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Modification of Bitumen by Recycled Post-Consumer Low Density Polyethylene with Surface Activated Using Air Ion Irradiation

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ABSTRACT

Air ion irradiated recycled low density polyethylene (i-LDPE$_R$) was investigated as a modifier in bitumen and the results of the physical and chemical tests were presented in this paper. The recycled LDPE (LDPE$_R$) additive was obtained from greenhouse film, exposed to sunlight, in Italy. Air ion irradiation method has been applied for LDPE$_R$ surface activation, in order to form strong chemical bonding between bitumen and LDPE$_R$. Five samples were prepared with different i-LDPE$_R$ modifier content, wt. %: 1, 3, 5, 7 and 9. Complex shear modulus (G*) and phase angle (δ) of pure and modified bitumens were measured by using dynamic shear rheometer (DSR) at different traffic speed and in-service pavement temperature, while the morphology was examined by florescent microscope. Tests results reveal that a gradually increment in i-LDPE$_R$ modification leads to a decrease in penetration and an increase in softening point, which indicate an increasing stiffness for the bitumen.

Keywords: bitumen, air ion irradiation, modification, post-consumer, recycled polyethylene

1. INTRODUCTION

Bituminous materials are utilized extensively in many engineering applications, primarily pavement and airfield runaway constructions. However, recently, highway systems are exposed to additional load due to increased traffic levels, new axle designs and increased number of trucks. There is an effort to improve properties of bitumen by using additives to prevent highway systems from several deterioration (Read and Whiteoak, 2003). Although there are several additives for bitumen, modification by means of polymer is the most common method in pavement applications. Polymers are conventionally utilized in bitumen to enhance temperature susceptibility by increasing stiffness at high temperature, decreasing stiffness at low temperature as well (Isacsson and Lu, 1999; Airey, 2002). In addition to traditional polymers such as Styrene Butadiene Styrene (SBS), Ethylene vinyl acetate (EVA) etc., recently some altered polymers are employed in bitumen. Different polyolefins, such as low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) have been used as a modifier in bitumen and generally tend to provide enhanced mechanic properties. (Garcia-Morales et al., 2004; Habib et al., 2011). Although several polymers are used in bitumen satisfactorily, finding new fields for waste or recycling materials has also become crucial in all engineering branch by reason of environmental sensitivity. Cost reduction is also another important issue for pavement engineering due to high price of polymers (Gad et al., 2010). The aim of this work is to study the effect of recycled LDPE ($LDPE_R$) as modifier on structure-properties relationships for bitumen. In order to provide strong polymer/bitumen bonding, surface of the recycled LDPE was activated by using air ion beam irradiation. The study contains a laboratory evaluation of the ion-irradiated recycled LDPE (i-$LDPE_R$) modified bitumen (i-$LDPE_R$/B) in terms of morphology and physical-chemical properties. Fluorescence microscopy has been used to observe morphologic changes, while rheological testing has been undertaken by means of dynamic shear rheometry. To understand the influence of ion-irradiation on structure and efficiency of the $LDPE_R$ FTIR spectroscopy has also been conducted.

2. EXPERIMENTAL

2.1 Materials

In this study, the bitumen having 160/220 penetration grade was selected as a binder for all tests. The recycled LDPE's being used as additive in bitumen were procured from Sicily, Italy. The recycled LPDE materials were obtained from greenhouse film, exposed to sunlight and other external environmental factors as well. In order to fabricate recycled LDPE, the waste films were all washed, dried and cut to pieces by an industrial scale and finally extruded. The chemical composition of the $LDPE_R$ recycled LDPE used was LDPE 65-70%, LLDPE 12-17%, EVA copolymer 12-15%, T_m = 109^{o}C, E = 180MPa, TS = 16MPa, EB = 500%,MFI190/2.16 = 0,29 g/10 min and MFI230/2.16 = 0,95 g/10 min.

2.2 Air ion irradiation Method

Ion beam is a charged particle beam consists of ions. It has many uses in various industries and can be used for sputtering or etching and for ion beam analysis. This method enables a certain change in chemical structure that leads to create stronger bonds between polymer and bitumen by emerging new C-C bonds. In this research, the air ion irradiation process was done at 0.5 m^3 area surrounding by protection walls at 25 C^o, in normal air pressure (760mm). $LDPE_R$ particles exposed to current density ranging from $3x10^7$ to $8x10^7/cm^3$ for ten hours by means of an automatic controlled system.

2.3 Preparation of Samples

In order to provide a homogenous mixture, after completing , the air ion irradiation process, i-$LDPE_R$ grains were first milled, then the crumbled particles sieved with 0.6 mm sieve. The amount of additive used was, wt. %: 1, 3, 5, 7 and 9 by total weight of the binder which is enough to measure employability range of polymer additive and convenient with literary as well. 160/220 penetration grade bitumen was heated for 90 minutes at 163 °C, and then poured into the flask of the high shear mixer (Silverson LSM) adjusted to 1000 rpm. Subsequently the (i-LDPE$_R$ was added to bitumen by portions) in 15 minutes at certain intervals and then the mixing rate was increased to 4000 rpm and mixing was continued for 45 minutes. After the end of the mixing process, the samples were removed from the flask and divided into small containers, covered with aluminum foil and stored for various testing. The different binders were coded as follows:

Base bitumen – "B";
Base bitumen + 1% i-LDPE$_R$ – "B-1-i-LDPE$_R$";
Base bitumen + 3% i-LDPE$_R$ – "B-3-i-LDPE$_R$";
Base bitumen + 5% i-LDPE$_R$ – "B-5-i-LDPE$_R$";
Base bitumen + 7% i-LDPE$_R$ – "B-7-i-LDPE$_R$";
Base bitumen + 9% i-LDPE$_R$ – "B-9-i-LDPE$_R$";

3. TESTING PROGRAM

3.1 Morphology

Observing the dispersions of the polymers within the bitumen is fundamental to estimate behavior of the modified bitumen in applications. To this end, fluorescent microscopy was used. Florescent microscopy allows 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. The method of sample preparation for fluorescent microscopy followed the regular procedure consisted of a heating and cooling process. The samples were examined under a Carl Zeiss Primo Star generated from a 40 W halogen lamp and able to magnify up to 1000X. Images taken with three different magnifications by means of different objective lenses were evaluated.

3.2 Conventional Bitumen Tests

The samples of the pure and modified bitumen were subjected to conventional tests so as to examine physical changes, namely, penetration test (ASTM D5), softening point test(ASTM D36), ductility test (ASTM D 113). By using penetration and softening point values, penetration index was calculated for each sample of bitumen that shows the temperature susceptibility of bitumen. A classical approach related to PI calculation has been given in the Shell Bitumen Handbook (Read and Whiteoak, 2003) as shown in the following equation:

$$PI = \frac{1952 - 500 \times \log(Pen_{25}) - 20 \times SP}{50 \times \log(Pen_{25}) - SP - 120} \tag{1}$$

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

3.3 Rotational Viscosity Test

The viscosity of bitumen binders can be measured within the range of 0.01 Pa.s (0.1 poise) to 200 Pa.s (2000 poise) (Bahia and Anderson 1995). A Brookfield viscometer (DVRV-II Pro

Extra) was used in for the viscosity tests of the pure and the modified bitumens. Two different viscosity values were taken at 135 ^oC and 165 ^oC, so as to evaluate more precisely.

3.4 Dynamic Shear Rheometer Test

The dynamic shear rheometer (DSR), was used to determine the viscoelastic behavior of modified bitumen binders especially at intermediate to high service temperatures. The parameters obtain from the DSR tests can indicate the performance of the modified bitumen against rutting. (Zaniewski and Pumphrey, 2004; McGennis et al., 1994). The AASHTO TP5 standard test method requires that a thin bitumen specimen be sandwiched between two parallel metal plates held in a constant temperature medium. One plate remains fixed while the other oscillates, at an angular frequency (ω) of 10 radians per second for 10 cycles, with respect to the other (Zaniewski and Pumphrey, 2004). A higher complex modulus (G^*) and a lower phase angle (δ) are coveted results for rutting resistance. It is meant to be the bitumen become stiffer if an increased G^* results obtained after polymer modification. The bitumen exhibiting a lower δ has a greater elastic component, thus allowing more of the total deformation to be recovered. The relationship $G^*/\sin\delta$ was chosen as the parameter for SHRP specifications with respect to rutting resistance of bitumen binders (McGennis et al., 1994). Testing the bitumen samples at 10 radians per second frequency is equivalent to a traffic speed of 100 km/hr. For decreasing free flaw traffic levels, a lower frequency could be used to evaluate the behavior of the modified bitumen under heavy traffic (Kennedy et al., 1994). Three different frequencies are selected to reflect the free flow, decresing free flow and heavy traffic. Anton Paar Physica SmartPave Plus dynamic shear rheometer was used at several mid and high temperatures in this study to indicate dynamic mechanical properties of the pure and the modified bitumens.

4. RESULTS AND DISCUSSION

4.1 Conventional Bitumen Tests

Conventional test results were conducted on base and the modified bitumen are given in Table 1. The results reveal that penetration decreases progressively with increasing amount of i-$LDPE_R$ modifier. Accordingly, B-9-i-$LDPE_R$ binder has the lowest penetration value. Softening point values increases with increasing i-$LDPE_R$ proportion which also promote penetration test results. Increasing rate of the polymer modifier, induce to increase gradually softening point temperatures. For instance, softening point increases to 60.3 ^oC from 38.7 ^oC by adding 5% i-$LDPE_R$. Therefore, the results of penetration and softening point tests show that i-$LDPE_R$ modifier provides increased stiffness compared to the pure bitumen. As can be seen from Table 1, there is a substantial reduction in ductility associated with i-$LDPE_R$ content. In general, above of the 100cm is an expected results for ductility test for typical pavement asphalt. Consequently, addition of i-$LDPE_R$ polymer could violate the ductility specifications. Polymer modification reduces the temperature susceptibility of the bitumen. Higher values of PI signify lower temperature susceptibility which means modified binder could be used a larger temperature range. In other words, bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation (Read and Whiteoak, 2003; ASTM D5-97, 1998).

Table 1. Conventional test results of base and modified bitumen.

Properties	B 160/220	B 160/220 + i-LDPE$_R$, wt.%				
		1	3	5	7	9
Penetration 25^{o}C, 0,1mm	195.5	158.2	133.3	117.7	68.4	63.5
Softening Point, ^{o}C	38.7	41.1	43.4	51.0	59.5	67.8
Ductility, cm	103	88	81	72	63	53
Penetration Index (PI)	-0.73	-0.59	-0.38	1.53	1.77	3.13

4.2 Morphology

The morphology of i-LDPE$_R$ modified bitumen was observed with a fluorescent microscope and images were taken with different objectives lenses that are 4X, 10X and 40X, respectively. Figure 1.a provides a general appearance of the modified bitumen, whereas Figure 1.c shows a detailed image on texture and allow to observe the phases and the structure of the modified bitumen. The Images given in Figure 1 belong to B-9-i-LDPE$_R$, the highest polymer content among the all blends studied. Two main phase can be easily seen, that are a continuous bitumen-rich phase (brown color) and a dispersed polymer phase (yellow). Expecting few greater particles, other i-LDPE$_R$ polymers are mostly ranging from 3 to 10 μm in diameter and are largely well dispersed in bitumen. While modifier particles with a size greater than 30 μm were not seen generally in the modified bitumen samples, it can be understood that polymer particles have become swollen by absorbing an amount of the bitumen content. A third phase can be observed in the image taken with a 40X lens (Figure 1.c) that might means a chemical bond was created between bitumen and polymer phase after ion beam process.

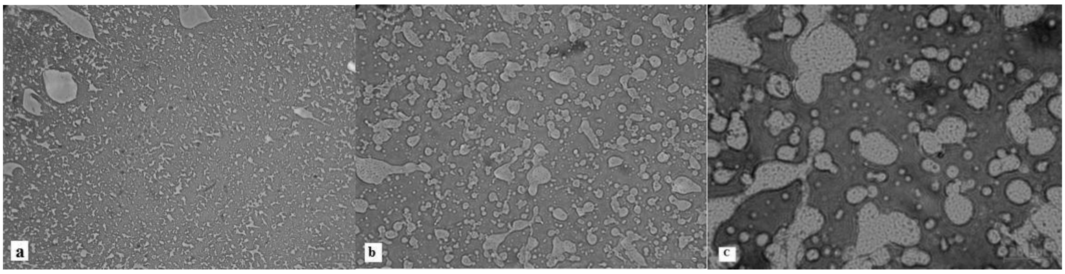

Figure 1. (a, b, c) Surface image of i-LDPE$_R$ modified bitumen at different magnification

4.3 RV Test Results

Rotational viscosity values and modification indices (η) of the binders employed in this study are shown in Table 2. Modification indices are ratio of the viscosity of modified bitumen to base bitumen and reflect degree of the increment in viscosity. As can be seen from Table 2, the viscosity values increase with increasing content of i-LDPE$_R$ additive at both temperatures conditions. Especially, the sample B-9-i-LDPE$_R$ has a significant increase in viscosity compared to the base bitumen, it also can be clearly seen from the values of the modification indices which is 6.65 at 165 °C. The increments at both 135 °C and 165 °C are similar. For instance, modification indice calculated for B-7-i-LDPE$_R$ is 3.93 at 135 °C, while it is 3.73 at 165 °C.

Table 2. Rotational viscosities of pure and modified bitumens

Binder types	Rotational viscosity at 135^{o}C (cP)	Rotational viscosity at 165^{o}C (cP)	$\eta_{\text{i-LDPER/B}}$ / η_{Bitumen} at 135^{o}C	$\eta_{\text{i-LDPER/B}}$ / η_{Bitumen} at 135^{o}C
B	203	65	1.00	1.00
B-1-i LDPE$_R$	250	82.5	1.23	1.27
B-3-i-LDPE$_R$	380	122.5	1.87	1.88
B-5-i-LDPE$_R$	700	207.5	3.45	3.19
B-7-i-LDPE$_R$	798	242.5	3.93	3.73
B-9-i-LDPE$_R$	1285	432.5	6.33	6.65

4.4 DSR Test Results

The rheological behaviors of pure and i-LDPE$_R$ modified bitumens at from mid temperature to high temperatures (10-75 ^{o}C) have been characterized by using the Dynamic Shear Rheometer (DSR). Two different spindle diameters (8 and 25 mm) and testing gaps (1 and 2mm) were selected depending on test temperature. Table 3 shows frequencies used in the test procedure which were accepted as equivalent to different frequencies of traffic. In order to examine the effects of i-LDPE$_R$ modifier against rutting. DSR test parameters are given in Table 4. The mechanism of polymer modification can be explained by plotting complex modulus and phase angle vs. temperature for the base and modified bitumen in Fig. 2,3 and 4.

Table 3. Traffic speeds equivalent frequencies

Traffic speed, km/hr	Traffic speeds equivalent frequencies, Hz (rad/sec)
Low, 6 km/hr	0.1 Hz (0.628 rad/sec)
Medium, 45 km/hr	0.72115 Hz (4.53 rad/sec)
High, 120 km/hr	1.9355 Hz (12.15494 rad/sec)

Table 4. DSR test parameters

Test parameters		
Mode of loading	Controlled-strain	
Frequencies, Hz	0.1 Hz, 0.72115 Hz, 1.9355 Hz	
Temperatures, ^{o}C	10, 15, 20, 25	30, 35, 40, 45, 50, 55, 60, 65, 70, 75
Diameter spindle, mm	8	25
Testing gap, mm	2	1

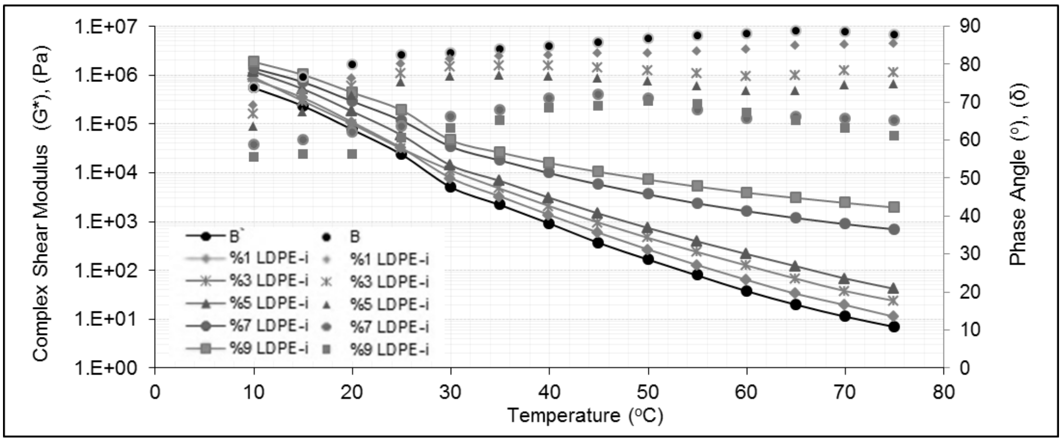

Figure 2. Curves of complex shear modulus and phase angle at 0.1 Hz for base and i-LDPE$_R$ modified bitumens.

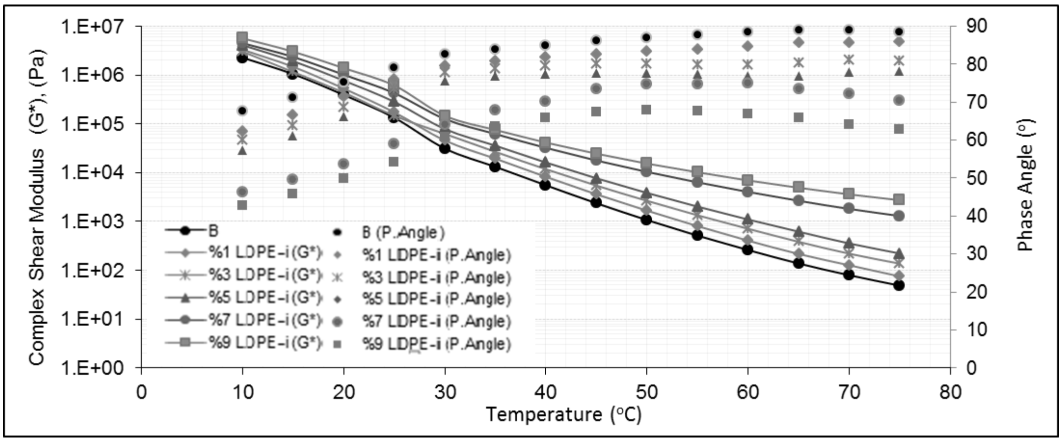

Figure 3. Curves of complex shear modulus and phase angle at 0.72115 Hz for base and i-LDPE$_R$ modified bitumens.

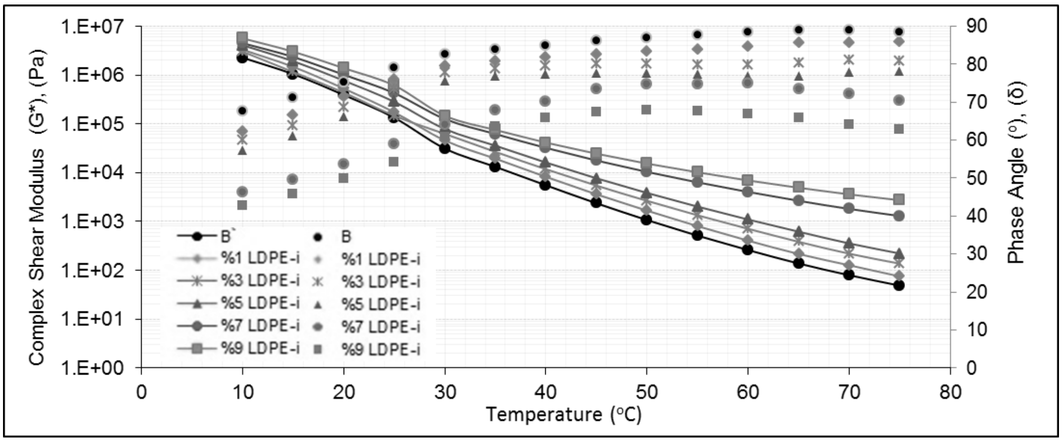

Figure 4. Curves of complex shear modulus and phase angle at 1.9355 Hz for base and i-LDPE$_R$ modified bitumens.

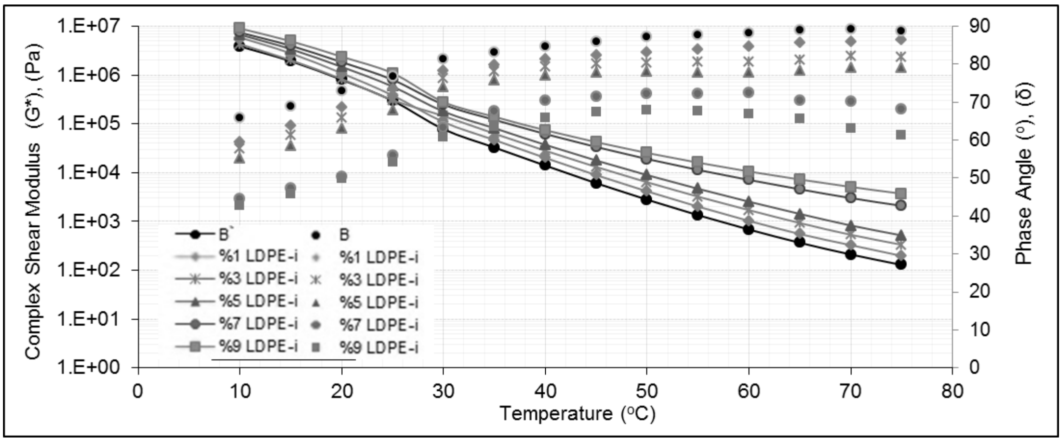

Figure 5. G*/sinδ (Pa) at 0.1 Hz for base and i-LDPE$_R$ modified bitumens.

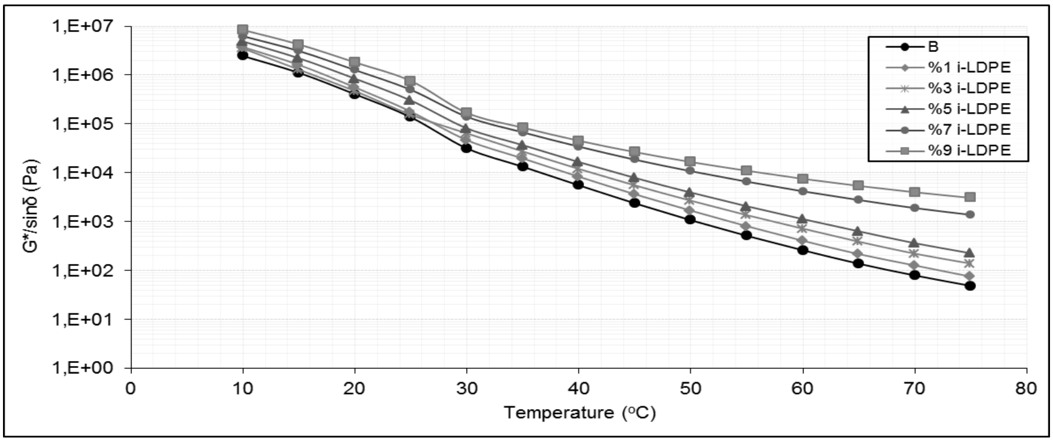

Figure 6. G*/sinδ (Pa) at 0.72115 Hz for base and i-LDPE$_R$ modified bitumens.

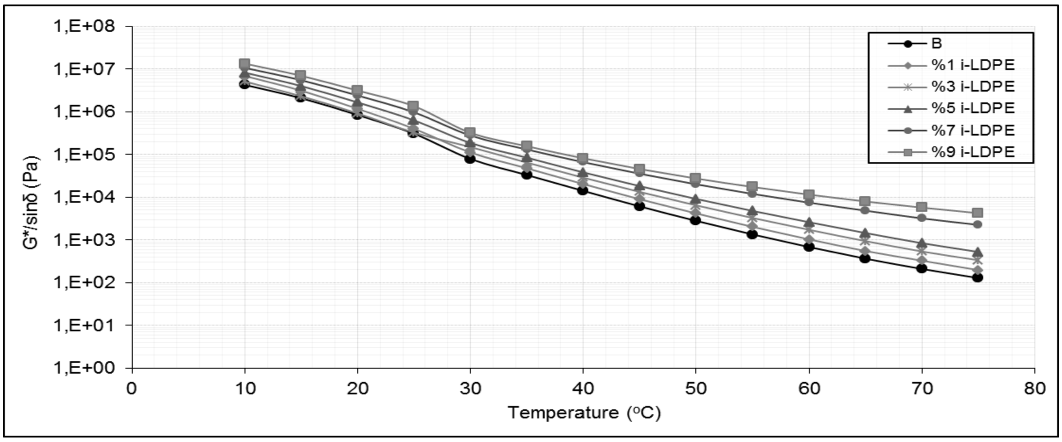

Figure 7. G*/sinδ (Pa) at 1.9355 Hz for base and i-LDPE$_R$ modified bitumens.

The isochronal plots reveal that, the all modified bitumens have greater complex modulus than the base bitumen. In addition, blends show a relatively consistent increase in G* with increasing amount of the modifier i-LDPE$_R$ that indicate an increasing stiffness of the modified binders. This improvement in terms of deformation stability is a sign of gained resistance against ruts formation in pavements. The phase angle (δ) is generally regrad as elasticiy of bitumen. The values of phase angle for the samples of modified bitumen are lower compared to pure bitumen. The decrease in phase angle values by i-LDPE$_R$ modification is point to that the modified bitumens were become more elastic which can also lead to lesser rut damage. Changes in rutting parameters ($G^*/\sin\delta$) with increasing temperature are shown in Figures 5, 6 and 7. It is clearly seen that rutting parameters of B-9-i-LDPE$_R$ are obiviously higher than the ones of all the other samples at all frequencies. The increment of the rutting parameter increase with increasing modifier content and that all same for low, medium and high frequencies. These results show that using i-LDPE$_R$ as addivitve in bitumen can provide remarkable positive effects against rutting.

5. CONCLUSIONS

i-LDPE$_R$ modified bitumen has been investigated by means of conventional, chemical and dynamic mechanical tests. The dispersing efficiency of i-LDPE$_R$ in bitumen was observed and analyzed as well. Results show that rheological properties of bitumen are improved by means of i-LDPE$_R$ modification. The images taken with fluorescence microscope reveal formation of multiphase system with bitumen continuous phase, i-LDPE$_R$ dispersed phase and the mixed phase (interfacial layer), which is a sign of reactive compatibilization of the blend components by virtue of chemical bonding. The appearance of reactive C=C bonds in i-LDPE$_R$ macromolecules after irradiation of the LDPE$_R$ by ion beam is evidenced by means of FTIR spectroscopy. Conventional penetration, softening point, ductility and rotational viscosity tests have proved the increased stiffness (hardness) and improved temperature susceptibility of i-LDPE$_R$ modified bitumens. The results obtained from the DSR tests show that i-LDPE$_R$ modifier provides an increased complex shear modulus (G*) values and rutting parameters ($G^*/\sin\delta$), and decreased phase angle (δ) values compared to the base bitumen. Complex shear modulus, rutting parameters increase with increasing in i-LDPE$_R$ modifier content in the blends while phase angle decreases, thereby, using i-LDPE$_R$ as a modifier in bitumen increase durability of flexible pavement by means of increased stiffness and elasticity.

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