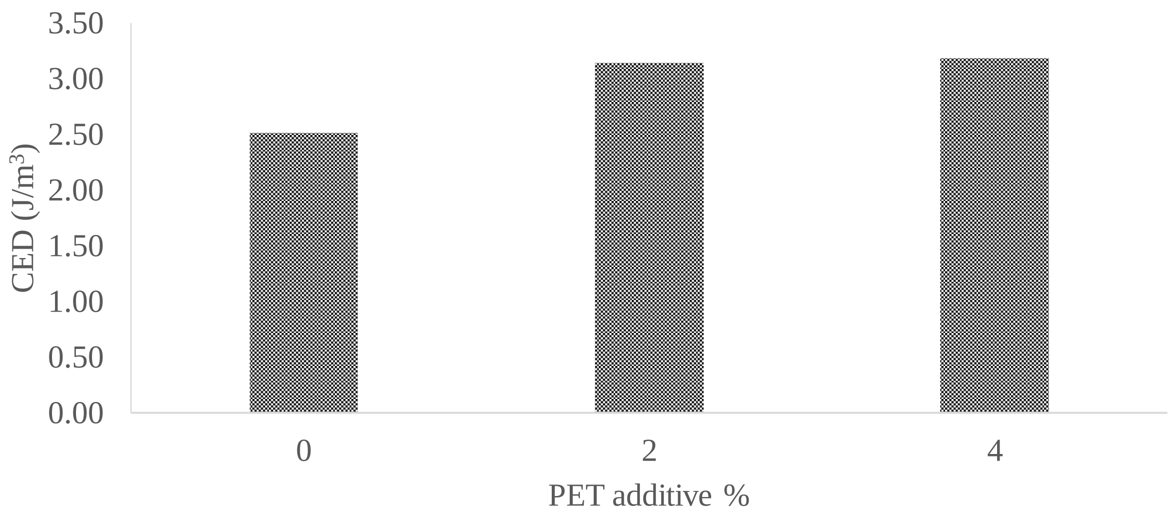


Figure 8. CED results of PET modified binders

3.3 Modification of Asphalt Binder

All modified binders were prepared by mixing virgin binder and PET additive through a high shear mixing process at a temperature between 170 ºC and 180 ºC with a mixing speed of 4000 rpm for 1 hour [14]. Along with the virgin binder, modified binders with 2% and 4% PET additives by weight of virgin binder labelled 2-PET and 4-PET were prepared in this study.

3.4 Sample Preparation

Asphalt mixtures of the different binders were prepared using RAP at 0% (Control), 15%, 30% and 50% to replace part of the aggregates. The total contribution of the recycled binder from the RAP was considered in the design of mixes. Volumetric properties and analysis were conducted to determine the optimum binder content for the control mix and recycled mixes as per ASTM D6927. The aggregates were firstly heated to 160–170°C before preparing the HMA mixtures. 75 blows per side were used to compact the mixtures with a Marshall hammer. In this laboratory work; for each mixture, samples were prepared in triplicate and the average results are presented.

4. Experimental Procedure

4.1 Conventional binder properties and Viscosity

All asphalt binders were first subjected to the basic rheological property tests, including penetration and softening point tests as per ASTM D5 and ASTM D36 respectively. To obtain the viscosities of various binders, Brookfield viscosity tests were conducted as per ASTM D4402 using a DV-II Brookfield rotational viscometer. For these tests, the samples were maintained in the thermo-container for about 30 min at the chosen test temperature before testing.

4.2 Marshall Test

Stability and flow analysis were performed on the different mixtures according to ASTM D1559. Before conducting the tests, the samples were firstly placed in a water bath at 60°C for 30 min of immersion. The values determined by Marshall testing provides performance prediction measures of the mixtures. The test measures the maximum load that can be sustained by the test sample at the loading rate of 50.8 mm/minute. This maximum load at failure is designated as stability. During loading, a dial gauge which is attached computes the specimen's plastic flow or deformation due to the loading. The flow value is recorded in increments of 0.25 mm simultaneously as the maximum load is reached.

4.3 ITSM Test

Indirect tensile stiffness modulus (ITSM) test was performed as per ASTM D4123 to measure the stiffness modulus of specimens, which is considered an important property of an asphalt mixture. It has been shown to designate the ability of pavement layers to dispense traffic loads among themselves and defined as the measure of the response of asphalt pavement layers to the applied stresses and corresponding strains [28-30]. In this test, recurring haversine load pulses at the frequency of 1 Hz (0.1 s loading and 0.9 s rest) were used. The stiffness modulus was then calculated according to the following equation:

$$Sm = \frac{\mathrm{P}\ (\mathrm{v}+0.27)}{\mathrm{tH}} \qquad (2)$$

where Sm is stiffness modulus (MPa), P is repeated load (N), t is the sample's thickness (mm), H is the recoverable horizontal deformation (mm) and ν is the Poisson ratio (an assumed Poisson ratio of 0.35 was used). The tests were performed for unaged samples and samples conditioned through long term oven ageing by placing on a placed on a rack in an oven at 85^{o}C for 120 h (5 days) following the AASHTO R 30-02 test protocol.

5. Results and Discussion

5.1 Conventional binder properties and Viscosity

The conventional binder properties of the various binders are shown in Figure 9. The addition of the PET additive was characterised by an increase in softening point and decrease in penetration values. It was evident that the addition of the additive increases the stiffness of the virgin binder. For example, the penetration values of the virgin binder were seen to decrease by 15% and 20% respectively by the addition of the PET additive at 2% and 4%. The viscosity test was carried out in the temperatures prescribed to determine the change in viscosity of PET modified binders, as represented in Figure 10. The specifications require that the maximum value of viscosity should be less than 2000 cP at 135^{o}C. It was seen that all binders met the requirements, and the inclusion of the PET additive marginally increased the viscosity of the virgin binder. At the temperature of 150^{o}C, virgin binder showed a viscosity of around 200 cP, whereas 2-PET and 4-PET exhibited slightly higher viscosities of around 240 and 270 cP, respectively. At the temperature of 165^{o}C which the mixing temperature is, all binders exhibited viscosities of less than 200 cP, which indicates that workability of binder will not be a concern in the preparation of the mixtures.

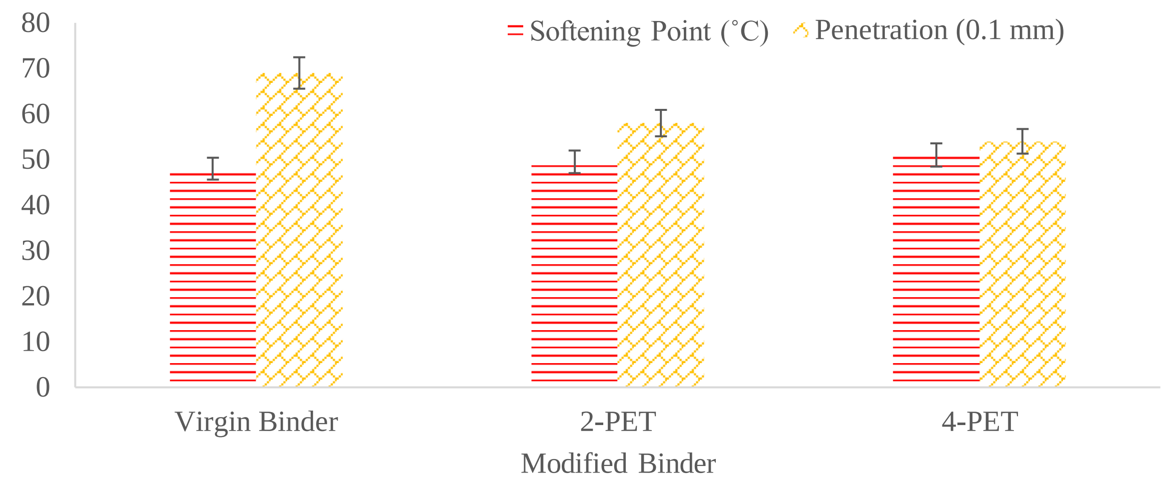


Figure 9. Softening point and penetration values

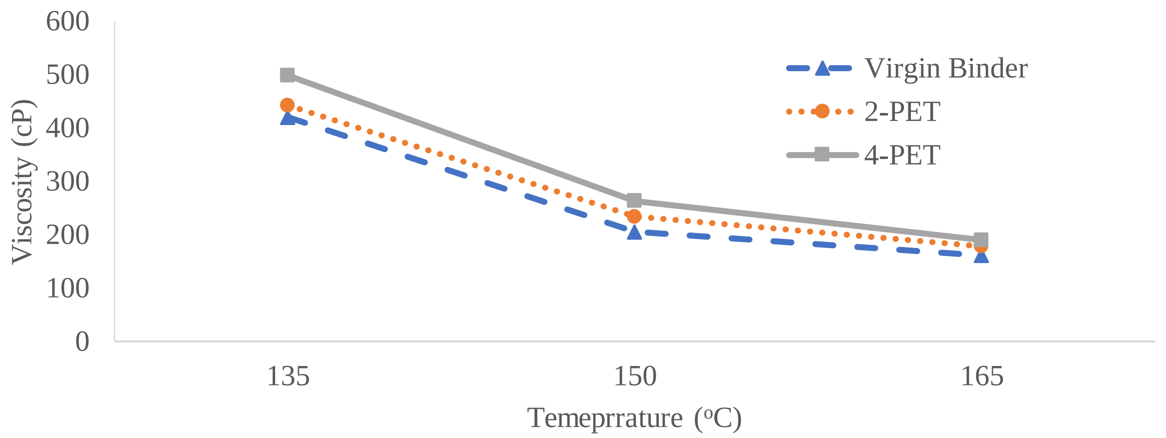


Figure 10. Viscosities of the prepared binders

5.2 Marshall Test

5.2.1 Stability

The various Marshall properties of the prepared mixtures are detailed in Table 2. Marshall stability in particular is often regarded as a vital factor in asphalt mixture design and signifies the capacity of mixtures to resist deformation as a result of applied loads [31]. Figure 11 shows the different stability values of the mixtures with various RAP content. It was seen that all samples prepared met the acceptance requirements of 10 kN and the stability increased with increase in RAP content, mainly due to the availability of stiffer RAP binder, which leads to more rut resistant mixtures [1]. Mixtures prepared using the 2-PET additive showed the highest stability values, with an average increase of around 15-30 % as compared to the virgin binder mixtures. The increase in stability with the incorporation of PET additives can be attributed to difference in polarity between the amine comprising additives and aggregate which increases adhesion tendencies [7]. However, similar to other commercial chemical additives, this effect may be most noticeable at an optimum additive content wherein the distribution of charges between the various molecular fractions in bitumen and amines are most compatible [32]. Such a trend was seen in the study where the mixtures prepared with 4-PET displayed lesser stability than the 2-PET mixtures, which suggests that 2% of PET additive content is more appropriate to maintain maximum stability of mixtures.

Table 2. Marshall properties of mixtures.

Sample	**Mixture**	**Stability (kN)**	**Flow (mm)**	**Air Void (%)**	**Bulk Density (g/cm^3)**
Virgin Binder	Control	13.53	2.42	3.21	2.29
	15% RAP	16.98	2.24	3.32	2.31
	30% RAP	16.58	2.1	3.19	2.31
	50% RAP	19.97	2.45	3.15	2.32
2-PET	Control	15.19	2.41	3.32	2.29
	15% RAP	18.18	2.03	3.4	2.29
	30% RAP	20	2.4	3.31	2.31
	50% RAP	22.12	2.57	3.42	2.31
4-PET	Control	13.4	2.27	3.65	2.3
	15% RAP	15.69	2.24	3.54	2.31
	30% RAP	18.26	2.69	3.43	2.31
	50% RAP	20.24	2.81	3.21	2.32

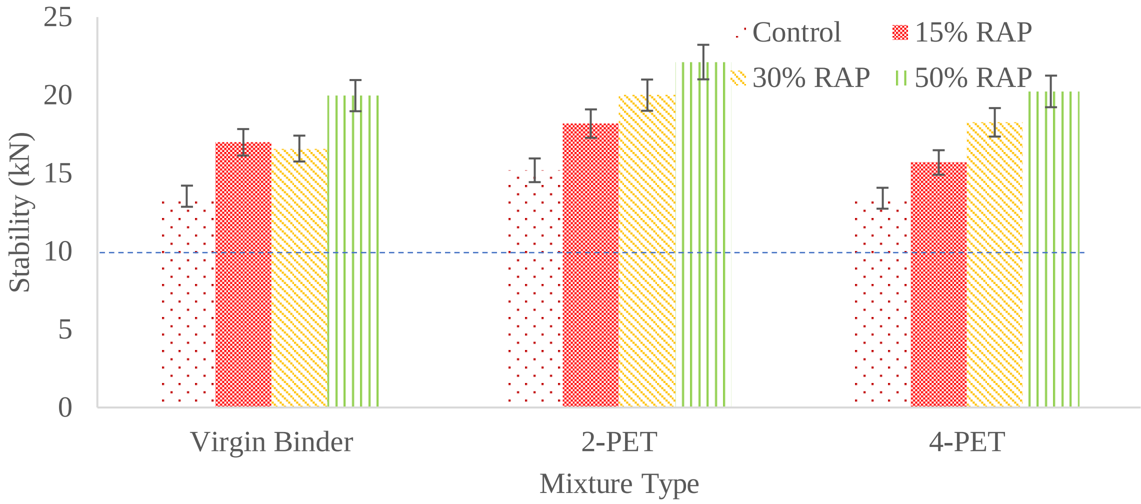


Figure 11. Stability values of mixtures

5.2.2 Flow

The flow value is defined as the total movement or vertical deformation occurring in the sample between no load and maximum load during the stability test and considered a gauge of the plasticity and flexibility properties of mixtures [33]. A high flow value indicates that an asphalt mixture has plastic behaviour and may be susceptible to permanent deformation. Low flow values on the other hand may indicate insufficient binder content in the mixture which may make it prone to long-term durability issues. As per specifications, the optimum flow value for a mixture design is between 2-4 mm. It was observed as seen in Figure 12 that all exhibited flow values were similar and within the adequate range limit. The addition of the PET additive did not significantly change the flow values of the modified mixtures as compared to the virgin mixtures. This is anticipated as the PET additive is mainly composed of plastomeric components, hence its influence on binder elasticity is minimal.

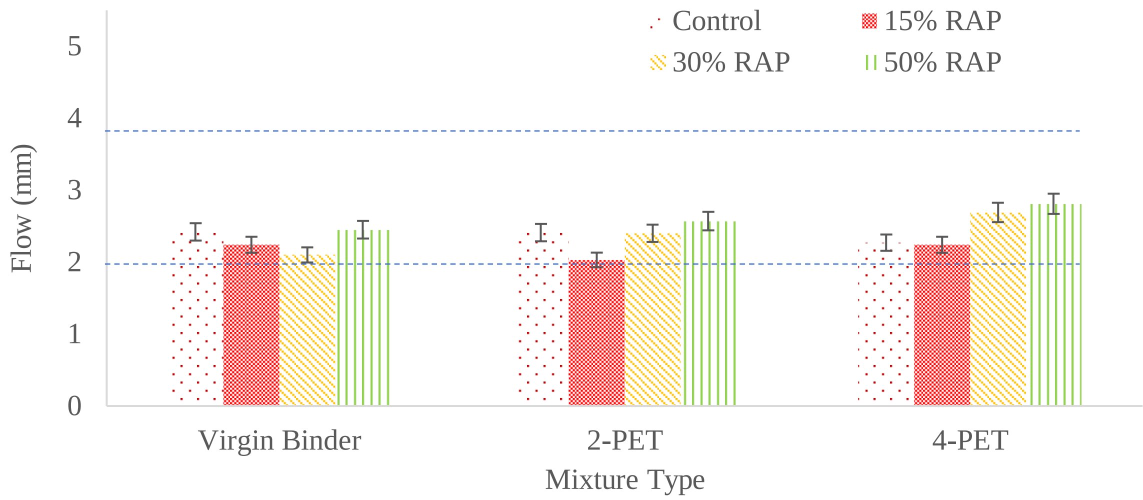


Figure 12. Flow values of mixtures

5.2.3 Marshall Quotient

The Marshall Quotient (MQ) is considered a good indicator of a mixtures resistance to permanent deformation [32]. MQ values were calculated for the various mixtures as represented in Figure 13. A higher MQ value indicates a tauter mixture, hence more resistant to permanent deformation. The PET modified control mixtures showed higher MQ values than the virgin mixtures. All samples prepared with 2-PET showed higher a MQ than 4-PET which might indicate that 2% addition of PET provides the optimum percentage of additive in terms of workability and mixture performance, especially for RAP content over 15 %. Previous studies based on binder properties have noted similar percentages of around 1.5% - 3%, might deliver the most balanced mixture performance [7,14].

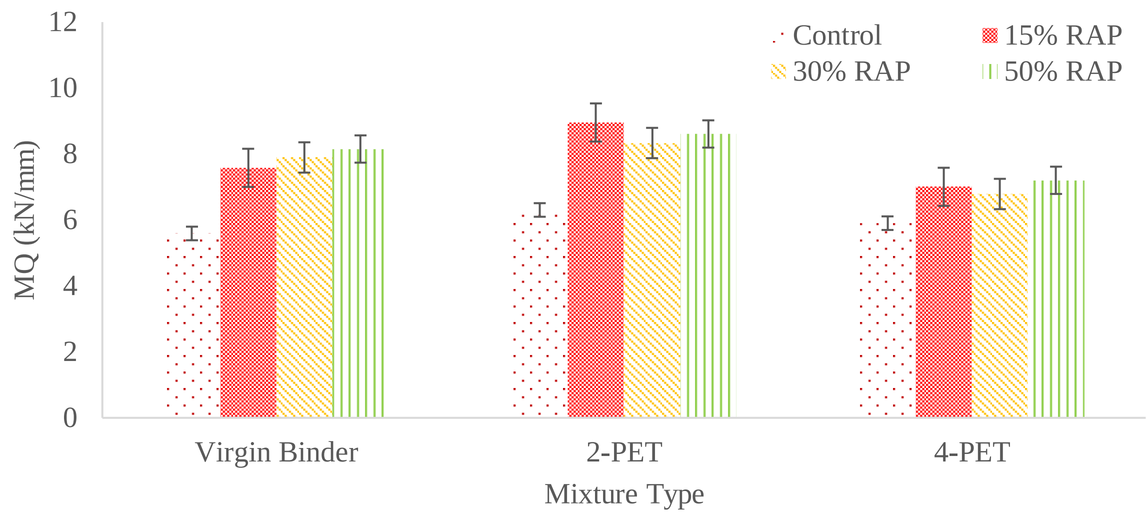


Figure 13. MQ values of mixtures

5.3 ITSM

Results of the ITSM tests at 20°C for different mixtures before and after ageing are shown in Table 3. It was observed that the mixtures prepared with the PET additive exhibited higher stiffness modulus in comparison to the mixtures with the virgin binder. Naturally, this stiffness modulus was seen to increase with the rise in RAP content. To study the rate of increase in stiffness with age, an ageing index, which is the ratio of ITSM value after ageing to the initial ITSM value, was calculated as represented in Figure 14. The mixtures with PET modified binder showed a lower ageing index as compared to the mixtures prepared with the virgin binder, indicating that the PET additives can significantly help negate the further stiffening of aged binder with time. It is hence expected that such modified mixes can yield longer pavement service life due to better ageing resistance properties as compared to the conventional RAP mixes which are generally prone to fatigue cracking problems.

Table 3. ITSM results of mixtures

Stiffness (MPa)				
	Mixture	**Virgin Binder**	**2-PET**	**4-PET**
Before Ageing	Control	1942	2860	2959
	15% RAP	2259	3025	3338
	30% RAP	2331	3205	3410
	50% RAP	2814	4084	4306
After Ageing	Control	3236	4098	4187
	15% RAP	4098	4909	5103
	30% RAP	4500	5144	5306
	50% RAP	6024	7175	7184

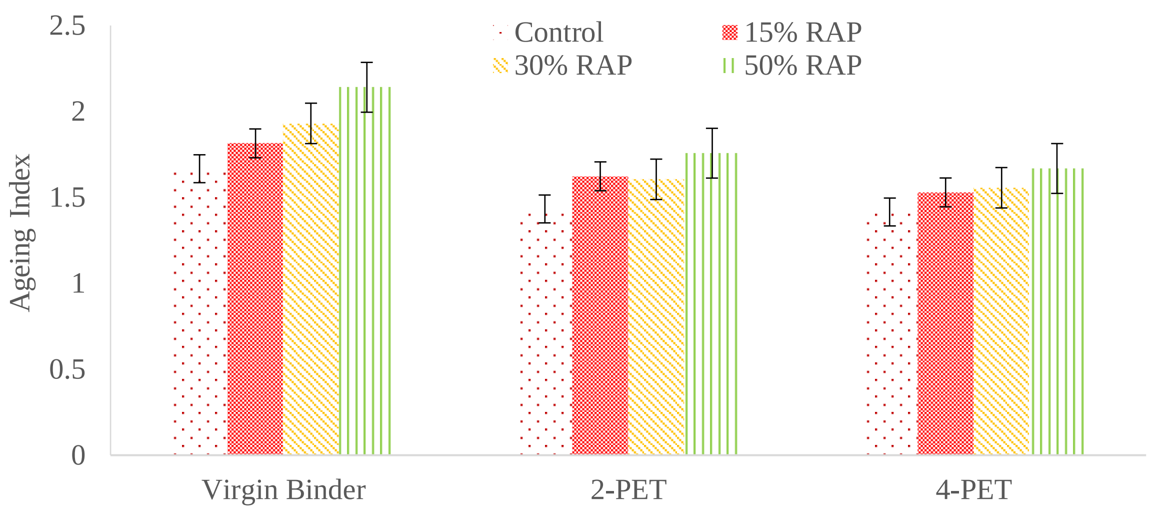


Figure 14. Ageing index of mixtures

6. Findings and Conclusion

In this study, the feasibility of incorporating waste PET as a performance enhancing additive for asphalt mixtures containing RAP was examined. An aminolysis process was used to degrade PET into amine-based additives. Based on the experimental results, the following findings were obtained:

- The PET additive after aminolysis was successfully characterised through FTIR analysis, which showed absorption peaks at 1503 cm^{-1}, 1540 cm^{-1} and 1630 cm^{-1} for the aromatic group and amide groups, respectively.

- According to the MDS, the addition of the PET additive increases the density of the asphalt binder, while the CED values indicated that PET additive molecules may increase the intermolecular interaction within the asphalt binder, thereby increasing performance properties.
- The viscosity of the asphalt binder increased with the addition of the PET additive.
- The RAP mixtures prepared with the 2-PET additives showed higher stability and MQ values indicating better performance against pavement distresses such as deformation and rutting.
- The ITSM test results indicated that RAP mixtures with PET additive are more resistant to ageing as compared to mixtures prepared with virgin binders, signifying better long-term performance.

Overall, the work conducted in this study has verified that the incorporation of PET additives has significant constructive effects on the performance properties of RAP mixtures. It is expected that the usage of such waste materials for pavement applications represents an environmentally and economically viable option for practitioners. It is recommended that further studies be conducted regarding cost-benefit analyses and life cycle assessment before ascertaining the viability for field trials.

7. Acknowledgement

The authors would like to thank the Hong Kong Research Grant Council (Project Number: 15 214615) and Hong Kong Environment and Conservation Fund (Project Number: 84/2017) for providing the financial support for the study presented in this paper.

8. References

[1] Al-Qadi I, Elseifi M, Carpenter S. Reclaimed asphalt pavement: a literature review. Illinois Center for Transportation, Urbana, IL, USA. 2007.

[2] North Carolina Department of Transportation, NCDOT. FHWA/AASHTO RAP ETG survey. 2007.

[3] Materials Engineering and Research Office MTO. RAP usage survey. 2008.

[4] Kodippily S, Holleran G, Henning TFP. Deformation and cracking performance of recycled asphalt paving mixes containing polymer-modified binder. Road Materials and Pavement Design. 2017;18(2):425-439

[5] Hassani A, Ganjidoust H, Maghanaki AA. Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement. Waste Manage Res. 2005;23:322–327.

[6] Yildirim Y. Polymer modified asphalt binders. Construction and Building Materials. 2007;21(1):66–72.

[7] Padhan RK, Gupta AA, Badoni RP, et al. Improved performance of a Reactive Polymer based Bituminous Mixes–effect of cross linking agent. Road Materials and Pavement Design. 2015;16 (2):300-315.

[8] Zia KM, Bhatti HN, Bhatti IA. Methods for polyurethane and polyurethane composites, recycling and recovery: a review. Reactive & Functional Polymers. 2007;67(8):675–692.

[9] Firas A, Dumitru P. Recycling of PET. European Polymer Journal. 2005;41(7):1453–1477.

[10] Garcia-Morales M, Partal P, Navarro FJ, et al. Effect of waste polymer addition on the rheology of modified bitumen. Fuel. 2006; 85:936–943.

[11] Ameri M, and Nasr D. Properties of asphalt modified with devulcanized polyethylene terephthalate. Pet Sci Technol. 2016;34:1424–1430.

[12] Gürü M, Çubuk MK, Arslan D, et al. An approach to the usage of polyethylene terephthalate (PET) waste as roadway pavement material. J Hazard Mater. 2014;279:302–310.
[13] Padhan RK, Gupta AA, Badoni RP, et al. Performance improvement of a crumb rubber modified bitumen using polyoctenamer and cross linking agent. Road Materials and Pavement Design. 2017;18(4):999-1006.
[14] Leng Z, Sreeram A, Padhan RK, et al. Value-added application of waste PET based additives in bituminous mixtures containing high percentage of reclaimed asphalt pavement (RAP), Journal of Cleaner Production 2018; 196: 615-625
[15] Li DD, Greenfield ML. Chemical compositions of improved model asphalt systems for molecular simulations. Fuel. 2014; 115: 347-356.
[16] Oldenburg TBP, Huang H, Donohoe P, et al. High molecular weight aromatic nitrogen and other novel hopanoid-related compounds in crude oils. Organic geochemistry. 2004;35(6):665-678.
[17] Strausz OP, Peng PA, Murgich J. About the colloidal nature of asphaltenes and the MW of covalent monomeric units. Energy & fuels. 2002;16(4);809-822.
[18] Lira-Galeana C, Hammami A. Wax precipitation from petroleum fluids: A review. Developments in petroleum science. 2000;40:557-608.
[19] Simanzhenkov V, Idem R. Crude oil chemistry. CRC Press. 2003.
[20] Li DD, Greenfield ML. High internal energies of proposed asphaltene structures. Energy & Fuels. 2011;25(8):3698-3705.
[21] Koopmans MP, Leeuw JWD, Lewan MD, et al. Impact of dia- and catagenesis on sulphur and oxygen sequestration of biomarkers as revealed by artificial maturation of an immature sedimentary rock. Organic Geochemistry. 1996;25(5–7):391-426.
[22] Koopmans MP, Leeuw JWD, Damsté JSS. Novel cyclised and aromatised diagenetic products of β-carotene in the green river shale. Organic Geochemistry. 1997;26(97):451-466.

[23] Marynowski L, Rospondek MJ, Reckendorf RMZ, et al. Phenyldibenzofurans and phenyldibenzothiophenes in marine sedimentary rocks and hydrothermal petroleum. Organic Geochemistry. 2002;33(7):701-714.

[24] Cai C, Zhang C, Cai L, et al. Origins of palaeozoic oils in the tarim basin: evidence from sulfur isotopes and biomarkers. Chemical Geology. 2009;268(3–4):197-210.

[25] Mullins OC. The modified yen model. Energy & Fuels. 2010;24(4):2179-2207.

[26] Dickie JP, Yen TF. Macrostructures of the asphaltic fractions by various instrumental methods. 1967; 39:727-734.

[27] Bristow GM, Watson WF. Cohesive energy densities of polymers. part 2.—cohesive energy densities from viscosity measurements. Transactions of the Faraday Society. 1958;54: 1742-1747.

[28] Gómez-Meijide B, Pérez I. Effects of the use of construction and demolition waste aggregates in cold asphalt mixtures. Construction and Building Materials. 2014;51:267–277.

[29] Kok BV, Yilmaz M. The effects of using lime and styrene–butadiene–styrene on moisture sensitivity resistance of hot mix asphalt. Construction and Building Materials. 2009;23(5):1999–2006.

[30] Moreno-navarro F, Sol M, Rubio-Gamez C, et al. Reuse of thermal power plant slag in hot bituminous mixes. Construction and Building Materials. 2013;49:144–150.

[31] Akbulut H, Gurer C, Cetin S. Use of volcanic aggregates in asphalt pavement mixes. Proceedings of the Institution of Civil Engineers – Transport. 2011;164(2):111–123.

[32] Little DN, Allen DH., Bhasin A. Chemical and Mechanical Processes Influencing Adhesion and Moisture Damage in Hot Mix Asphalt Pavements. In: Modeling and Design of Flexible Pavements and Materials. Springer, Cham; (2018)

[33] Hot Mix Asphalt Materials. Mixture Design and Construction, National Center for Asphalt Technology. 1991:225.

Table 1. Gradation of Mixture.

	Mixture Gradation	RAP gradation
Sieve Size (mm)	Pass ratio (%)	
14	100	100
10	85.0	94.1
5	58.0	87.8
2.36	38.0	70.0
1.18	26.0	50.2
0.6	17.9	32.7
0.3	11.0	19.2
0.15	3.4	9.7
0.075	3.0	3.4

Table 2. Marshall properties of mixtures.

Sample	Mixture	Stability (kN)	Flow (mm)	Air Void (%)	Bulk Density (g/cm^3)
Virgin Binder	Control	13.53	2.42	3.21	2.29
	15% RAP	16.98	2.24	3.32	2.31
	30% RAP	16.58	2.1	3.19	2.31
	50% RAP	19.97	2.45	3.15	2.32
2-PET	Control	15.19	2.41	3.32	2.29
	15% RAP	18.18	2.03	3.4	2.29
	30% RAP	20	2.4	3.21	2.31
	50% RAP	22.12	2.57	3.42	2.31
4-PET	Control	13.4	2.27	3.65	2.3
	15% RAP	15.69	2.24	3.54	2.31
	30% RAP	18.26	2.69	3.43	2.31
	50% RAP	20.24	2.81	3.21	2.32

Table 3. ITSM results of mixtures

Stiffness (MPa)				
	Mixture	**Virgin Binder**	**2-PET**	**4-PET**
Before Ageing	Control	1942	2860	2959
	15% RAP	2259	3025	3338
	30% RAP	2331	3205	3410
	50% RAP	2814	4084	4306
After Ageing	Control	3236	4098	4187
	15% RAP	4098	4909	5103
	30% RAP	4500	5144	5306
	50% RAP	6024	7175	7184

Figure 1. Synthesis of PET additives from waste PET bottles.

Figure 2. Structure of PET.

Figure 3. Mechanism of aminolysis of PET.

Figure 4. FTIR spectra of PET additive.

Figure 5. TGA/DSC analysis of PET additive.

Figure 6. Structures of 12 components in asphalt binder and PET additive.

Figure 7. Density results of binders with different PET contents.

Figure 8. CED results of PET modified binders.

Figure 9. Softening point and penetration values

Figure 10. Viscosities of the prepared binders.

Figure 11. Stability values of mixtures.

Figure 12. Flow values of mixtures.

Figure 13. MQ values of mixtures.

Figure 14. Ageing index of mixtures.