

## Research Article

# Effect of Gamma-Irradiated Recycled Low-Density Polyethylene on the High- and Low-Temperature Properties of Bitumen

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This paper describes polymer modification of bitumen with gamma-irradiated recycled ( $\gamma$ -LDPE<sub>R</sub>) low-density polyethylene. The recycled low-density polyethylene (LDPE<sub>R</sub>) was obtained from greenhouse films exposed to sunlight at least one year. The surface of the LDPE<sub>R</sub> was treated by gamma beam irradiation that provided formation of free radicals and some functional groups that may contribute to the creation of strong chemical bonds between polymer modifier and bitumen. Five different samples of bitumen/ $\gamma$ -LDPE<sub>R</sub> compositions with the modifier content, wt. %: 1, 3, 5, 7 and 9, were prepared. The effects of the  $\gamma$ -LDPE<sub>R</sub> on original and aged bitumen were investigated by means of morphological, chemical, and physical testing program, including FTIR spectroscopy, conventional tests, rotational viscosity (RV), dynamic shear rheometer (DSR), and bending beam rheometer (BBR) tests. Superior performing asphalt pavements (Superpave) specifications were used to analyze mechanical test results as well as to determine the performance grades (PG) of the binders. Optimum usage of the  $\gamma$ -LDPE<sub>R</sub> as modifier in bitumen were suggested after testing program. The results reveal the stiffening effect of the  $\gamma$ -LDPE<sub>R</sub> on bitumen that provide enhanced temperature susceptibility and also promise better performance grades (PG) with  $\gamma$ -LDPE<sub>R</sub> polymer modification.

## 1. Introduction

The modification of bitumen by means of polymers is the most widespread method in flexible pavement applications. The polymers such as Styrene Butadiene Styrene (SBS), Ethylene vinyl acetate (EVA) are satisfactorily used to enhance temperature susceptibility by increasing stiffness at high temperature and decreasing stiffness at low temperature [1–4]. In addition to SBS, various polymers are utilized in bituminous materials. Polyolefins such as low-density polyethylene (LDPE), high density polyethylene (HDPE), and polypropylene (PP) have been used as modifier, for generally to enhance mechanical properties of bitumen [5–8].

On the other hand, using recycled polymers contributes to reducing amount of waste materials; it has many benefits, such as environmental protection, lower energy

consumption, and their affordable cost. Therefore, it is fundamental to find an application area for recycled polymers, in order to increase their commercial use [9–11].

The aim of this work is to study the effect of recycled LDPE (LDPE<sub>R</sub>) as modifier on bitumen by means of morphologic, chemical, and mechanical test methods. However, there is no chemical reaction between LDPE<sub>R</sub> and bitumen which results in a two-phase mixture after the preparation of modified bitumen. In order to provide strong polymer/bitumen bonding, surface of the recycled LDPE was activated by using gamma beam irradiation. The surface activation helps to create double bonds ( $>C=C<$ ) that can interact with bitumen.

The study contains a comprehensive laboratory evaluation of the  $\gamma$ -irradiated recycled LDPE ( $\gamma$ -LDPE<sub>R</sub>) modified bitumen ( $\gamma$ -LDPE<sub>R</sub>/B) in terms of morphology and physical-chemical properties. Fluorescence microscopy has been used

TABLE 1: Physical properties of the base bitumen.

Properties	Standard	160/220
Penetration (25°C; 0.1 mm)	ASTM D5	195.5
Softening point (°C)	ASTM D36	38.7
Ductility (25°C; cm)	ASTM D113	103
Penetration index (PI)	—	-0.73
Specific gravity (25°C; gr/cm <sup>3</sup> )	ASTM D70	1.03

to observe morphological changes, while rheological testing have been undertaken by means of dynamic shear rheometer (DSR) and bending beam rheometer (BBR). To understand the influence of  $\gamma$ -irradiation on structure and efficiency of the LDPE<sub>R</sub> recycled LDPE, Fourier transform infrared (FTIR) spectroscopy has been performed as well.

## 2. Experimental

**2.1. Materials.** The binders were prepared with the type of bitumen having 160/220 penetration grade. Physical properties of the bitumen are given in Table 1. The LDPE<sub>R</sub> used as modifier in bitumen was supplied from Sicily, Italy. The LDPE<sub>R</sub> was obtained from greenhouse films exposed to sunlight, as well as to other external environmental factors for one year. The waste films were washed, dried, cut into the pieces of dimensions 12 × 12 mm, and finally extruded. The chemical composition of the LDPE<sub>R</sub> used was LDPE 65–70%, LLDPE 12–17%, EVA copolymer 12–15%,  $T_m = 109^\circ\text{C}$ ,  $E = 180\text{ MPa}$ ,  $\text{TS} = 16\text{ MPa}$ ,  $\text{EB} = 500\%$ ,  $\text{MFI}190/2.16 = 0,29\text{ g}/10\text{ min}$ , and  $\text{MFI}230/2.16 = 0,95\text{ g}/10\text{ min}$ .

**2.2. Gamma Irradiation Activation Method.** In order to provide a chemical bonding between bitumen and polymer modifier, gamma irradiation method was applied to the LDPE<sub>R</sub> [12]. Gamma irradiation method is used in several applications such as food processing, cancer treatments, and some sterilization systems. Gamma irradiation is electromagnetic of high frequency and rays are ionizing radiation. It provides a reformed chemical composition of the materials exposed to decay that might contribute to creating strong bonds between polymer modifier and bitumen. The irradiation source was an electron accelerator—complex electric device, where the transition from regimes of treatment with charged particles (electrons) to regimes of treatment with stream of gamma quanta of a wide range of energies is possible. The LDPE<sub>R</sub> granules were  $\gamma$  irradiated with a dose of 20 kGy.

**2.3. Preparation of Samples.**  $\gamma$ -LDPE<sub>R</sub> granules were obtained as pellet shaped. In order to work with smaller pieces, they were milled by using grinder and the particles were sieved with No 50. The amount of additives was selected as %: 1, 3, 5, 7, and 9 by total weight of the binder which is enough to examine the effect of the polymer modified bitumen. High shear mixer was employed for preparing sample. 160/220 penetration grade bitumen was heated for 90 minutes at 163°C and then poured into the mixer flask adjusted to 500 rpm. Subsequently, the  $\gamma$ -LDPE<sub>R</sub> was added

to bitumen by portions in 15 minutes at certain intervals and then the mixing rate was increased to 1300 rpm and mixing was continued for 150 minutes. After the end of the mixing process, the samples were removed from the flask, divided into small containers, covered with aluminum foil, and stored for various testing.

The different binders were coded as follows:

- (i) base bitumen–“B<sub>i</sub>”
- (ii) base bitumen + 1%  $\gamma$ -LDPE<sub>R</sub>–“B-1- $\gamma$ -LDPE<sub>R</sub>”
- (iii) base bitumen + 3%  $\gamma$ -LDPE<sub>R</sub>–“B-3- $\gamma$ -LDPE<sub>R</sub>”
- (iv) base bitumen + 5%  $\gamma$ -LDPE<sub>R</sub>–“B-5- $\gamma$ -LDPE<sub>R</sub>”
- (v) base bitumen + 7%  $\gamma$ -LDPE<sub>R</sub>–“B-7- $\gamma$ -LDPE<sub>R</sub>”
- (vi) base bitumen + 9%  $\gamma$ -LDPE<sub>R</sub>–“B-9- $\gamma$ -LDPE<sub>R</sub>”

### 2.4. Testing Program

**2.4.1. Fourier Transform Infrared Spectroscopy.** Fourier transform infrared (FTIR) spectroscopy was used to characterize various functional groups in asphalt and polymer modifier. FTIR spectra were recorded with a Bruker Tensor 27 DTGS spectrometer between 4000 and 450 cm<sup>-1</sup> using the attenuated total reflection (ATR) mode. For each spectrum, 32 consecutive scans with a resolution of 4 cm<sup>-1</sup> were averaged.

**2.4.2. Morphology.** In order to determine the grade of the dispersion of the modifier within the bitumen, fluorescent microscopy was used. Florescent microscopy allows researchers to study the morphology of bitumen by using a principle in which polymers become swollen after absorbing some of the constituents of the original bitumen [13].

The method of sample preparation for fluorescent microscopy followed the regular procedure that is consisted of heating, homogenizing, and cooling process. The samples were examined under a Carl Zeiss Primo Star generated from a 40 W halogen lamp and magnify up to 1000X.

**2.4.3. Conventional Bitumen Tests.** The samples of the base and modified bitumen were subjected to conventional tests that are, namely, penetration (ASTM D5), softening point (ASTM D36), and ductility (ASTM D 113). By using penetration and softening point values, penetration index was calculated for each sample of bitumen to investigate the temperature susceptibility of bitumen. A classical approach related to PI calculation has been given in the Shell Bitumen Handbook [14] as shown in the following equation:

$$\text{PI} = \frac{1952 - 500 \times \log(\text{Pen}_{25}) - 20 \times \text{SP}}{50 \times \log(\text{Pen}_{25}) - \text{SP} - 120}, \quad (1)$$

where  $\text{Pen}_{25}$  is the penetration at 25°C and SP is the softening point temperature of the unmodified and modified bitumen.

**2.4.4. Rotational Viscosity Test.** The rotational viscometer determines the bitumen viscosity by measuring the torque necessary to maintain a constant rotational speed of a cylindrical spindle submerged in a bitumen specimen held

at a constant temperature, described in AASHTO TP48. Unlike the capillary viscometers used with the viscosity-graded method, the rotational viscometer can evaluate modified bitumen binders. Viscosity of bitumen binders can be measured within the range from 0.01 Pa·s (0.1 poise) to 200 Pa·s (2000 poise) [15]. Though this test, which is one of the Superpave Performance Grade (PG) asphalt binder specification, can be conducted at various temperatures for different purposes, the test performed for Superpave PG asphalt binder specification is always conducted at 275°F (135°C). In order to observe the changes in viscosity at various temperatures, a second viscosity reading is taken generally at 165°C. A Brookfield viscometer (DVRV-II Pro Extra) was used in this study for the viscosity tests of the base and the modified bitumens. Viscosity values were measured at 135°C and 165°C, respectively.

**2.4.5. Dynamic Shear Rheometer Test.** The most commonly used methods for the fundamental rheological characterization of bitumen are dynamic mechanical methods using oscillatory type testing, generally conducted within the region of linear viscoelastic response by using a dynamic shear rheometer (DSR). In order to characterize the viscoelastic behavior of bitumen binders at intermediate and high service temperatures, DSR is used in Superpave specification providing an indication of the rutting resistance of bitumen immediately following the construction. It is also possible to evaluate the resistance to rutting at high service temperatures in the early stages of pavement life and fatigue cracking at immediate service temperatures in the later stages of service life by DSR [16].

The principal viscoelastic parameters obtained from DSR are the complex shear modulus ( $G^*$ ) and the phase angle ( $\delta$ ).  $G^*$  is defined as the ratio of maximum (shear) stress to maximum strain, a measure of the total resistance to deformation when the bitumen is subjected to shear loading. The phase difference between stress and strain in an oscillatory test is named as  $\delta$ , a measure of the viscoelastic balance of the material behavior [17].

In this study, the principal viscoelastic parameters such as  $G^*$ ,  $\delta$ , rutting parameter ( $G^*/\sin\delta$ ), and high-temperature performance grades of the base and modified bitumens were determined by DSR test.

**2.4.6. Bending Beam Rheometer Test.** The bitumen binder plays a critical role in the thermal cracking potential of hot mix asphalt (HMA) pavement. HMA pavements with a high stiffness modulus at low temperatures are susceptible to thermal cracking. Bitumen binders become harder, or stiffer, as the ambient temperature decreases. Given that the stiffness of an HMA pavement is directly proportional to the stiffness of bitumen binder, high stiffness at low temperatures increases the potential of thermal cracking. The bending beam rheometer (BBR) was developed to determine the stiffness of bitumen binders at low service temperatures and to evaluate the potential of the binder for thermal cracking [16].

Creep tests were conducted at -6, -12, and -18°C which are equivalent to -16, -22, and -28°C, respectively, in low

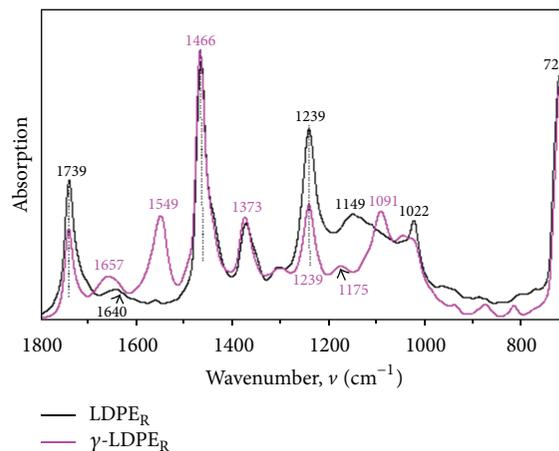


FIGURE 1: The normalized FTIR spectra of the LDPE<sub>R</sub> and  $\gamma$ -LDPE<sub>R</sub>.

temperature performance grade, using a BBR according to ASTM D6648-01. The bitumen beam (125 mm long, 12.5 mm wide, and 6.25 mm thick) was submerged in a constant-temperature bath and kept at the test temperature for 60 min. After preloading procedure, a constant load of 100 g (980 mN) was then applied to the rectangular beam supported at both ends by stainless steel half-rounds (102 mm apart), and the deflection of center point was measured continuously. Creep stiffness (S) and creep rate ( $m$ -value) of the binders were determined at several durations of loading ranging from 8 to 240 s [18]. The creep stiffness is an indicator of the specimen's ability to resist the constant creep load and the creep rate is the rate at which the creep stiffness changes with loading time [16]. For an adequate low-temperature cracking resistance, the creep stiffness must be less than 300 MPa and the  $m$ -value must be greater than 0.3 to be in compliance with Superpave specification [19].

### 3. Results and Discussions

**3.1. FTIR Spectroscopy.** In Figure 1, the normalized FTIR spectra (the band at  $\nu \approx 720 \text{ cm}^{-1}$  has been used as internal standard) of the virgin LDPE<sub>R</sub> and  $\gamma$ -LDPE<sub>R</sub> are shown. As can be seen from Figure 1, there is no significant difference in position and intensity of the main absorption bands at  $\nu \approx 720, 1022, 1373, \text{ and } 1466 \text{ cm}^{-1}$ , which are the characteristics for vibrations of C-C and C-H bonds of hydrocarbon chain of virgin LDPE and  $\gamma$ -LDPE<sub>R</sub>. However, the new peaks are additionally observed at  $\nu \approx 1091, 1175, 1549, \text{ and } 1657 \text{ cm}^{-1}$  in the spectrum of  $\gamma$ -LDPE<sub>R</sub> accompanied by decreasing intensity of the peaks at  $1239 \text{ cm}^{-1}$  and  $1739 \text{ cm}^{-1}$ . These new peaks evidence formation of unsaturated bonds in macromolecular chains of gamma-irradiated LDPE (the peak with maximum at  $\nu \approx 1657 \text{ cm}^{-1}$  corresponds to the non-conjugated C=C bond) that is occurred as a result of high-energy action of the gamma-rays on LDPE. At irradiation treatment free radicals appear at breakage of polymer chains, which can then transform to different groups and bonds including formation of double bonds ( $>\text{C}=\text{C}<$ ). Certainly,

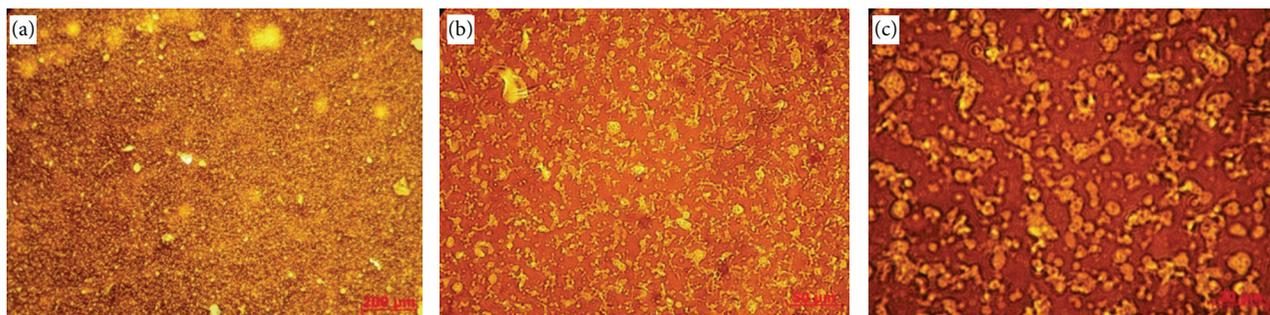


FIGURE 2: (a) 50X magnification, (b) 200X magnification, and (c) 500X magnification.

TABLE 2: Characteristic properties of base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens before and after short-term ageing.

Properties	Binder types					
	Base	1- $\gamma$ -LDPE <sub>R</sub>	3- $\gamma$ -LDPE <sub>R</sub>	5- $\gamma$ -LDPE <sub>R</sub>	7- $\gamma$ -LDPE <sub>R</sub>	9- $\gamma$ -LDPE <sub>R</sub>
Penetration (25°C; 0.1 mm)	195.5	168.8	135	102	83.1	57.2
Softening point (°C)	38.7	42.5	48.4	64.2	60.3	70.5
Ductility (cm) at 25°C	103	92	84	77	69	63
Penetration index (PI)	-0.73	0.23	1.31	1.85	2.54	3.28
	After ageing					
Change of mass (%)	0.76	0.68	0.65	0.40	0.37	0.35
Penetration (25°C; 0.1 mm)	102	85.6	125	93.8	76.5	52.5
Retained penetration (%)	52	50.7	92.5	91.9	92	92
Softening point (°C)	42.7	45.3	49.5	65.1	61.1	66.5
Change in softening point (°C)	4	2.8	1.1	0.9	0.8	-4

the unsaturated bonds formed in  $\gamma$ -LDPE<sub>R</sub> are reactive towards the unsaturated bonds of bitumen components that provides effective reactive compatibilization of the blends of modifier with bitumen through the chemical reactions of the surface functional groups of the activated polyethylene and the double bonds of the bitumen components. In air, the free radicals formed can react with oxygen forming some oxygen-containing functional groups in polymer structure (e.g., C(O)O- group of organic acids or esters with a maximum around  $\nu \approx 1549 \text{ cm}^{-1}$  and -C-O-C- bond in ethers with an absorption bands around  $\nu \approx 1091, 1175$ ). These groups can also contribute to physical-chemical compatibilization of  $\gamma$ -LDPE<sub>R</sub> with bitumen.

**3.2. Morphology.** The morphology of  $\gamma$ -LDPE<sub>R</sub> modified bitumen was observed with a fluorescent microscope. The images given in Figure 2 belong to B-9- $\gamma$ -LDPE<sub>R</sub>, the highest polymer content among the all binders. The surface images were taken with using different magnification (i.e. 50X, 200X and 500X). Figure 2(a) shows the texture of the modified bitumen in general, whereas Figure 2(c) shows a detailed image on texture and allows observing the phase structure of the modified bitumen. Two major phases that can be clearly seen (Figures 2(a), 2(b), and 2(c)) are a continuous bitumen-rich phase (brown) and a dispersed polymer phase (yellow). Excluding a few greater particles, the main amount of  $\gamma$ -LDPE<sub>R</sub> is mostly ranging from 3 to 10  $\mu\text{m}$  in diameter and

is quite well dispersed in bitumen. While modifier particles with a size greater than 30  $\mu\text{m}$  were not seen generally in the modified bitumen samples, it can be said that polymer particles have been swollen by absorbing an amount of the bitumen content. A third phase (mixed phase) can be observed in the image taken at the 500X magnification (Figure 2(c)) formed in interface region obviously due to chemical bonding between bitumen and gamma-irradiated polymer particles.

**3.3. Conventional Bitumen Test.** In order to understand the effect of  $\gamma$ -LDPE<sub>R</sub> additives on physical properties of the bitumen, conventional tests were conducted. The results, including both before and after short-term ageing, are given in Table 2. As can be seen, penetration decreases continuously with increasing amount of  $\gamma$ -LDPE<sub>R</sub> polymer content.

Hence, B-9- $\gamma$ -LDPE<sub>R</sub> binder has the lowest penetration value with 57.2. Softening point test results support penetration results, as it increases with increasing  $\gamma$ -LDPE<sub>R</sub> polymer content. These physical tests results point out a significant increase in stiffness of the bitumen with increasing amount of the polymer modifier. There is no specification limits for ductility, it is generally expected to be higher than 100 cm. Consequently, decreasing ductility means, binders become more brittle with increasing amount of  $\gamma$ -LDPE<sub>R</sub> modifier.

The PI values increase progressively from -0.73 to 3.28, as modifier content increases that signifies  $\gamma$ -LDPE<sub>R</sub> polymer

TABLE 3: Viscosity values of the of base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens.

Binder types	Rotational viscosity (cP)		$\eta_{\text{modified}}/\eta_{\text{pure}}$		Temperature range (°C)	
	135°C	165°C	135°C	165°C	Mixing	Compaction
B	202.5	65.5	1	1	135–142	122–128
B-1- $\gamma$ -LDPE <sub>R</sub>	250	80	1.23	1.22	142–148	129–135
B-3- $\gamma$ -LDPE <sub>R</sub>	380	122.5	1.88	1.87	152–159	139–145
B-5- $\gamma$ -LDPE <sub>R</sub>	702.5	208	3.47	3.18	165–171	154–159
B-7- $\gamma$ -LDPE <sub>R</sub>	798	330	3.94	5.04	187–195	170–177
B-9- $\gamma$ -LDPE <sub>R</sub>	1286	435	6.35	6.64	189–195	175–181

modified bitumen can be used in a wider temperature range than base bitumen.

The tests performed on aged samples reveal that  $\gamma$ -LDPE<sub>R</sub> additives have a positive effect on ageing properties of bitumen, as mass loss of the bitumen diminishes. Furthermore, the results of all the samples are within the limitation of change of mass (i.e., 1%). After short-term ageing, the retained penetration tends to increase as  $\gamma$ -LDPE<sub>R</sub> content increases which shows that increasing polymer content helps to diminish the effects of ageing on bitumen binders.

**3.4. Rotational Viscosity Results.** Rotational viscosities performed at 135 and 165°C for base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens are shown in Table 3. For all the samples, mixing and compaction temperatures were determined from the viscosity versus temperature graph given in Figure 3. The results reveal a gradual increase in viscosity with modification. As in the penetration and softening point test, this increasing in viscosity gives a clear indication of the stiffening effect of  $\gamma$ -LDPE<sub>R</sub> modification. Modification indices, which can be calculated as the viscosity of modified bitumen divided by the viscosity of base bitumen, especially have greater values for B-5- $\gamma$ -LDPE<sub>R</sub>, B-7- $\gamma$ -LDPE<sub>R</sub>, and B-9- $\gamma$ -LDPE<sub>R</sub> binders. Calculated mixing and compaction temperatures for the base and modified binders tend to increase continuously. Although there are no viscosity values exceeding the Superpave specifications (i.e., 3000 cP) for both base and modified bitumen, this increase in mixing and compaction temperatures means that the workability of bitumen considerably decreases. Besides, mixing temperature of B-7- $\gamma$ -LDPE<sub>R</sub> and B-9- $\gamma$ -LDPE<sub>R</sub> binders reaches 195°C, which can be considered as unfavorable result, because it means that the energy consumption will increase to high levels in applications.

**3.5. Dynamic Shear Rheometer Test.** In this study, high-temperature performances grades of base and modified bitumens were investigated by means of DSR tests. The fundamental rheological parameters for bitumen such as  $G^*$ ,  $\delta$ , and  $G^*/\sin \delta$  were also determined for original and aged samples in this DSR testing program, and the results are given in Table 4 and Figure 4. Table 4 also contains the high-temperature performance grades (PG) calculated with minimum rutting parameter ( $G^*/\sin \delta$ ) criteria of 1 kPa for original samples and 2.2 kPa for aged samples recommended in Superpave binder specifications. As can be seen, the

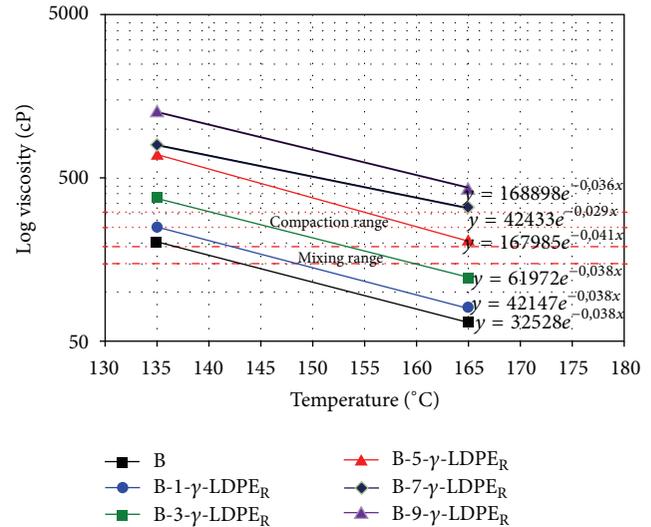


FIGURE 3: The mixing-compaction temperatures for the base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens.

values of  $G^*$ , the measure of the total resistance of bitumen against the deformation subjected to the shear stress, increase significantly for both original and aged samples with increasing  $\gamma$ -LDPE<sub>R</sub> modifier content. This result determines that binders become hardened after  $\gamma$ -LDPE<sub>R</sub> modification. Therefore, it can be said that the  $\gamma$ -LDPE<sub>R</sub> modified binders are more durable than original binders against shear stress deformations.

The phase angle ( $\delta$ ) is generally considered to be more sensitive to the chemical structure than the complex modulus,  $\delta$  generally tends to decrease as the amount of modifier increases, and, therefore, predominantly viscous behavior with increasing temperatures,  $\gamma$ -LDPE<sub>R</sub> modifier improves the elastic response of the modified binders.

The effect of  $\gamma$ -LDPE<sub>R</sub> modification on the rheological parameters ( $G^*$  and  $\delta$ ) leads to an increased rutting parameter ( $G^*/\sin \delta$ ) of binders that promises an improvement of the rutting deformation. As values of  $G^*/\sin \delta$  within the limitations, DSR test is maintained to the next test temperatures.

The increased  $G^*/\sin \delta$  parameters also affect the PG of the binders. There is a significant increase in PG with increase of  $\gamma$ -LDPE<sub>R</sub> modifier, especially content of 5, 7, and 9%. For instance, high-temperature performance grades step up to

TABLE 4: DSR test results of the original and aged of base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens.

Binders	Temperature (°C)	G* (KPa)	$\delta$ (°)	G*/sin $\delta$ (KPa)	Specification limits (Pa)	Performance grading	
B	Original	52	4.64	86.6	4.65	≥1000	PG 52-Y
		58	1.85	87.4	1.85		
		64	0.766	88.2	0.767		
	Aged	52	3.06	87.1	3.07	≥2200	
		58	1.39	87.2	1.39		
		64	1.88	84.9	1.89		
B-1- $\gamma$ -LDPE <sub>R</sub>	Original	52	2.75	80.7	2.78	≥1000	PG 58-Y
		58	1.31	77.3	1.35		
		64	0.702	72.7	0.735		
	Aged	52	9.47	82.3	9.56	≥2200	
		58	4.07	84	4.10		
		64	1.88	84.9	1.89		
B-3- $\gamma$ -LDPE <sub>R</sub>	Original	52	3.60	85.8	3.61	≥1000	PG 58-Y
		58	1.66	85.5	1.66		
		64	0.843	84.3	0.84		
	Aged	52	10.6	78.7	10.6	≥2200	
		58	4.66	77.9	4.76		
		64	2.42	74.7	2.42		
B-5- $\gamma$ -LDPE <sub>R</sub>	Original	52	5.36	81.6	5.42	≥1000	PG 64-Y
		58	2.47	79.9	2.51		
		64	1.27	77.1	1.30		
	Aged	52	16.8	80	17.1	≥2200	
		58	7.07	82.4	7.13		
		64	3.14	83.7	3.16		
B-7- $\gamma$ -LDPE <sub>R</sub>	Original	52	7.69	84.5	7.72	≥1000	PG 64-Y
		58	3.34	85.4	3.35		
		64	1.62	85.4	1.63		
	Aged	52	20.7	77.7	21.2	≥2200	
		58	9.04	80.2	9.18		
		64	4.26	81.7	4.30		
B-9- $\gamma$ -LDPE <sub>R</sub>	Original	52	10.3	71.9	10.8	≥1000	PG 76-Y
		58	5.37	68.4	5.78		
		64	3.13	64.6	3.47		
	Aged	70	1.99	60.7	2.28	≥2200	
		76	1.33	57	1.59		
		82	0.881	53.4	1.10		
B-9- $\gamma$ -LDPE <sub>R</sub>	Original	52	51.4	69.1	55	≥2200	PG 76-Y
		58	25	70.9	26.4		
		64	13	71.7	13.7		
	Aged	70	5	70.3	5.31	≥2200	
		76	2.89	68.2	3.11		
		82	1.78	65.2	1.96		

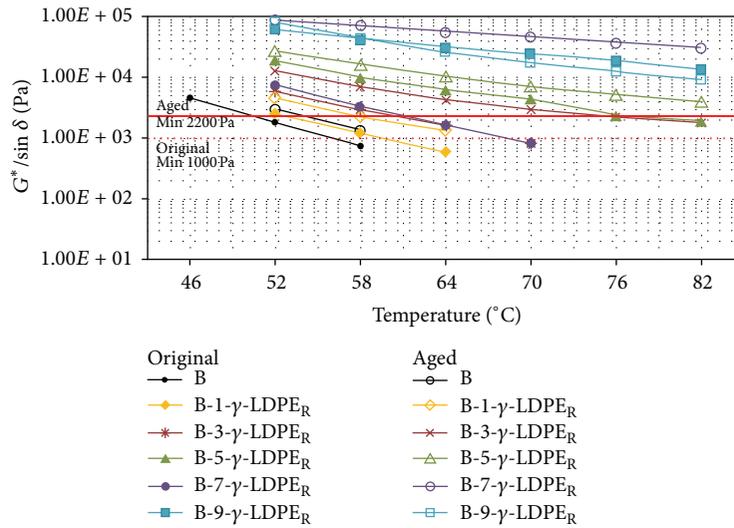


FIGURE 4: Rutting parameter of binders.

TABLE 5: Creep stiffness and  $m$ -value of the binders at a loading time of 60 s and different temperatures.

Binder types	Creep stiffness (MPa)			$m$ -value			Performance grading (PG)
	$-16^{\circ}\text{C}$	$-22^{\circ}\text{C}$	$-28^{\circ}\text{C}$	$-16^{\circ}\text{C}$	$-22^{\circ}\text{C}$	$-28^{\circ}\text{C}$	
B	42.13	99.50	199.05	0.479	0.432	0.309	PG Y-28
B-1- $\gamma$ -LDPE <sub>R</sub>	40.71	139.69	219.12	0.381	0.343	0.281	PG Y-22
B-3- $\gamma$ -LDPE <sub>R</sub>	67.61	146.12	228.33	0.325	0.318	0.274	PG Y-22
B-5- $\gamma$ -LDPE <sub>R</sub>	66.93	156.68	248.98	0.324	0.301	0.285	PG Y-22
B-7- $\gamma$ -LDPE <sub>R</sub>	78.77	176.58	—	0.311	0.267	—	PG Y-16
B-9- $\gamma$ -LDPE <sub>R</sub>	79.39	143.8	—	0.310	0.263	—	PG Y-16

64-Y and 76-Y from 52-Y, when content of the modifier is 5 and 9%, respectively.

**3.6. Bending Beam Rheometer Test.** In order to study the influence of polymer additives on the low-temperature creep responses of bitumen, the bending beam rheometer test was employed at different loading times of 8, 15, 30, 60, 120, and 240 s and temperatures of  $-16^{\circ}\text{C}$ ,  $-22^{\circ}\text{C}$ , and  $-28^{\circ}\text{C}$ . Table 5 contains of compares creep stiffness and  $m$ -values obtained at three temperatures and at a loading time of 60 s. The creep stiffness values and  $m$ -values of the base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens are also graphed in Figures 5 and 6. As can be seen, creep stiffness of binders increases with increasing polymer modifier content. It can be said that this result was expected, as conventional and rotational viscosity test results indicate the effect stiffening of  $\gamma$ -LDPE<sub>R</sub> modification. Although it is known that binders with higher creep stiffness are not convenient for cold regions, as we can see from the results, the creep stiffness values of binders obtained do not exceed Superpave specifications (i.e., 300 MPa) at any test temperatures. As to  $m$ -value, there is a trend to exceed limitations with increasing polymer modifier content. Consequently, binders of B-7- $\gamma$ -LDPE<sub>R</sub> and B-9- $\gamma$ -LDPE<sub>R</sub> are failed at  $-22^{\circ}\text{C}$  to remain within specifications (i.e., 0.3) whereas the rest of the binders step up to next testing

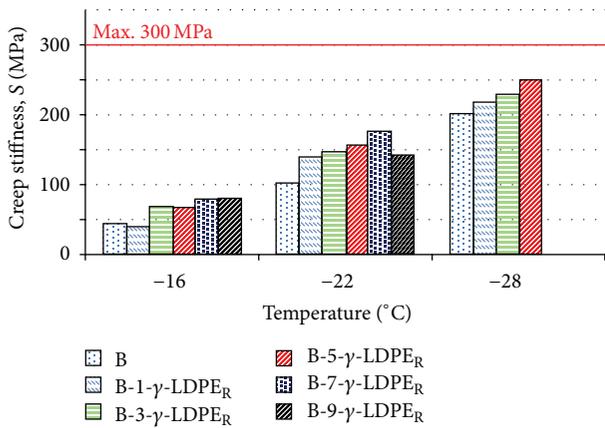
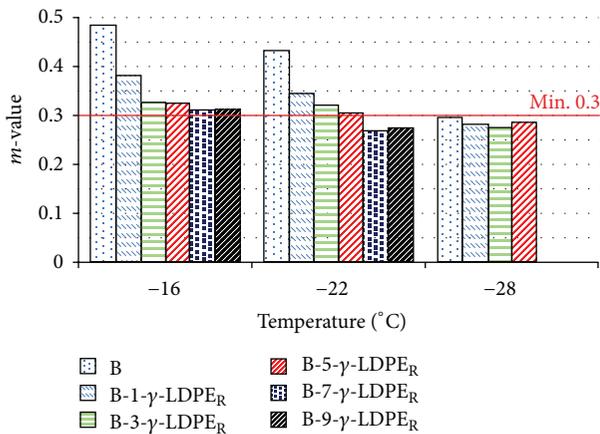
temperature. However, any of the binders were not able to provide  $m$ -value specification at  $-28^{\circ}\text{C}$  excepting base bitumen. Since creep stiffness is within the limitations,  $m$ -values determine the low-temperature performance grade of binders. Hence, there is a slightly decreasing trend in low-temperature performance grades as polymer modifier content increases. As can be seen from Table 5, it steps down to  $-22$  and  $-16$  from  $-28^{\circ}\text{C}$ , as polymer modified content is increased to 1% and 7%, respectively.

**3.7. The Effect of  $\gamma$ -LDPE<sub>R</sub> on Performance of Modified Bitumen.** As it was discussed above,  $\gamma$ -LDPE<sub>R</sub> has positive the effect on high temperature performance grades, while it decreases slightly low temperature performance grades. Thus, in order to clarify the total effects of  $\gamma$ -LDPE<sub>R</sub> on the performance and to recommend for optimum usage of  $\gamma$ -LDPE<sub>R</sub> in bitumen, Table 6 was prepared to show dependence of the modifier content on failure temperatures of binders for DSR and BBR test. Table 6 also contains the PG of the binders.

The results indicate that, the improvement at high temperatures can be seen clearly at even low polymer modification. For instance, B-1- $\gamma$ -LDPE<sub>R</sub>, which is able to be used in regions with a wider temperature range, as improvement of the binder, is  $4.53^{\circ}\text{C}$ . As content of polymer modifier increases, the improvement also continues to increase.

TABLE 6: The effect of  $\gamma$ -LDPE<sub>R</sub> on high and low service temperatures and on performance grade (PG).

Binder types	Fails at HT (°C)	Fails at LT (°C)	HT (°C) improvement	LT (°C) decrement	Improvement/decrement	Performance grading (PG)
B	54.3	-28.78	—	—	—	PG 52-28
B-1- $\gamma$ -LDPE <sub>R</sub>	61	-26.61	6.7	2.17	4.53	PG 58-22
B-3- $\gamma$ -LDPE <sub>R</sub>	63.5	-24.45	9.2	4.33	4.87	PG 58-22
B-5- $\gamma$ -LDPE <sub>R</sub>	66.9	-22	12.6	6.78	5.82	PG 64-22
B-7- $\gamma$ -LDPE <sub>R</sub>	68.6	-20.5	14.3	8.28	6.02	PG 64-16
B-9- $\gamma$ -LDPE <sub>R</sub>	80.5	-17.95	26.2	10.83	15.37	PG 76-16

FIGURE 5: Creep stiffness values of the base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens.FIGURE 6:  $m$ -values of the base and  $\gamma$ -LDPE<sub>R</sub> modified bitumens.

Thereby, temperature improvement of B-3- $\gamma$ -LDPE<sub>R</sub> and B-5- $\gamma$ -LDPE<sub>R</sub> binders rises up to 4.87 and 5.82°C, respectively. B-9- $\gamma$ -LDPE<sub>R</sub> has the largest improvement with 15.37°C. However, although failure temperatures are more precise than PG classifications, it is necessary that analyzing the effect of the polymer modifier by using both the failure temperatures and PG.

The PG of the base bitumen was found as PG 52-28, whereas B-1- $\gamma$ -LDPE<sub>R</sub> was a binder of PG 58-22. It can

be understood that there is no improvement since high-temperature performance grade steps up to one level (52 to 58) while the decreasing in the low-temperature PG is the same (-28 to -22). However, in fact, as can be seen above there is an improvement in terms of failure temperatures.

B-3- $\gamma$ -LDPE<sub>R</sub> has the same PG (58-22) with B-1- $\gamma$ -LDPE<sub>R</sub>, whereas B-5- $\gamma$ -LDPE<sub>R</sub> has PG 64-22, which indicates there is an improvement in terms of both failure temperatures and PG. As for B-7- $\gamma$ -LDPE<sub>R</sub>, low-temperature performance grading steps down to two level compared with base bitumen (-16), thereby B-7- $\gamma$ -LDPE<sub>R</sub> has a poorer PG than B-5- $\gamma$ -LDPE<sub>R</sub>. The B-9- $\gamma$ -LDPE<sub>R</sub> has the biggest PG (76-16) along all the binders due to vast high-temperature improvement. It might be interpret as a benefit; however, this stiffening effect causes some problems in application while binder is being mixed and compacted. Nevertheless, it is undesirable due to high energy consumptions, as discussed in RV results.

Consequently, in spite of gradual increasing in temperature improvement as polymer content increases, as can be seen B-7- $\gamma$ -LDPE<sub>R</sub> and B-9- $\gamma$ -LDPE<sub>R</sub> have a lower temperature grade of -16 that also indicates that there must be a limitation to the usage of  $\gamma$ -LDPE<sub>R</sub>. According to the rheological test (DSR and BBR), and considering RV results it can be suggested that the usage of  $\gamma$ -LDPE<sub>R</sub> polymers as modifier in bitumen with content of 5% as B-5- $\gamma$ -LDPE<sub>R</sub> has the most stable results due to the previously mentioned reasons.

#### 4. Conclusion

$\gamma$ -LDPE<sub>R</sub> modified bitumen has been investigated by means of conventional, chemical, and mechanical tests. It was found that the rheological properties of bitumen are enhanced with  $\gamma$ -LDPE<sub>R</sub> polymer modification as identified by testing program. The surface images of the binders obtained with fluorescence microscopy revealed formation of multiphase system with bitumen continuous phase,  $\gamma$ -LDPE<sub>R</sub> dispersed phase, and mixed phase (interfacial layer), which is a sign of the presence of chemical bonding between bitumen and gamma-irradiated polymer particles.

FTIR spectroscopy confirmed the appearance of reactive (>C=C<) bonds in  $\gamma$ -LDPE<sub>R</sub> macromolecules after gamma irradiation of the LDPE<sub>R</sub>. Conventional tests, such as penetration and softening point, indicate a significant increase in stiffness of the bitumen with increasing amount of the  $\gamma$ -LDPE<sub>R</sub> modifier.

After short-term ageing by means of RTFOT, all the modified binders are within the Superpave limitations. Furthermore,  $\gamma$ -LDPE<sub>R</sub> polymer has a positive effect on bitumen ageing. In addition to the observed stiffening effect of  $\gamma$ -LDPE<sub>R</sub> on bitumen, RV test results also suggest that using  $\gamma$ -LDPE<sub>R</sub> as modifier more than 5% in bitumen can cause some mixing and compacting problems in applications.

The results obtained from the DSR tests show that  $\gamma$ -LDPE<sub>R</sub> modifier provides an increased complex shear modulus ( $G^*$ ) values and rutting parameters ( $G^*/\sin \delta$ ) and decreased phase angle ( $\delta$ ) values which means the  $\gamma$ -LDPE<sub>R</sub> modified binders are more resistant against rutting compared to the base bitumen. This improvement also affects the PG of the binders that increases gradually with increasing modifier content. However, there must be a limitation for the usage of the  $\gamma$ -LDPE<sub>R</sub> polymer due to BBR results that indicate an increasing creep stiffness and decreasing  $m$ -value as polymer content increases.

Consequently, in this paper, with taking into account the rheological tests and RV results, it was suggested that the optimum usage of  $\gamma$ -LDPE<sub>R</sub> is 5% by weight of bitumen.

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