A simple treatment of electronic-waste plastics to produce asphalt binder additives with improved properties

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Abstract: This study evaluated the performance of e-waste modified asphalt binders. E-waste
modifiers Acrylonitrile Butadiene Styrene (ABS), Acrylonitrile Butadiene Styrene-
Polycarbonate (ABS-PC) and High Impact Polystyrene (HIPS) were used after 100 percent of

the material passed through a #50 (300 μm) sieve. A conventional asphalt binder, PG58-28 binder, was used as a control. The e-wastes were blended with the control binder as untreated (UT) and chemically treated (T) modified binders. Chemically treated (T) modifiers were processed with cumene hydroperoxide before blending into PG58-28, to promote covalent molecular bonding between the e-waste plastic and asphalt. Results showed that untreated e-waste modified asphalt binders were stiffer and more elastic behavior than the control binder, but when these same e-waste plastics were first treated with cumene hydroperoxide, the increases were significantly higher. Use of chemically treated e-waste modifiers also significantly improves the resistance to rutting of asphalt binders, as shown by the work dissipated per loading based on the analysis conducted at 1.59 Hz. The improved results are attributed to the cumene hydroperoxide promoting direct covalent molecular bonding between e-waste plastic powders and the asphalt binder. These results suggest that when polymer modifiers are used in asphalt, radical reactions, at least at the interface with the modifier, should be promoted rather than prevented by added radical inhibitors.

Keywords: Recycled electronic-waste plastic, asphalt modification, rheological, free radical initiator, peltier system, activation energy

1. Introduction

The use of polymers in asphalt pavements has grown rapidly since the early 1970s [1], though the earliest patented modification process of polymer modified asphalt was more than 100 years earlier, in 1843 [2]. Previous studies showed that the modification of asphalt binders using polymer materials significantly improved the properties of asphalt material in several ways, such as a reduction in temperature susceptibility, improved rheological characteristics, and enhanced material durability [2-8]. These enhancements can be seen through the improved functional properties of bituminous pavement, which include the resistance to rutting, fatigue, low temperature cracking, stripping, wear resistance, and aging [2, 9, 10]. The most common polymers used to modify the performance of bituminous binders are styrene butadiene styrene (SBS), styrene-butadiene rubber (SBR), ethylene-vinyl acetate (EVA), as well as virgin or waste polyethylene modifiers [6, 11, 12]. They are used because of their engineering behavior, (influenced by the morphology of the composite), availability, and lower production costs [12-14]. According to Airey [6], SBS copolymers derive their strength and elasticity through the cross linking of their molecules into a 3-D network. The rigid polystyrene end blocks are thought to convey their strength to the polymer while the center polybutadiene block gives the asphalt binders exceptional elasticity. However, Isacsson and Lu [5] and Whiteoak [15] stated that the effectiveness of crosslinking molecules in asphalt binders deteriorates rapidly above 100°C, the glass transition temperature for polystyrene. The strength and elasticity of the polystyrene domain copolymer are restored though when the temperature falls below 100 °C.

Another potential, but still little studied, material additive for asphalt binder modification is electronic waste (e-waste) plastic. E-waste comprises approximately 23.3% by weight of computers that are disposed of worldwide [16]. The rapid growth of electronic gadgets and

computer technologies is making e-waste disposal a significant issue, resulting in negative environmental impacts [17]. The utilization of e-waste to modify asphalt not only relieves pressure on landfills by providing a valuable use for electronic waste plastics but also leads to substantial savings in infrastructure resources. Several studies have been conducted involving the use of e-waste include: Yokoyama and Iji [18], Anandhan et al. [19], Li et al. [20], Achilias et al. [21], Jeong et al. [22], Colbert and You [23, 24] Perez-Belis et al. [25], Wang and Xu [26], and Mueller et al. [27]. A recent study by our group, Colbert and You [23] and Colbert et al. [28], studied the benefit of using acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) plastics as asphalt binder modifiers. The results showed that the e-waste modified asphalt binders met the virgin binder high temperature performance criteria. Furthermore, the e-waste modified asphalt binders were found to be stiffer at low temperatures compared to virgin asphalt binders. The addition of low percentages of e-waste yielded an adequate low temperature performance compared to neat asphalt binders.

In addition to the use of e-waste to improve the properties of asphalt binders, the addition of free radical initiators was also tested in this study to enhance the performance of e-waste modified asphalt binders. Peroxide and hydroperoxide initiators like cumene hydroperoxide (CHP) decompose to produce alkoxy ($\text{RO} \bullet$) and/or hydroxy ($\text{HO} \bullet$) radicals (**Fig. 1**) that can go on to abstract a labile hydrogen (as $\text{H} \bullet$) from the plastic and/or the asphalt, thereby producing new radical (**Fig. 2**). These new radicals can then couple giving covalent bonding between the additive and the binder to promote interfacial adhesion and between different parts of the asphalt itself to enhance branching (**Fig. 2**). **Fig. 3** shows how a new radical ($\text{RO} \bullet$) produced as shown in **Fig. 1**, can abstract an $\text{H} \bullet$, leading to a reactive radical on a polymer backbone (e.g. a styrene unit in ABS or SBS with the labile H atom shown in bold) or a labile hydrogen on hydrocarbon

components that are commonly present in bituminous asphalt (the above representative aromatic component shows seven labile hydrogen atoms) leading to new reactive radicals. The last line in **Fig. 3** shows the coupling of radicals, such as a styrenic radical from e-waste (e.g. ABS) and a radical on an activated aromatic component of asphalt.

Fig. 1.

Fig. 2.

Fig. 3.

These bonding scenarios were proposed to show how radical reactions can be used beneficially to improve the tensile strength, intermolecular interaction, and the molecular weight of an e-waste modified asphalt binder. However, in contrast to this approach, other studies have investigated the possible benefits of preventing radical reactions in asphalts. A study conducted by Li et al. used anti-oxidants as free-radical scavengers to prevent radicals from reacting and altering the more susceptible butadiene block in styrene-butadiene-styrene (SBS) modified asphalt (5 %), and by doing so, improved the aging resistance of [29]. A typical anti-oxidant scavenging reaction is illustrated in **Fig. 4**. However, it is important to recognize that butadiene repeat units possess C=C bonds and that bond can react over time, making that segment more brittle. Here, we are targeting different radical reactions that can promote branching and covalent bonding between the polymer modifier and asphalt binder. The effects of these modifications on aging remain to be studied.

Fig. 4.

The ultimate goal of this study is to demonstrate that there is value in using e-waste plastic in the bituminous materials to improve the durability of asphalt pavements, and the use of e-waste in asphalt pavements could be a major value-added outlet for this growing waste resource. Secondly, we demonstrate that the useful properties gained from adding e-waste polymers to asphalt binders are significantly improved by including free-radical initiators in the formulation to serve the dual purpose of rheology modifiers and adhesion and branching promoters between the phases.

2. Materials

Fig. 5 shows the e-waste modifiers that were used in this study: Acrylonitrile Butadiene Styrene (ABS), Acrylonitrile Butadiene Styrene-Polycarbonate (ABS-PC), and High Impact Polystyrene (HIPS). Formerly, the e-waste plastics were refined using a heavy-duty shredder and grinder to reduce the plastic particles to powdered computer plastics [23]. ABS is characterized as a heterogeneous multi-phase polymer that consists of a rubber component and a combination of styrene acrylonitrile [30]. Additionally, ABS has a good impact strength, rigidity, toughness and a good chemical resistance [21]. While, based on Balart et al. [31], ABS and PC waste plastic exhibited lower mechanical properties compared to virgin plastics, they retained their properties favorable to various engineering plastics in the market. However, it was found that ABS-PC is not recycled efficiently using conventional recycling methods, contributing to its reduction in value and demand among plastic recyclers [30].

The modifiers were used under two different conditions, which are untreated (UT) and chemically treated (T). The treated modifier was initially sprayed with hydro-peroxide before blending into the conventional asphalt binder, PG58-28. The treatment of e-waste powders was anticipated to reinforce molecular bonding between e-waste plastics and asphalt binders. The intended result of this molecular bonding was to enhance low and high temperature performance of modified asphalt binders.

Fig. 5.

3. Methodology

3.1 Preparation of treated and untreated e-waste modified asphalt binder

A high shear mixer was used to combine the asphalt binder, e-waste powders, and hydroperoxide (only for the chemically treated e-waste asphalt binders) together for 45 minutes at 5000 RPM and at 3000 RPM for 15 minutes to ensure complete melting and blending of the e-waste modifiers within the asphalt binder. The asphalt binders used for this investigation includes: 5% ABS-UT modified asphalt binder, 5% ABS-T modified asphalt binder, 5% ABS-PC-UT modified asphalt binder, 5% ABS-PC-T modified asphalt binder, and a control asphalt binder. The control asphalt binder was a neat binder PG58-28 that was delivered from an asphalt mixture production plant in Gladstone, Michigan.

Cumene hydroperoxide was used as the free radical initiator for this investigation. The explanations of the treatment were clearly described by Colbert [23] and are illustrated in **Fig. 6**. The treatment of e-waste plastics took place through three steps:

- 1) Contact between melted e-waste plastic chains and thermally generated peroxide radicals occur at an appropriate melting temperature. For a given polymer the melting or softening temperature can vary significantly depending on the polymer source and thermal history, but for ABS plastics this is often around 105 °C. ABS-PC is typically amorphous though its T_g is often ~125 °C. HIPS melting point is often reported to be anywhere from 180 to 260 °C. Therefore, at our processing temperatures HIPS probably did not melt sufficiently for any significant covalent bonding to have occurred between it and the binder. However, the initiator would still promote reactions with the asphalt binder itself.
- 2) The radical's abstract hydrogen atoms, causing a range of different reactions, include chain scissions depending on the conditions.
- 3) Finally, molecular weights can rebuild, improving strength properties [32].

Fig. 6.

3.2 Oscillatory test on the e-waste modified asphalt binder

A HAAKE RheoStress 6000 dynamic shear rheometer (DSR) was used to evaluate the rheological properties of asphalt binders modified using various types of e-waste modifiers through a Peltier system. By using this system, the test was conducted without using water as a medium to control the temperature of the specimen, which is commonly used in the standard dynamic shear rheometer (DSR) procedures. Prior to testing, the DSR specimens were prepared using untreated and treated Acrylonitrile Butadiene Styrene (ABS-UT and ABS-T) and untreated and treated Acrylonitrile Butadiene Styrene-Polycarbonate (ABS-PC-UT and ABS-PC-T)

modifiers which were blended into a control asphalt binder, PG58-28, at 5% and 15% by weight. The results of those modified binders were compared to the dynamic rheological properties of the neat PG 58-28 binder. The specimens were tested at 12% strain, a frequency of 1.592 Hz, and at a temperature range of 46°C to 82°C. The HAAKE Rheometer DSR and the prepared sample in a rubber mold are shown in **Figs. 7(a) and (b)**, respectively. The results are shown in **Figs. 8~15**.

Fig. 7.

3.3 Bending Beam Rheometer test on the e-waste modified asphalt binder

A Cannon Bending Beam Rheometer (BBR) was used to evaluate the low temperature susceptibility of asphalt binders modified using different types of e-waste modifiers. Prior to testing, the BBR specimen was prepared using 5% by weight of Acrylonitrile Butadiene Styrene (ABS) and High Impact Polystyrene (HIPS) modifiers which were blended into a control asphalt binder, PG58-28. The results of those e-waste modified binders are compared to the low temperature properties of the m-value and creep stiffness with the neat PG 58-28 binder. The specimens were tested at -18°C. Four modified formulations were tested in addition to the control binder. The modified PG 58-28 binders contained 5% by weight of HIPS-UT, HIPS-T, ABS-UT or ABS-T. The results are shown in **Fig. 16**.

3.4. Analysis of activation energy of e-waste modified asphalt binder

When a fluid flows, the layers of the fluid molecules slide over each other while the intermolecular forces resist the motion, causing resistance to flow in the molecular structure of

the fluid [33]. Therefore, for a fluid to begin flowing, a certain level of energy is required and should be higher than that of the intermolecular forces, which is called the activation energy. The effect of e-waste material on the intermolecular forces was evaluated in terms of the activation energy in this study. Arrhenius equation (Equation 1) was used to model the viscosity–temperature dependency of e-waste asphalt binders

$$\nu = Ae^{\frac{E_f}{RT}} \quad (1)$$

where:

ν = viscosity (Pa's),

A = a regression constant,

E_f = the activation energy for flow (kJ/mol),

T = temperature (°K) and

R = the universal gas constant (8.314 J/mol/°K).

4. Results and Discussions

4.1 Oscillatory testing results

The mechanical response of viscoelastic materials depends on their loading and the given temperature of the material. Oscillatory testing is the best method to understand the complex behavior of modified asphalt binders [34]. Six modified formulations were tested in addition to the control binder, which were 5% untreated ABS modified binder (5% ABS UT), 15% untreated ABS modified binder (15% ABS UT), 5% untreated ABS-PC modified binder (5% ABS-PC UT), 5% ABS treated binder (5% ABS T), 15% ABS treated binder (15% ABS T), and 5% ABS-PC treated (5% ABS-PC T). In shear mode, the complex modulus (G^*) and phase angle (δ) at different temperatures were evaluated and recorded for the various e-waste plastics modified

asphalt binders. The G^* indicates the total resistance of the asphalt binder to deformation under an applied load, while the δ represents the relative distribution of the asphalt binder's total response between the viscous and elastic components. Bahia and Anderson [34] observed that the δ of asphalt is a function of temperature, loading time, and composition, which can be related to the properties of the modifiers used in this study. A value of 0° for δ indicates that the asphalt binder exhibits a completely elastic nature, while a 90° value indicates a completely viscous behavior. The Elastic Modulus (G') and Viscous Modulus (G'') were also determined and presented in a Cole-Cole rheology plot to illustrate the contribution of the elastic and viscous portions within the e-waste modified asphalt binder.

4.1.1 Effects of treated and untreated e-waste powder on G^* and δ of modified asphalt binders

Both parameters (G^* and δ) are crucial to the performance of the binder. During every loading cycle, failure is dependent on the amount of strain or stress developed by the continuous cyclic loading and the degree of deformation that can be recovered or dissipated in the asphalt binder. Theoretically, the stiffness and the rate of relaxation of the asphalt binder is directly related to the results of G^* and δ , respectively [34]. A higher G^* value and a lower δ are favorable and indicate a good resistance to rutting; however, a higher relaxation rate and lower stiffness is essential and favorable for resistance to thermal cracking. **Figs. 8~10** display the results for G^* and δ over a continuous temperature range from 46°C to 82°C for the modified e-waste and control (PG58-28) binders.

Fig. 8(a) shows the results for the control binder (PG58-28) and the binders modified with 5% ABS-UT and ABS-T. The hydroperoxide-treated ABS-T modified binder has the highest G^* values throughout the test compared to the 5% ABS-UT binder. This increase in

stiffness could be the result of good dispersion and adequate molecular bonding of e-waste plastics with the asphalt binder. The phase angle, serving as an index to characterize the viscosity of the asphalt binder, suggests that 5% ABS modified asphalt binders are less viscous and have a better elasticity since their curves are always under the neat binder curve; especially for the 5% ABS-T binder (**Fig. 8(b)**). Based on these conditions, both ABS-UT and ABS-T e-waste modified asphalt binders are more resistant to rutting than the control, with the ABS-T modified asphalt significantly outperforming the ABS-UT modified asphalt and the control based on the G^* and δ curves.

Fig. 8.

Fig. 9 shows the G^* and δ graphs of the control asphalt binder and binders modified with 5% by weight of ABS-PC-UT and ABS-PC-T, and it shows the same trends observed with the binders modified with ABS-UT and ABS-T. The ABS-PC-T modified binder has the largest G^* (**Fig. 9(a)**) while the G^* of the ABS-UT and control binders are significantly lower. The G^* from the ABS-PC-T modified asphalt binder did, however, decline rapidly between 46-52 °C, before recovering a little by 55 °C. Despite this significant decline, the ABS-PC-T modified asphalt binder consistently maintained a higher G^* than the other asphalt binders. The reason for the drastic decline is not obvious, but it may be due to some chemical change facilitated by the radical initiator, since it is not observed in the binder modified with ABS-PC-UT. The 5% ABS-PC-UT binder is shown to have phase angle δ values similar to those of the control binder over the DSR temperature range between 82-90° while the ABS-PC-T modified binder has significantly lower δ values, which repeats the pattern seen for the 5% ABS-T modified binder in

Fig. 8(b). The data shows that the stiffness and the rate of relaxation of the PG58-28 binder are only slightly improved with 5% ABS-PC-UT powder. However, the modification by ABS-PC-T seems to possess a good enhancement of visco-elastic properties including those at higher temperature ranges, which might result in a better performance of the pavement at the maximum in-service temperatures.

Fig. 9.

The effect of the amount of modifier was tested for the untreated e-waste. **Fig. 10(a)** compares the effect of increasing the amount of added e-waste (ABS-UT) from 5% to 15% by weight. Increasing the amount of ABS-UT in the binder to 15 % yielded the highest G^* obtained, which was much greater than that of either the control binder or the binder modified with just 5% ABS-UT. Again, at higher temperatures, the G^* of both modified resins declined significantly and from 70-82 °C, were not significantly different from the control binder. The phase angle δ , resulting from increased quantities of ABS-UT, was similar to that resulting from adding initiator. Modification of the binder with 5% ABS-UT slightly altered the phase angle compared to that of the control binder over the DSR temperature range between 46-82 °C; however, blending 15% ABS-UT into the binder drastically reduced the δ over the temperature range of approximately 85-65°, as presented in **Fig. 10(b)**. Overall, the e-waste modified asphalt binders are stiffer and more elastic compared to the control binder, and asphalt viscosity increases with increasing percentages of e-waste modifiers as mentioned by Colbert and You in their paper [23]. Furthermore, the application of the hydroperoxide before blending the powder into the conventional asphalt binder has tremendously helped in improving the high temperature

performance of the modified asphalt binders by reinforcing the molecular bonding between e-waste plastics and asphalt binders.

Fig. 10.

4.1.2 Cole-Cole curve

Figs. 11 and 12 display the results of the elastic modulus (G') and viscous modulus (G'') to illustrate the rheological behavior of the modified e-waste binders. **Fig. 11** compares the results of ABS-T and ABS-UT modified binders with those of the unmodified control binder while **Fig. 12** presents the results of the 5% ABS-PC-UT and ABS-PC-T modified asphalt binders. In general, the e-waste modified asphalt binders exhibited a higher stiffness and viscosity compared to the control binder, as shown by the linear curves presented from the Cole-Cole charts in **Figs. 11 and 12**. The results show that using ABS-T and ABS-PC-T plastics with the asphalt binder increases both the elastic and viscous modulus compared to the ABS-UT and ABS-PC-UT modified asphalt binders. The asphalt modified with ABS-PC-UT had the lowest G' and G'' coefficients for all the e-waste plastic modified binders, followed by the ABS-UT modified binder. It seems that the PC component is not helpful in this approach. The results confirm the benefit of the initiator to the formulation since the binder modified by 5% ABS-T resulted in a higher G' and G'' coefficient, implying an increase in the elastic and viscous modulus compared to the control PG 58-28 and untreated 5% ABS binders. The presence of treated e-waste plastic particles in the binder allows the matrix to respond to deformation, and it should favor a high temperature rutting resistance under traffic loading.

Fig. 11.

Fig. 12.

The Cole -Cole curve can be used to validate the data for a master curve at any frequency or temperature [35]. Acceptable data from a Cole-Cole chart are independent of temperature and frequency and forms a single curve. As shown in **Fig. 12**, the correlation between G' and G'' is linear for all of the binder samples, irrespective of e-waste type and treatment. Therefore, it can be implied that the data presented in **Figs. 8~10** is valid.

4.1.3 Resistance to Rutting

Figs. 13 and 14 display the results of the $G^*/\sin(\delta)$ Superpave rutting parameter for the e-waste modified and control asphalt binders. In SHRP specifications, the rheological parameter, $G^*/\sin(\delta)$, was used to express the role of the asphalt binder to prevent rutting. This value indicates the total resistance of the asphalt binder to damage under repeated loading (G^*) and the relative amount of energy recovered or dissipated into non-recoverable deformation ($\sin(\delta)$) during the loading cycles [36]. Higher asphalt binder stiffness is favorable to avoid excessive deformation of the pavements, and it should be adequately elastic so that it can return to the original condition after unloading. Therefore, the $G^*/\sin(\delta)$ should be adequately large, especially in the early life of a pavement and when exposed to high temperatures during summer days. **Fig. 13** shows that the ABS modified asphalt binders exhibited a better resistance to rutting compared to control binder over the entire temperature range, especially for the 5% ABS-T binder and 15% ABS-UT binder. The sample prepared using the 5% ABS-UT modifier was

found to have marginally increased the rutting parameter, where the $G^*/\sin(\delta)$ values are slightly higher compared to control sample (PG58-28) at the test temperature within the range of 46°C to 64°C. In general, a higher percentage of ABS resulted in an increased rutting parameter value for the e-waste modified asphalt binders. Based on the overall results, the ABS-T modified asphalt binder has better resistance to rutting.

Fig. 13.

Fig. 14 displays the $G^*/\sin\delta$ results for the ABS-PC modified e-waste asphalt binders. Again the results for the binder modified with 5% ABS-PC-T are greater than those for the ABS-PC-UT and the untreated control binder. The results of ABS-PC-T outperform the other binders except for a 4 °C temperature range from 52-56 °C where the ABS-PC-UT seems to be better than the ABS-PC-T modified binder. The results for the ABS-UT modified binder are slightly better than the unmodified control binder until approximately 70°C where the $G^*/\sin(\delta)$ values for the control binder and the binder with 5% ABS-PC-UT are similar. .

Fig. 14.

Fig. 15 shows the work dissipated for the resistance to rutting based on the analysis conducted at 1.59Hz at four different temperatures between 58°C and 76°C. Based on the constant strain (0.001%), the calculation was performed using the following equation.

$$W_c = \pi \sigma_0^2 / (G^* / \sin \delta) \quad (2)$$

367

368 Where:

369 W_c = Work dissipated per load cycle

370 σ_o = Stress applied during load cycle

371 G^* = Complex modulus

372 δ = Phase angle

373 In the field, when the load (loading and unloading) is applied, the work from each load is
374 transferred to the pavement. A portion of the work is absorbed by the pavement and reflected as
375 elastic rebound. The remaining work is converted into pavement distresses such as rutting,
376 fatigue cracking, and crack propagation. For this investigation, strain is considered a constant
377 where high dissipated energies per load cycle are favorable prior to having a better resistance to
378 rutting. By the addition of chemically treated e-waste modifiers into the asphalt binder, the
379 amount of dissipated energy per load cycle seems to have increased tremendously. Based on the
380 dissipated energy results, chemical e-waste treatment improved the resistance to rutting by an
381 average of 30 times greater than that of the unmodified asphalt binder. However, polymer
382 modifications of asphalt binders using untreated e-waste powder should be avoided since it
383 would not considerably improve the high temperature performance of asphalt binder due to
384 unstable molecular bonding between the e-waste particles and the asphalt binder.

385

386 **Fig. 15.**

387

388 Based on the W_c results, the asphalt binder modified using 15% ABS-T has a
389 performance comparable to the asphalt binder modified with 5% ABS-PC-UT regardless of

testing temperatures. Additionally, there is no difference in the rutting resistance between the asphalt binder modified using 5% ABS-T and 15% ABS-UT but the performance is comparable. Overall, the best results have been achieved using the 5% ABS-PC-T modified asphalt binder because it gives the highest resistance to rutting throughout the tested temperature range. However, it is recommended to use an appropriate amount of e-waste powder to modify the asphalt binders to obtain a favorable performance, not only at high temperatures but also when experiencing other conditions, where the failure could be due to thermal cracking or fatigue cracking. Furthermore, if seeking to apply similar (initiator-treated) polymer-modifiers to asphalt binders, researchers need to take into consideration that the modification of a bituminous material may result in excessive hardening due to different processing histories including stirring and the processing time at the specified temperature range, and therefore, the final properties could be influenced by the oxidation of the bituminous phase

4.2 Effects of e-waste powder on creep stiffness and m-value of modified asphalt binders

The creep stiffness and m-value (the rate of change in creep stiffness) are crucial parameters to consider in determining the thermal cracking performance of the asphalt. Asphalt binders which are resistant to thermal cracking will have a combination of a creep stiffness under 300 MPa and an m-value greater than 0.3. **Fig. 16** displays the results for the creep stiffness and corresponding m-values for asphalt binders modified with 5% ABS-T, ABS-UT, HIPS-T, and HIPS-UT along with the unmodified control binder (PG58-28). The m-value is given after 60 seconds at -18°C and -21°C.

Fig. 16.

Fig. 16 shows that the m-value slightly decreases from the control value for the asphalt binders modified with treated and untreated ABS and treated and untreated HIPS. Creep stiffness is slightly increased from the control binder for the 5% ABS and HIPS modified binders at both -18°C and -21°C. From the results, the addition of 5% ABS-UT resulted in a 7.4% increase in creep stiffness at -18°C and a 6% increase in creep stiffness at -21°C versus the control binder. When the binder was modified with 5% ABS-T, there was a 10.7% increase in creep stiffness at -18°C and a 17.4% increase in creep stiffness at -21°C versus the control binder. The modified binders also had a higher creep stiffness and lower m-value than the 5% HIPS binders for both treated and untreated cases, resulting in a 3.7% increase for the 5% HIPS-UT binder and a 4.7% increase in creep stiffness for the 5% HIPS-T versus the control binder at -18°C. The treated 5% ABS-T binder resulted in the highest creep stiffness and lowest m-value as temperatures decreased from -18°C to -21°C, implying that there is an increase in susceptibility to thermal cracking versus the control PG 58-28 and 5% ABS-UT binders. The presence of treated e-waste plastic particles in the binder allows the matrix to have a decreased rate of change in stiffness at lower temperatures.

4.3. Effects of e-waste powder on activation energy of e-waste modified asphalt binders

Table 1 presents the activation energies of asphalt binders. The addition of e-waste powder increases the activation energy of 5% ABS-UT, 5% ABS-PC-UT, and 15 % ABS-UT samples by 1.48%, 1.52%, and 5.21%, respectively, in comparison to that of the control binder. Meanwhile, the activation energy of 5% HIPS-UT is 1.23 times higher than that of the control binder, which indicated that the intermolecular forces of the e-waste modified binder is stronger

than that of the control binder. Theoretically, a higher activation energy implies a better structural integrity against permanent deformation due to stronger intermolecular forces resisting the motion of the molecular layers initiated by the external force (i.e. traffic loading). Hence, it results in a higher resistance to rutting, which is consistent with the results of $G^*/\sin(\delta)$ presented in **Figs. 13 and 14**.

Table 1.

In contrast, Table 1 shows that the activation energy of 5%ABS-T and 5%ABS-PC-T are -38.43 % and -57.06 %, respectively. The negative value indicates that the activation energy of the chemically treated e-waste binders is lower compared to the control asphalt binder, PG58-28. Without a proper analysis, the result can be misinterpreted where the intermolecular forces of such binder samples are relatively weaker and, consequently, exhibit less strength in deformation compared to the control asphalt specimen. However, the results of $G^*/\sin(\delta)$ for the modified binder clearly show a higher performance at the sweep temperature. The explanation for this observation can be made via evaluation of the gradient of $G^*/\sin(\delta)$ where the correlation between $G^*/\sin(\delta)$ and temperature is mathematically interpreted as shown in Equation 4, which is developed based on the continuous function presented in Equation 3.

$$\lim_{T \rightarrow T_{n,i}} G^*/\sin(\delta) = f(T) \quad (3)$$

$$46^\circ\text{C} \leq T \leq 82^\circ\text{C}$$

$$\begin{aligned}
G^*/\sin(\delta)\text{Gradient} &= \frac{\Delta G^*/\sin(\delta)}{\Delta T} = \frac{\partial[G^*/\sin(\delta)]}{\partial T} \\
&= \frac{(G^*/\sin(\delta))_n - (G^*/\sin(\delta))_i}{T_n - T_i} \quad (4) \\
&46^\circ\text{C} \leq T \leq 82^\circ\text{C}
\end{aligned}$$

Where:

$(G^*/\sin(\delta))_n$ = Final $G^*/\sin(\delta)$

$(G^*/\sin(\delta))_i$ = Initial $G^*/\sin(\delta)$

T_i = Initial temperature

T_n = Final temperature

From the Gradient of $G^*/\sin(\delta)$ results presented in Table 1, two trends can be found.

The first trend is that the absolute values of gradient of $G^*/\sin(\delta)$ of some samples from 46°C to 52 °C are higher than the gradients from 52°C to 82°C, as shown by the gradients of 5 % ABS-T and 5 % ABS-PC-T presented in Equation 5. The second trend shows a pattern opposite from the first trend where the values of the gradient of $G^*/\sin(\delta)$ of samples from 46°C to 52 °C are lower than those from 52°C to 82°C. Based on the overall findings, the control, 5 % ABS-UT, 5 % ABS-PC-UT, 15 % ABS-UT, and 5 % HIPS-UT exhibited results consistent with the second trend. However, it can be seen that the values of the gradient of $G^*/\sin(\delta)$ of the second trend from 52°C to 82°C are very close to the total gradient of $G^*/\sin(\delta)$, which is measured from 46°C to 82°C. For example, the absolute values of the gradient of $G^*/\sin(\delta)$ of the control sample from 46°C to 82°C and 52°C to 82°C are 7.47 and 7.6, respectively.

$$\left\{ \begin{array}{l} \text{The Trend 1: } [\text{Gredient of } G^*/\sin(\delta)]_{46^\circ\text{C to } 52^\circ\text{C}} > [\text{Gredient of } G^*/\sin(\delta)]_{52^\circ\text{C to } 82^\circ\text{C}} \\ \text{The Trend 2: } [\text{Gredient of } G^*/\sin(\delta)]_{46^\circ\text{C to } 52^\circ\text{C}} < [\text{Gredient of } G^*/\sin(\delta)]_{52^\circ\text{C to } 82^\circ\text{C}} \end{array} \right. \quad (5)$$

Referring to the activation energies of 5 % ABS-T and 5 % ABS-PC-T asphalt binders, the $G^*/\sin(\delta)$ of both binders dramatically decreases from 46°C to 52°C, which is consistent with the curves shown in **Figs. 13(a)** and **14**, while the $G^*/\sin(\delta)$ values only slightly change at the lower rate from 52°C to 82°C. Such an obvious change in the material behavior (based on the result trend) shows that the rate of reduction in the binder stiffness (in terms of $G^*/\sin(\delta)$) is smaller at elevated temperatures, indicating a lower temperature susceptibility. It is essential to carefully understand this phenomenon and avoid any misinterpretations of the result. The lower activation energy of the chemically treated e-waste binders can be interpreted based on the reduction in complex viscosity over the temperature sweep at the higher rate. Prior to this, it is recommended to analyze the activation energies considering the results of $G^*/\sin(\delta)$ to avoid being misled on the performance of the modified binders.

5. Conclusions

In this study, three e-waste plastic powders, ABS, ABS-PC, and HIPS, were added to the control asphalt binder to modify the performance. The effects of a free radical initiator on the properties of e-waste modified asphalt binder were also evaluated. The main intention of using this initiator was to improve the branching and stability of the modified asphalt binder and to promote interfacial adhesion between binder and polymer-modifier by direct chemical bonding. A peltier system was used to evaluate the rheological properties of the modified asphalt binder

specimens. The bending beam rheometer was used to evaluate and compare the low temperature performance of ABS and HIPS modified asphalt binders. Based on the results, several conclusions can be made as follows:

- i. The e-waste modified asphalt binders have exhibited a higher stiffness and more elastic behavior compared to the control binder, PG58-28.
- ii. Using 5% of ABS-T and ABS-PC-T to modify the binder yielded greater increases in the elastic and viscous modulus than were achieved using the same amount of ABS-UT and ABS-PC-UT in the asphalt binders, showing direct benefit from the added initiator.
- iii. Generally the HIPS-T modified asphalt properties were not so different from HIPS-UT asphalt, unlike with the other e-waste plastics. This may attributed by the high melting temperature of the HIPS, reducing the beneficial interfacial bonding to the asphalt. However, the initiator would still promote reactions in the asphalt phase.
- iv. The ABS modified e-waste binders have greater $G^*/\sin(\delta)$ values at low to intermediate temperatures than the control. However, ABS-PC and ABS binders have similar values for rutting parameters from temperatures ranging from 70 to 82°C.
- v. It is highly recommended to evaluate the effects of e-waste materials on the intermolecular forces of the binder samples based on the analysis of the activation energies. Additionally, it is also suggested to analyze the activation energies based on an asphalt rheological parameter such as $G^*/\sin(\delta)$.

The overall significance of this work is that rather than using anti-oxidants to inhibit radical formation within the binder, some properties are enhanced by the addition of free radical initiators that increase the radical formation in polymer-modified asphalt binders

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List of Figures

Fig. 1. Peroxide (ROOR) and hydroperoxide (one or both R's = H) free radical initiators

decompose to produce alkoxy (RO•) and/or hydroxy (HO•) radicals that will initiate chemical changes leading to interfacial adhesion.

Fig. 2. Example of how generated radicals may lead to increased branching in asphalt

components. Here, a representative activated aromatic radical couples with a representative activated saturated radical.

Fig. 3. Reaction sequence showing how a radical initiator (e.g. RO–OR) forms reactive radicals.

Here we show abstraction of an H• from a styrene repeat unit and from a representative asphalt hydrocarbon, which then couple, giving branching by covalent bond giving a strong interface.

Fig. 4. Reaction showing how a typical anti-oxidant works by providing an easily abstracted H•, and leaving behind a new but unreactive radical.

Fig. 5. E-waste computer plastic used in this study (a) ABS, (b) ABS-PC and (c) HIPS

Fig. 6. Treatment process of e-waste plastics using free radical initiator to produce active radicals on e-waste polymer backbones, leading to interfacial bonding with asphalt

Fig. 7. (a) HAAKE RheoStress 6000 DSR, (b) Prepared sample

Fig. 8. (a) Complex Modulus and (b) phase angle of specimens prepared with 5 % ABS-UT and ABS-T at different temperatures.

Fig. 9. (a) Complex Modulus and (b) phase angle of specimens prepared with ABS-PC-UT and ABS-PC-T at different temperatures.

Fig. 10. Effects of different percentages of ABS-UT and temperature on G^* and δ

Fig. 11. Cole-Cole curve of ABS e-waste modified binders, a) Untreated 5% ABS versus control, b) Treated 5% ABS versus control

Fig. 12. Cole-Cole curve of ABS-PC e-waste modified binders, a) Untreated 5% ABS-PC versus control, b) Treated 5% ABS-PC versus control

Fig. 13. Superpave rutting parameter for e-waste modified binders, a) Effect of 5% ABS-UT and 5%ABS on $G^*/\sin \delta$, b) Effect of 5% ABS-UT and 15%ABS-UT on $G^*/\sin \delta$

Fig. 14. Comparison between Superpave rutting parameter of 5% ABS-PC-UT and 5%ABS – PC-T

Fig. 15. Work dissipated energy for rutting prevention

Fig. 16. Effects of chemical treatment of ABS and HIPS modified binders on (a) m-value and (b) creep stiffness at -18°C and -21°C

696   **List of Tables**

697

698   **Table 1.** Activation energy for e-waste modified binders

699

List of Figures

Fig. 1. Peroxide (ROOR) and hydroperoxide (one or both R's = H) free radical initiators decompose to produce alkoxy (RO •) and/or hydroxy (HO•) radicals that will initiate chemical changes leading to interfacial adhesion.

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Reactive radical   Generic anti-oxidant

Unreactive radical

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(a) Acrylonitrile Butadiene Styrene (ABS)

(b) Acrylonitrile Butadiene Styrene-Polycarbonate (ABS-PC)

(c) High Impact Polystyrene (HIPS)

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(a) HAAKE RheoStress 6000

(b) E-waste Binder in Rubber Mold

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(a)

(b)

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Fig. 13. Superpave rutting parameter for e-waste modified binders, a) Effect of 5% ABS-UT and 5%ABS on $G^*/\sin \delta$, b) Effect of 5% ABS-UT and 15%ABS-UT on $G^*/\sin \delta$

Fig. 14. Comparison between Superpave rutting parameter of 5% ABS-PC-UT and 5%ABS – PC-T

Fig. 15. Work dissipated energy for rutting prevention

(a)

(b)

Fig. 16. Effects of chemical treatment of ABS and HIPS modified binders on (a) m-value and (b) creep stiffness at -18°C and -21°C

List of Tables

Table 1. Activation Energy for e-waste modified binders

Asphalt	Activation Energy (kJ/mol)	Difference (%)	G*/sin(δ) Gradient		
			Total range	Split range	
			46<T<82	46<T<52	52<T<82
Control	112,330.45	NA	-7.47	-6.82	-7.6
5% ABS-UT	114,001.57	1.48	-7.59	-6.42	-7.85
5% ABS-T	69,160.01	-38.43	-4.707	-5.63	-4.60
5% ABS-PC-UT	114,043.14	1.52	-7.58	-6.92	-7.73
5% ABS-PC-T	48,228.68	-57.06	-3.38	-17.29	-3.38
15% ABS-UT	11,8191.82	5.21	-7.99	-6.69	-8.29
5% HIPS-UT	251232.45	123.65	-17	-10.61	-18.84