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Effect of waste plastic as modifier on thermal stability and degradation kinetics of bitumen/waste plastics blend

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ABSTRACT

Different modified bituminous binders are used in pavement construction for improved durability and for enhanced performance in resisting cracking and permanent deformation of bituminous layers. Waste plastics, whose disposal is a matter of concern, have been used successfully for modifying bitumen. This paper reports the thermogravimetric studies conducted on waste plastic modified bituminous binders. Modified bituminous binders prepared using different plastic contents (0–7 wt% by weight of bitumen) were investigated. The activation energies were determined from thermogravimetric analysis (TGA) data using Kissinger and the Flynn–Wall–Ozawa methods, which do not require knowledge of the reaction mechanism. Modified bitumen (WPMB5) with 5 wt% plastic was found to have the highest thermal stability compared to other binders investigated. Differential scanning calorimetry (DSC) studies were carried out to find crystalline melting temperature and fusion enthalpy. Rheological parameters of modified binders prepared with different plastic contents also suggest that the 5 wt% plastic content is expected to yield optimal performance.

1. Introduction

Bituminous binders used in road construction must perform adequately under a wide temperature regime. The binder must remain flexible enough to withstand stresses without cracking at low temperature during winter, but remain cohesive at high summer temperature (up to 60 °C). Bitumen, a black complex colloidal substance obtained from the bottom of the vacuum distillation columns in the crude oil refineries, is a natural polymer of low molecular weight [1]. It is highly viscoelastic in nature [2]. Bitumen is composed of saturates, aromatic hydrocarbons, resins, and asphaltenes (SARA) where the asphaltenes are dispersed into a liquid oily matrix of saturates aromatics and resins [3]. It has been widely used all over the world for road paving applications, due to its high impermeability, good adhesiveness to aggregates, high elasticity, and cost effective [4].

60/70 penetration grade (VG-30 viscosity grade) bitumen was used in many of the recently completed highway projects in India for construction of bituminous layers. Though these binders supplied by different refineries satisfy the relevant specifications [5,6], the performance of the pavements subjected to extreme conditions of traffic and temperature has not been satisfactory. Different types of modified bituminous binders have been used successfully in some projects. Crumb rubber modified bitumen (CRMB) and polymer modified bitumen (PMB) are the commonly used modified binders. Research works on different types of PMBs are available in literature. The feasibility of using waste plastic has also been examined by different researchers [7,8]. Use of waste plastic as modifier serves the dual purpose of enhancing binder performance and providing a means for recycling the plastic and is a much better disposal solution compared to other options such as incineration and land filling. The modifiers should be compatible and miscible with bitumen and the modified binders should resist degradation at mixing temperature and maintain desired properties during the service life of pavement. Low compatibility between bitumen and polymer can lead to phase separation [9,10]. High energy mixing process is required to thoroughly disperse the polymers in the binder [11].

Since the binders are subjected to high temperatures during construction process and during the service life of the pavement, knowledge of thermal degradation behaviour of the modified binders is essential for understanding the long term performance of the pavements. The literature survey reveals that studies on thermal decomposition of waste plastic modified bitumens are few in number. The present investigation was taken up with the objective of evaluating the thermal degradation characteristics of bituminous binders modified using different proportions of waste plastics. The modified binders were being developed to provide enhanced performance in road pavement subjected to heavy vehicular traffic and high service temperature.

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Thermogravimetric analysis (TGA) was used to evaluate the thermal behaviour and stability parameters of neat and modified bitumen [12]. Different polymer modified binder samples were prepared in the present study by varying the proportion of waste plastic (WP) from 0 to 7 wt% (by weight of bitumen). 60/70 penetration grade was used for modification. TGA kinetic study was carried out on this binder to evaluate the effect of polymer content on the thermal degradation properties of the binder. TGA, differential scanning calorimetry (DSC) results, and rheological properties of the binders were used to identify the optimum content of waste plastics to be used for modification of pristine bitumen. The TGA results obtained for the binders were analyzed using Kissinger and Flynn–Wall–Ozawa kinetic methods as detailed in the following section.

1.1. Theoretical background

The pyrolysis process of bitumen can be represented by the following reaction:

$$\text{Bitumen} + \text{waste plastics} \xrightarrow{\text{k}} \text{volatiles} + \text{solid residue}$$

The basic equation for kinetic analysis is shown in Eq. (1):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{(-E/RT)} f(\alpha) \tag{1}$$

In Eq. (1) A and E are Arrhenius parameters (the pre-exponential factor and the activation energy, respectively), $f(\alpha)$ is the reaction model, R is the gas constant, T is the temperature, t is the time, and α is the extent of conversion. Rearrangement of Eq. (1) gives the following relationship for non-isothermal degradation corresponding to the given conversion is represented as:

$$g(\alpha) = \int_0^{T_\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A_\alpha}{\beta} \int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dt \tag{2}$$

At non-isothermal condition the equation is stated as below:

$$\frac{1}{\beta} \int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT - \frac{1}{\beta_0} \int_0^{T_{\alpha,0}} \exp\left(-\frac{E_\alpha}{RT}\right) dT = 0 \tag{3}$$

where T_α and E_α are experimental values of the temperature and activation energy, respectively corresponding to a given conversion at heating rate of β. $T_{\alpha,0}$ found as a solution of Eq. (3) is a temperature at which a given conversion will be reached at an arbitrary heating rate, β_0. Solving Eq. (3) for different conversion, dependency of α on T at an arbitrary heating rate can be predicted and the experimental data are simulated in this way [13–15].

1.2. Kissinger method (differential method)

The Kissinger method [16] has been used in the literature to determine the activation energy from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The activation energy can be determined by the Kissinger method without a precise knowledge of the reaction mechanism, using the equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln[n(1-\alpha_{\max})^{n-1}]\right\} - \frac{E}{RT_{\max}} \tag{4}$$

where β is the heating rate, $T_{\max}$ is the temperature corresponding to the inflection point of the thermal degradation curves which corresponds to the maximum reaction rate. A is the pre-exponential factor, $\alpha_{\max}$ is the maximum conversion, n is the reaction order and R is the gas constant (8.314 J/mol K). From a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ and fitting to a straight line, the activation energy (E_a) can be calculated from the slope of the graphs.

Table 1
Physico-mechanical properties of waste plastics.

Parameter	Thickness (mm)	Density (gm/cm^3)	Tensile strength (MPa)	Elongation at break (%)
Values	0.2 –0.4	0.96	16.71	12.9

1.3. Flynn–Wall–Ozawa method (integral method)

Flynn–Wall–Ozawa method [17,18] represents a relatively simple method of determining activation energy directly from weight loss versus temperature data obtained at several heating rates, using the equation:

$$\log\ \beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \tag{5}$$

T is the absolute temperature at different heating rate under the same conversional rate, where β, A, E, R have their usual significance. This is one of the integral methods that can determine the activation energy without knowledge of reaction order. It is used to determine the activation energy for given values of conversion. The activation energy for different conversion values can be calculated from a log β versus $1000/T$ plot.

2. Experimental investigations

Different bituminous blends were prepared by blending VG-30 viscosity grade (60/70 penetration grade) bitumen with different proportions of waste plastic. Physical and rheological parameters of these blends were evaluated. TGA and DSC tests were conducted for examining the thermal stability of the binders. Details of these investigations and the inferences drawn there from are presented in the following sections.

2.1. Preparation of waste plastic/bitumen blends

60/70 penetration grade (VG-30 viscosity grade) bitumen provided by Haldia Petrochemicals (India) was used as base binder. Waste plastic (WP) films of 2 mm × 2 mm dimension supplied by M/s K K Poly Flex (P) Ltd. (Bangalore, India) were utilized as a binder modifying agent. These waste plastic films were prepared by shredding used plastic bags, collected from Municipal Solid Waste (MSW). Different physico-mechanical properties of the WP are given in Table 1.

2.2. Sample preparation

Waste plastic bitumen blends were prepared using a 0.2 HP laboratory scale mechanical stirrer consisting of a three blade stirrer. This device was operated at 3500 rpm for 45 min at a blending temperature of 180 °C. Shell report suggests that the mixing temperature should not exceed 185 °C and the mixing time should be adequate enough for homogeneous dispersion of the waste plastic within the bitumen matrix [19]. Different polymer (waste plastic) concentrations, 0, 1, 3, 5, and 7 wt% (by weight of bitumen) were considered for preparing the blends.

2.3. Thermal analysis of the blends

2.3.1. Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed with TGA Q50 model of TA Instruments, USA, operated in the dynamic mode at different heating rates. Heating rates of 5, 10, and 20 °C/min were used. Samples (~10 mg) were placed in a platinum pan and the experiments were conducted in nitrogen environment with N_2 being supplied at a flow rate of 60 ml/min. The activation energies have been calculated by using Kissinger (differential method) and Flynn–Wall–Ozawa (integral methods) [16–18] method as described earlier. Conversion values 5–80% at each 5% conversion were used for estimating the activation energy values using Flynn–Wall–Ozawa method.

2.3.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out in DSC Q100 model of TA Instruments, USA. About 10–20 mg of samples was used for the DSC test to determine the glass transition temperature (T_g), melting points (T_m), and heat of fusion (ΔH_f) of the blend components from the thermograms. The cooling and heating cycles were programmed at a heating rate of 10 °C/min in the temperature range from −100 to +200 °C to provide the same thermal history for all the samples and to avoid the influence of the polymerization process on the thermal transitions of the polymer and the possible effects of crystallization and/or rearrangement during sample storage. The degree of crystallization (F_c) [9,20] can be determined from Eq. (6).

$$\%F_c = \frac{\Delta H_f}{\Delta H} \times 100 \qquad (6)$$

where ΔH_f is the observed fusion enthalpy of the blends and ΔH is the fusion enthalpy of 100% crystalline polymer obtained from literature.

2.4. Rheological properties of polymer modified bituminous blends

Different rheological parameters of the bituminous blends were determined to examine the influence of the thermal stability characteristics of the binders on the rheological performance of the binders. Penetration, softening point, ductility and dynamic shear rheometer (DSR) tests were conducted.

2.4.1. Penetration tests

The penetration tests were carried out at 25 °C according to ASTM D5 [21]. Bitumen was placed in water bath and the penetration of a standard needle under a total standard load (100 g) was measured and reported in tenth of mm.

2.4.2. Ductility

Ductility is a measure of the cohesive strength of a binder. The test is usually performed according to ASTM D113 [22] at a temperature of 27 °C and the sample is elongated at 5 cm/min until it breaks.

2.4.3. Ring and ball test (softening point temperature)

The softening points (ring and ball test) of different straight and modified bitumen were measured according to ASTM D36 [23].

2.4.4. Dynamic shear rheometer (DSR) tests

Complex modulus and phase angle were determined for all the binders at a test of 64 °C and a frequency of 10 rad/s. Bohlin ADS Automated Dynamic Shear Asphalt Rheometer with parallel plate geometry (25 mm in diameter) was used for this purpose.

3. Results and discussion

3.1. Thermal analysis

3.1.1. TGA

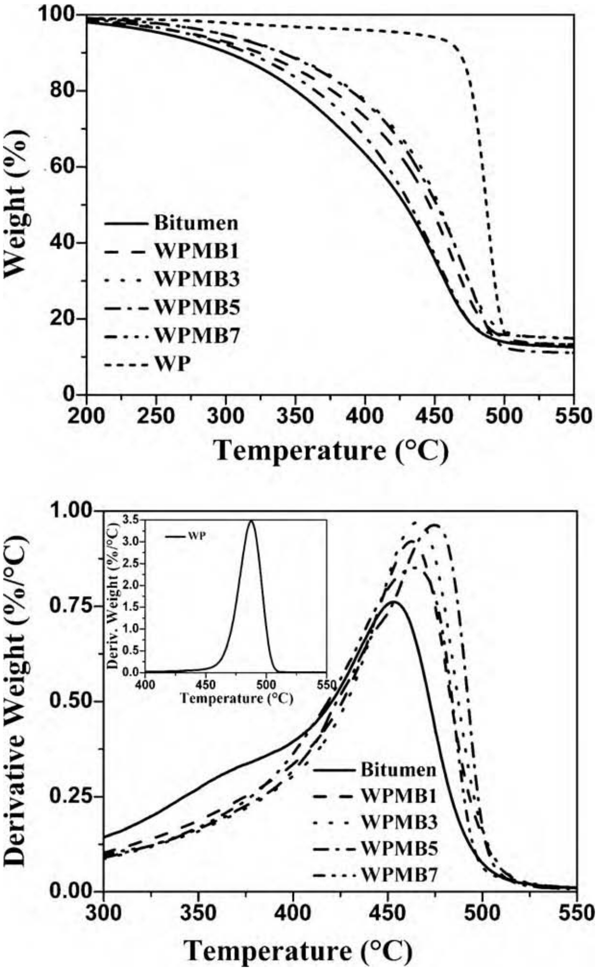

Fig. 1. TGA thermograms for pristine bitumen, waste plastics, and bitumen/WP blends containing 1, 3, 5, and 7 wt% WP loading at heating rate of 20 °C/min.

TGA studies have been carried out to determine thermal characteristics of materials such as thermal stability, degradation temperatures, etc. Fig. 1 shows typical TGA curves and the corresponding derivative thermogravimetric (DTG) curves obtained at a heating rate of 20 °C/min for bitumen, different blended binders and waste plastic. TGA thermograms correspond to single-stage degradation with well defined initial and final degradation temperatures, which might have been the result of a random chain scission process and subsequent pyrolysis of the samples. The onset temperature of thermal degradation (T_{onset}), 50% weight loss temperature ($T_{0.5}$), maximum decomposition temperature (T_{max}), and the yield of charred residue at 600 °C are given in Table 2. These results are obtaining by averaging the results from three runs for a particular sample. T_{onset}, $T_{0.5}$, T_{max}, and mean activation energy (E_a) reported in Table 2 are the average of three values. A derivative weight loss curve, DTG, can be used to indicate the point at which weight loss is most apparent. It is evident from TGA thermograms that below 200 °C there was no mass loss and above 200 °C volatilization of low molecular mass species took place along with pyrolysis. The shifting of the peak values of T_{onset}, $T_{0.5}$, and T_{max} is observed with higher polymer content due to higher thermal stability of the modifiers. Bitumen is a low molecular weight polymer and the oligomer part decomposed first, which results in decomposition of bitumen at lower temperature than PMBs [24]. Decomposition temperature increases with increase in polymer content in the blend due to high molecular weight and crystalline nature of the modifier, which makes them high temperature resistant. However, at higher modifier content (7 wt%) the decomposition temperature and the

Table 2
TGA and DTG thermogram data of pristine bitumen, waste plastics, and bitumen/WP blends containing 1, 3, 5, and 7 wt% WP loading at heating rate of 20, 10, and 5 °C/min.

Sample codes	T_{onset} (°C)	$T_{0.5}$ (°C)	T_{max} (°C)	Residue at 600 °C (wt%)	Heating rate (°C/min)
Bitumen	270	445	446	10	20
WPMB1	275	447	463	13	
WPMB3	295	452	466	13	
WPMB5	296	453	474	12	
WPMB7	273	452	463	13	
WP	431	486	488	13	
Bitumen	260	421	429	11	10
WPMB1	266	428	446	12	
WPMB3	270	433	449	14	
WPMB5	278	438	461	15	
WPMB7	271	429	443	16	
WP	407	469	470	12	
Bitumen	239	388	407	19	5
WPMB1	250	414	426	16	
WPMB3	254	416	430	17	
WPMB5	257	419	440	15	
WPMB7	248	412	423	18	
WP	389	452	455	13	

thermal stability are reduced as shown in Fig. 1 and represented in Table 2.

TGA is an excellent tool for studying the thermal degradation kinetics. It is widely used because of its experimental simplicity and the wealth of information obtained from a simple thermogram. The model free iso-conversional Kissinger and Flynn–Wall–Ozawa method, which is used to calculate kinetic parameters, such as the activation energy and it is not necessary to have a prior precise knowledge of the reaction mechanism. The maximum degradation temperature (T_{max}) for different PMBs and neat bitumen has been determined from the DTG curves. Using Kissinger's method, the various data for calculation of activation energies of the decomposition of WPMB1, WPMB3, WPMB5, WPMB7, and neat bitumen are reported in Table 3 and activation energy values by Kissinger and the average activation energy values by Flynn–Wall–Ozawa methods are given in Table 4. Typical Kissinger plots of $\ln(\beta/T_{max}^2)$ against $1000/T_{max}$ are shown in Fig. 2. Fig. 2 shows that the fitting straight lines are nearly parallel and thus confirm the applicability of this method. Using Flynn–Wall–Ozawa method the activation energy of the samples was determined at different degree of conversion ranging from 5% to 80% with a step of 5%. After 80% conversion there is only presence of residues for that reason it was not taken for calculation of E_a because after 80% conversion no change of the weight is shown. Typical Flynn–Wall–Ozawa method plot at 50% conversion for pristine bitumen, WP and various bitumen/WP blends is shown in Fig. 3. The E_a dependencies on α obtained for the thermal degradation of bitumen, WPMB1, WPMB3, WPMB5, WPMB7, and WP calculated by Flynn–Wall–Ozawa method are shown in Fig. 4. WP and modified binders demonstrate a significant variation in E_a and show considerable increase in E_a while bitumen shows a

Table 4
Comparison of activation energy calculated from both Kissinger and Flynn–Wall–Ozawa methods.

Sample codes	Activation energy, E_a (kJ/mol)	
	Kissinger method	Flynn–Wall–Ozawa method
Bitumen	132	125
WPMB1	151	133
WPMB3	161	152
WPMB5	171	169
WPMB7	145	132
WP	180	177

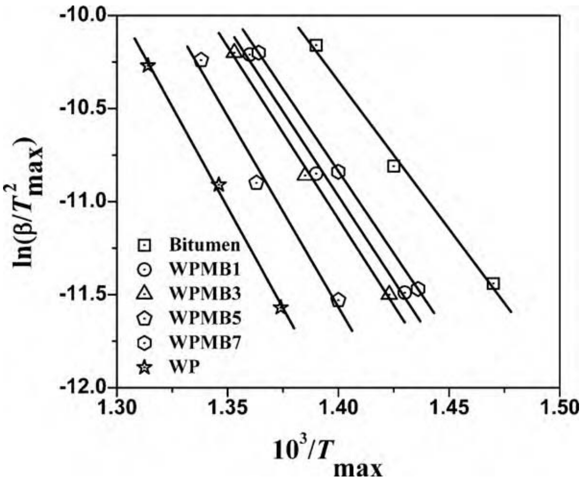

Fig. 2. Kissinger non-isothermal plots of heating rate versus temperature for different compositions at DTG peak temperature.

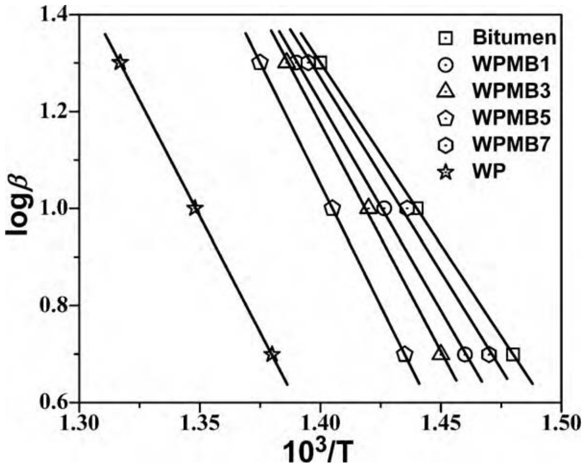

Fig. 3. Typical FWO plot at 50% conversion for bitumen, WPMB1, WPMB3, WPMB5, WPMB7 and WP samples.

Table 3
Data for calculating apparent activation energy by Kissinger method.

Sample codes	Heating rate (°C/min)								
	20			10			5		
	T_{max} (°C)	$1000/T_{max}$ (1/K)	$\ln(\beta/T_{max}^2)$	T_{max} (°C)	$1000/T_{max}$ (1/K)	$\ln(\beta/T_{max}^2)$	T_{max} (°C)	$1000/T_{max}$ (1/K)	$\ln(\beta/T_{max}^2)$
Bitumen	446	1.39	−10.16	429	1.425	−10.81	407	1.47	−11.44
WPMB1	462	1.36	−10.21	446	1.39	−10.85	426	1.43	−11.49
WPMB3	466	1.353	−10.2	449	1.385	−10.86	430	1.423	−11.5
WPMB5	474	1.338	−10.24	461	1.363	−10.9	441	1.4	−11.53
WPMB7	461	1.364	−10.2	443	1.4	−10.84	423	1.436	−11.47
WP	488	1.314	−10.27	470	1.346	−10.91	455	1.374	−11.57

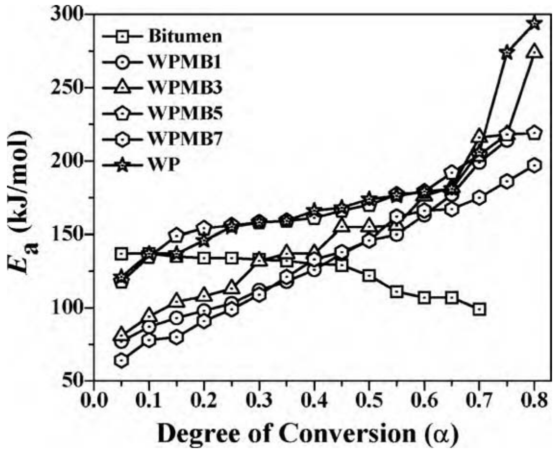

Fig. 4. The variation of E_a with degree of conversion of thermal degradation of bitumen, WPMB1, WPMB3, WPMB5, WPMB7 and WP samples determined from FWO method.

different trend; bitumen does not reveal a significant variation of E_a at lower degree of conversion and E_a decreases significantly at higher α values. The reason may be that bitumen is a low molecular weight polymer and degradation of bitumen is a heat liberating process i.e. exothermic process. Waste plastics are high molecular weight polymers and the degradation of WP and modified binders is endothermic process i.e. required more energy for thermal degradation.

It is observed in Table 4 that the activation energy values (E_a) computed using the Kissinger and Flynn–Wall–Ozawa (FWO) methods exhibit similar trend as the activation energy of bitumen is less than WPMBs, suggesting that the thermal stability of bitumen increases with increase in waste plastic content except for 7 wt% modifier at which the thermal stability started to decrease. The thermal stability of the bitumen/WP blend is substantially enhanced by the incorporation of crystalline waste plastic (with ordered structure) to the amorphous bitumen matrix. At lower polymer content, polymer appears to be in a continuous phase and swollen by the miscible components of the bitumen and forms an interconnected three-dimensional structure but at higher polymer content polymeric network collapses due to poor compatibility and coalescence of polymer molecules resulting in phase separation [25,26]. At 7 wt% modifier addition the blend became incompatible and poor degree of miscibility took place reflecting in the reduction of thermal stability. Both Kissinger and FWO methods were used to have a very meaningful comparison between the results obtained using the above two methods. It is evident from Table 5 that the activation energy values obtained from both the methods follow the same trend, which confirms that the optimum amount of WP that can be added into bitumen is around 5 wt%. From Table 4, it is observed that the activation energy values obtained from Kissinger method are higher than the activation energy values obtained by FWO method. The activation energy obtained from the Kissinger method is concerned to the maximum derivative peak temperature of the TGA thermogram whereas, the same calculated from the FWO method is associated with thermal degradation at different degree of conversion ranging from 5% to 80%. Hence, the value of E_a evaluated from fast method is not that much effective and practical as compared to the later.

3.1.2. DSC

DSC has been carried out to evaluate interaction of the bituminous components in the blend [27]. The effect of WP content on the T_g, T_m, ΔH_f, and crystallinity of the binders obtained from Fig. 5 are illustrated in Table 6. Fig. 5 shows that there is no significant change

Table 5
Activation energy (E_a) evaluated by Flynn–Wall–Ozawa method for pristine bitumen, waste plastic modified bitumen and waste plastics.

α	Bitumen			WPMB1			WPMB3			WPMB5			WPMB7			WP		
	E_a	R^2	95% CI[a]	E_a	R^2	95% CI	E_a	R^2	95% CI	E_a	R^2	95% CI	E_a	R^2	95% CI	E_a	R^2	95% CI
5	137	1.000		77	0.990		81	0.972		118	0.989		64	0.998		121	0.999	
10	137	0.980		87	0.990		94	0.966		135	0.999		78	0.994		137	1.000	
15	135	0.996		93	0.992		104	0.994		149	0.992		80	0.984		137	1.000	
20	134	1.000		98	0.990		108	0.999		154	0.987		91	0.990		146	0.999	
25	134	0.996		103	0.990		113	0.999		156	0.998		99	0.982		155	0.993	
30	133	0.996		112	0.998		132	0.999		158	0.998		109	0.986		158	0.998	
35	132	0.999		118	0.998		137	0.999		159	1.000		121	0.992		159	0.999	
40	130	0.999		126	0.997		137	0.990		161	1.000		133	0.992		166	0.998	
45	129	0.998	117.2, 132.35	137	1.000	110.4, 156.2	155	0.997	124.9, 179.8	166	0.994	154.8, 184.54	138	0.999	109.7, 154.3	168	0.998	152.1, 201.8
50	122	0.998		146	0.988		155	0.994		170	0.994		146	0.998		174	0.999	
55	111	0.999		150	0.996		156	0.996		177	0.994		162	0.994		176	0.999	
60	107	0.995		163	0.998		176	0.996		179	0.999		166	0.982		179	0.999	
65	107	0.995		177	0.007		182	0.998		192	1.000		167	0.986		181	0.994	
70	99	0.997		199	0.996		216	0.999		204	0.987		175	0.968		206	1.000	
75	–	–		214	1.000		218	0.999		218	0.998		186	0.992		274	1.000	
80	–	–		–	–		274	0.995		219	1.000		197	0.980		294	0.998	

[a] Confidence interval (CI).

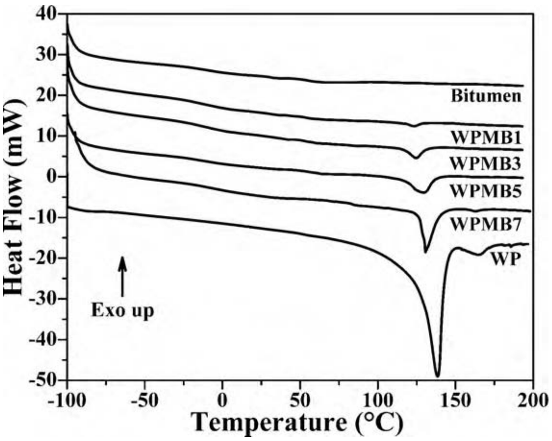

Fig. 5. DSC thermograms for pristine bitumen, waste plastics, and bitumen/WP blends containing 1, 3, 5, and 7 wt% WP loading at heating rate of 10 °C/min.

in glass transitions temperature (T_g) of bitumen and WPMBs. DSC curves revealed two sharp melting peaks, one peak at 132 °C and the other peak at 160 °C. These indicated the presence of different types of polymers in plastic waste including HDPE (crystalline melting temperature, $T_m \sim 132\,°C$) and PP ($T_m \sim 160\,°C$). The melting temperatures fell down to 123 °C for WPMB1, 125 °C for WPMB3, and 126.6 °C for WPMB5. A sharp endothermic melting peak is observed for WPMB1, WPMB3, and WPMB5 but for WPMB7 two melting peaks have been observed one sharp peak at 127.5 °C and a small peak at 160 °C. Heat of fusion ($\Delta H_f = 16.09$ J/g) of WPMB7 for maximum T_m is much higher than other modified binders (Table 6). The blend of bitumen and WP is incompatible in nature but the enthalpy of melting peak corresponds to the WP in lower modifier content blends are very low and also the peaks are small, indicating that there is some level of compatibility in the blend but for WPMB7 two melting peaks have been observed, which indicates incompatibility of polymers in bitumen matrix. It has been reported in the literature that some light components in bitumen such as paraffinic and aromatic compounds can easily migrate into the polymer-rich phase and cause the crystals to break to give lower melting temperatures and lower crystallinity [28–30]. So, the data availed from the present study indicate that there exist some good interaction between WP and bitumen matrix, which affects crystallization of polymer in the blend. Swelling of waste plastic by bitumen light component may be responsible for disrupting the crystalline part of the polymer and yielding crystallites with a smaller size distribution [30,31]. However, the incompatibility level is very high in the 7 wt% modifier filled blend, which is confirmed by the presence of two melting point peaks. ΔH_f divided by the polymer fraction in the blend represents the fraction of polymer that melts as the sample is heated i.e. the crystalline part of blend [9,30]. The melting enthalpy corresponding to wt% of waste plastic concentration in the blend (ΔH_{pol}) is the direct reflection of fraction crystallization (F_c). ΔH_{pol} value increases with increase in wt% WP content in the blend. The values of T_g, T_m, ΔH_f, ΔH_{pol}, and F_c are reported in Table 6. The waste plastic for blend preparation is mainly contains a mixture of HDPE and PP. The DSC thermogram shows a prominent crystalline melting peak corresponding to HDPE at 132 °C and a small peak at around 160 °C referred to the melting point of PP. The heat of enthalpy of HDPE melting peak is very high as compared to the PP, which indicates that the waste plastic contains major percentage of HDPE. Hence, the fraction of crystallinity (F_c) of the blends is evaluated by taking the HDPE melting point temperature peak as the standard one and reported in Table 6. In the case of pure crystalline HDPE the enthalpy of crystalline melting temperature obtained by means of X-ray scattering is 293 J/g as reported in the literature [32]. The F_c value increases with increase in polymer content in the blend. The F_c values have been changed significantly with the polymer/bitumen composition. The degree of crystallinity in the bitumen/WP blend is reduced prominently by the presence of amorphous bitumen phase within the WP and also it lowers the melting point of the crystalline regions within the polymer-rich phase by making the crystallites smaller.

Table 6
DSC thermogram data of pristine bitumen, waste plastics, and bitumen/WP blends containing 1, 3, 5, and 7 wt% WP loading at heating rate of 10 °C/min.

Parameter	WPMB1	WPMB3	WPMB5	WPMB7	WP
T_g (°C)	−16	−16	−17	−17	–
T_m (°C)	123	125	126.6	127.5	132.0
(ΔH_f)[a] (J/g)	0.9778	4.11	9.5	16.09	112.2
(ΔH_{pol})[b] (J/g)	97.78	137	190	230	–
$F_{c\ blend}$[c] (%)	33.42	46.82	65	78.6	–

[a] Enthalpy of polymer/bitumen blend.

[b] Melting enthalpy corresponding to polymer concentration percentage in the blend.

[c] Percentage of crystallinity in polymer/bitumen blend.

Table 7
Rheological properties of waste plastic/bitumen blends.

WP content (wt%)	Penetration point at 25 °C (1/10 mm)	Softening point (°C)	Ductility (cm)
0	69	44	>100
1	61.4	45.5	71.5
3	50.8	52.5	65.4
5	42	60	53
7	49	–[a]	31

[a] Because of severe phase separation bitumen rich part softened previously and the polymer-rich part remained in the ring.

3.2. Rheological properties of the binders

The data obtained from different rheological tests such as penetration point, softening point, ductility of WPMBs are presented in Table 7. The complex modulus values determined at 64 °C using dynamic shear rheometer is presented in Fig. 6. These properties are important for the performance of bituminous layers in pavements. Penetration value decreased at a near uniform rate from 69 dmm for neat bitumen to 42 dmm for WPMB5. However, penetration point increased to 49 dmm for WPMB7. As evident from DSC study, the bitumen/WP blend at 7 wt% shows phase separation between bitumen and WP. Softening point increased from 44 °C for bitumen to 60 °C for 5 wt% WP filled bitumen whereas, no soften-

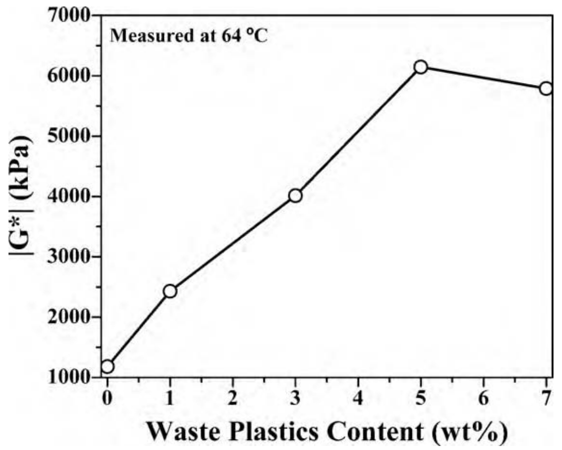

Fig. 6. The dependency of complex modulus ($|G^*|$) on wt% of waste plastic content at 64 °C.

ing point is found for WPMB7. The bitumen phase reached fluid condition before the softening of waste plastic for the binder prepared using 7 wt% plastics due to the presence of phase separation between bitumen and WP phase, which leads to the flowing out of part of the bitumen rich phase rapidly and the WP rich phase remains in the ring. The increase in softening point is favorable since bitumen with higher softening point may be less susceptible to permanent deformation or rutting [26,33]. The ductility was observed to decrease from 71.5 cm for 1 wt% binder to 31 cm for 7 wt% of binder. The ductility value signifies the property by virtue of which bitumen can exist in a thin film without breaking. The present results indicate that the binders become more brittle with increasing WP content. This may be due to the incompatibility of the blend, which leads to phase separation. Moreover, elongation of WP itself is very less (% elongation at break of these WP is 12.9%) due to its highly crystalline nature. The complex modulus $|G^*|$ represents the total resistance to deformation under load. From Fig. 5 it is found that the complex modulus increased in WPMBs with modifier percent up to 5 wt% after that it decreased, which may be due to the increase in the elasticity with wt% of polymer content. In case of 7 wt% polymer content the phase separation occurred due to the immiscibility of the blend that results in lower $|G^*|$ value.

4. Conclusions

The results obtained from the present investigation reveal that the performance of bitumen can be improved by addition of WP. The addition of WP to bitumen enhances the thermal, rheological, and physical properties of the modified binder prepared in a rotor-stator device. However, the extent of the effect is dependent on the polymer content in WPMB. The TGA/DTG results showed that bitumen decomposes more easily than modified bitumens because of the presence of more volatile content in bitumen. Unmodified bitumen was found to be thermally less stable than WPMBs. The optimum WP content is found to be 5 wt% based on the thermal stability results. DSC results show that the crystalline fraction increases with increasing in polymer content. At lower wt% WP content the interaction between bitumen and WP is significantly high because of the better swelling of polymer particles which further enables interaction of polymer particles with bitumen phase. Rheological properties obtained in the investigation indicate that polymer modification can be expected to improve the high temperature performance of the binders.

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