



## Bitumen Modification with Polysulphide Polymer Prepared from Heavy End Waste

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### ABSTRACT

Heavy end waste is produced as a by-product in purification unit of vinyl chloride monomer in petrochemical complexes. This waste should be recycled or reused with ensured safety. Preparation of polysulphide polymer from this waste is one of the solutions to reuse this waste. This paper deals with the effects of polysulphide polymer (PSP) and waste residue from distillation of heavy ends waste (WR) on the morphology, engineering and rheological properties of bitumen. To achieve this goal, polysulphide polymer was prepared from the distilled heavy ends waste which consists of a mixture of various chlorinated organic hydrocarbons and alkali polysulphide. Subsequently, bituminous blends were produced by mixing 60/70 penetration grade bitumen and 1, 3 and 5 wt% of PSP or WR. An optical microscopy was employed to study the morphology of samples. The observed morphology was attributed to physical interactions acting between the phases. The engineering properties of modified bitumen containing PSP and WR were also determined and compared with those of blank bitumen. The experimental results showed that softening point of the bitumen increased whereas its penetration decreased upon incorporation of PSP. In the case of WR, a reverse effect was observed. The experimental master curves of  $G'$  and  $G''$  obtained from the oscillatory rheological measurements using time-temperature superposition principle were reported. The shift factors used in constructing master curves indicated an Arrhenius type temperature dependency. The calculated flow activation energy of the bituminous blends showed higher resistance against their flow. It confirmed less rutting at high temperatures in comparison with that of the base bitumen.

### Key Words:

polysulphide;  
modified bitumen;  
waste;  
rheology;  
shift factor;  
temperature dependency.

### INTRODUCTION

Bitumen is a mixture of different hydrocarbons [1]. It is widely used as a binder in road paving, roofing systems, sealing compound and waterproofing applications [2,3] and generally in some coating materials [4]. Properties of the bitumen depend on the nature of the crude oil and the refining processes. Bitumen by itself often

cannot meet the performance requirements for applications such as paving, roofing system and water-proofing membranes. Therefore, approaches have been developed whereby polymers are added to the bitumen to increase properties such as low temperature flexibility and high temperature softening point [5,6]. Improvements

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in either low temperature or high temperature properties would cause widening range of service temperature [7,8].

Polymers were used to modify bitumen in improving their characteristics with enhanced performances [9]. Polymers used to modify the physical and rheological properties of bitumen are styrene butadiene styrene copolymer (SBS), styrene butadiene rubber (SBR) [10,11], ethylene vinyl acetate copolymer (EVA) [12], atactic polypropylene, ethylene-propylene copolymer and ethylene-propylene rubber [13], amorphous poly( $\alpha$  olefins), cellulose fibres, polyolefins [14], polyurethane and also epoxy resins [15]. Waste and recycled materials may also be used as modifying agents in bituminous materials [16,17], for example, wastes of EVA and ABS, recycled polymer [18], scrap tyre rubber [19,20] and wastes from petrochemical plants [21].

Styrene-butadiene-styrene (SBS) block copolymers and ethylene vinyl acetate (EVA) are two polymers which have been widely used in bitumen modification. This family of polymers improves low and high temperature behaviour of bitumens at relatively low concentrations (3-5%) [22]. EVA modifies bitumen by forming a tough, rigid, three-dimensional network which resists deformation. EVA has revealed as a good modifier which suppresses permanent deformation and thermal cracking on pavement [23].

One of the problems in chemical and petrochemical industries is the waste from chemical processes. The solution of this problem is well-known as: "three Rs", reduction, reuse and recycling. In PVC (polyvinyl chloride) plants the heavy end waste is generated during manufacture of chlorinated hydrocarbons. The heavy end waste is a side stream in distillation or purification unit of chlorinated hydrocarbons such as ethylene dichloride (EDC) or vinyl chloride monomer (VCM), epichlorohydrine (ECH), etc. It consists of a mixture of various organic chlorinated hydrocarbons [24,25]. Since these chlorinated or polychlorinated hydrocarbons pose a high risk to human health, traditionally they will either incinerate or recover as a chlorinated organic solvent. These methods, however, suffer several shortcomings. For example, the high temperature of incineration creates dioxin a highly

toxic atmospheric pollutant. Recovery of chlorinated solvent is also constrained by environmental concerns. High quantity of dichloro compounds found in the heavy end waste allows it to be polymerized with alkaline polysulphide to form polysulphide polymer. Thus, according to this, the environmentally hazardous heavy ends waste can now be converted into a useful polysulphide polymer without any environmental problems [26,27].

Organic polysulphide polymers are a class of important industrial compounds which have unusually good resistance to solvents and good low temperature properties [28]. These polymers which are prepared by the reaction between alkali metal polysulphide (for example,  $\text{Na}_2\text{S}_x$  where  $x = 1-5$ ) and  $\alpha,\omega$ -dihalo organic compounds have the general backbone structure:  $-\text{RS}_x\text{RS}_x\text{R}-$ . Wherein R is an organic moiety derived by removal of the halogens from an  $\alpha,\omega$ -dihalo organic compound, and  $x$  which ranges between about 2 and 5, may enter cross-linking at random intervals through the use of a small percentage of trihalide in the synthesis reaction. Polysulphide polymer shows good resistance to solvents and the environment and suitable low temperature properties which make them particularly useful in sealant applications [29].

The purpose of the present work is to study the benefit of the polysulphide polymer prepared by the heavy end waste addition on the bitumen performance. In that sense, blends of bitumen and polysulphide polymer have been prepared, and a further rheological and microstructural characterization, are mainly carried out. In our knowledge it is the first time that polysulphide polymer may be used in bitumen modification and the properties of the resulting blend are being reported.

## EXPERIMENTAL

### Materials

The materials used in this work were distilled heavy end waste of ethylene dichloride/vinyl chloride monomer unit of Bandar Imam Petrochemical Complex (BIPC, Mahshahr, Iran). Bitumen used in all modifications was a 60/70 penetration grade from Tehran refinery (crude from Asmari reservoir of

**Table 1.** Some physico-chemical characteristics of the bitumen 60/70 penetration from Tehran Refinery.

Physico-chemical properties	
Saturates (wt%)	15.66
Naphthene aromatics (wt%)	39.15
Polar aromatics (wt%)	35.04
Asphaltenes (wt%)	10.15
Penetration at 25°C (0.1 mm)	58.00
Softening point (°C)	50.00
Frass breaking temperature (°C)	-12.00
Performance grade (PG)	70-22
Penetration index (PI)	-0.859

Ahwaz in Khuzestan, south-west of Iran). The physical properties and composition of this bitumen are reported in Table 1. Sulphur, sodium hydroxide, magnesium chloride and hydrochloric acid were of technical grades.

### Procedures

#### *Preparation of Polysulphide Polymer*

Heavy end waste obtained directly from VCM plant was first distilled. The remaining waste (WR) in the black solid form was directly used as a bitumen modifier, and the lightly yellow liquid part was used to prepare polysulphide polymer by the following process:

Distilled heavy end waste (monomer), excess of sodium polysulphide and colloidal magnesium hydroxide were reacted at 70°C in a 1-L four-necked kettle. After addition of monomers, temperature was increased to 97°C and was kept for 4 h. Obtained polymer was washed out several times with hot water and decanted to remove salts. It was then dried at 80°C under vacuum for 2 h [30].

#### *Preparation of Modified Bitumen*

Modified bitumens (MB) were prepared by heating a 60/70 penetration grade bitumen in a duplex high-shear mixing system composed of Polytron 6000 (Kinematika Co., Switzerland). It was connected to a high-shear aggregate PT-DA 3020/2 along with a low-shear propeller mixer Polymix (Kinematika Co., Switzerland) operated at 165±5°C. Upon reaching 165±5°C, a pre-weighed amount of modifier (1, 3 or

5% by weight of the blend) was added slowly to the bitumen. Mixing was then continued at a speed of 8000 rpm for 30 min. When addition of the modifier was completed and while mixers were operating at low speed of rotation, samples for the penetration and ring and ball tests were taken from the mixer drain valve. Optical microscope samples were also taken during the transfer period. The remaining material in the mixing chamber was transferred into a metallic can and cooled down to room temperature. Samples for the rheological measurements were collected from this part of the blend.

#### *Morphological Analysis*

A polarization microscope has been used to investigate the morphology of the MBs by determining the state of dispersion of the polymer within the base bitumen. The MBs samples were placed on glass slides, kept for 15 min in an oven at 170-180°C, then, they were cooled to room temperature and each one was covered by another glass slide. The morphology of the samples was viewed under a Bel photonics polarization microscope MPL-15 model.

#### *Softening Point Temperature and Penetration Test*

The softening point (ring and ball test) of bitumen and PMBs was measured according to National Iranian Standards ISIRI 2951 (equivalent to ASTM D36) and the penetration tests were carried out at 25°C according to ISIRI 2950 (equivalent to ASTM D5) [31].

#### *Penetration Index*

The penetration index (PI) is a measure of temperature susceptibility of bitumen. The temperature susceptibility is defined as the change in the consistency of bitumen as a function of temperature. After determination of the penetration and softening point for all modified bitumen samples the penetration indexes were calculated by the following equation [4]:

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

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

### Rheometry

Dynamic mechanical analysis (DMA) was carried out using a rheometer MCR 300 Anton Paar which operated under a strain control. The parallel plate geometry with diameter of 25 mm was used. Dynamic rheological measurements were conducted at 30, 45, 60, 75 and 90°C, the shear-rate range of 0.1-500 s<sup>-1</sup>, with a gap of 1 mm and 10% strain for all tests. In dynamic measurements, the temperature was varied from 30 to 90°C (with 15°C steps), in order to construct master curves for the dynamic material functions at 30°C.

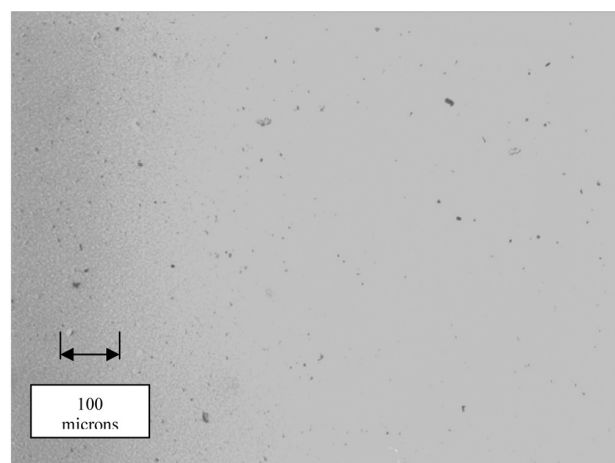
## RESULTS AND DISCUSSION

Heavy end waste of ethylene dichloride/vinyl chloride monomer unit, obtained from BIPC after fractional distillation was analyzed by gas chromatography. The composition of the heavy waste was 1,1,2-trichloroethane, 3,4-dichloro-1-butene, 1,1-dichloro-propane, 1,3-dichloro-2-butene, 1,3-dichloro-2-methylpropene, 1,4-dichloro-2-butene, 1,2-dichloro-ethane, 1,4-dichloro-2-butene. Remaining chlorohydrocarbons as a residual waste was a black solid substance. The resultant polysulphide polymer from distilled heavy end waste was brownish powder with a low mercaptan odour. The average molecular weight of the obtained polymer was 5000 g/mol, with mercaptan content of 1.64% and the specific gravity of 1.29 (25°C).

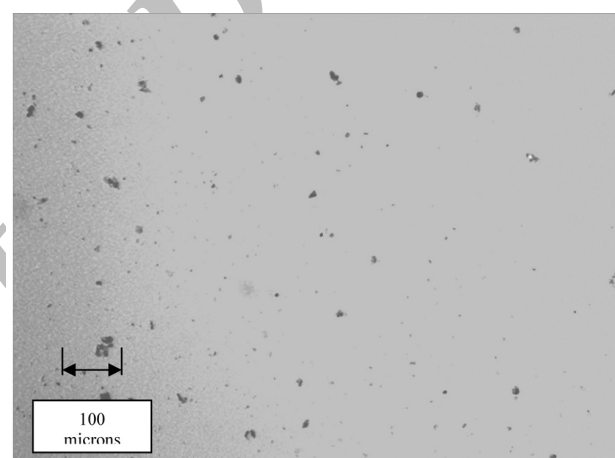
### Morphology

From a morphological point of view, the optical microscopic observations (Figures 1 and 2) do not show any significant difference between the PSP and WR modified bitumen. However, it should be noted that the natures of the dispersed phases of the blends are different. In the PSP-modified blends the dispersed phase is composed of polymeric material, whereas in the WR-modified blends the dispersed phase is composed from unknown solid particles which exist in the WR.

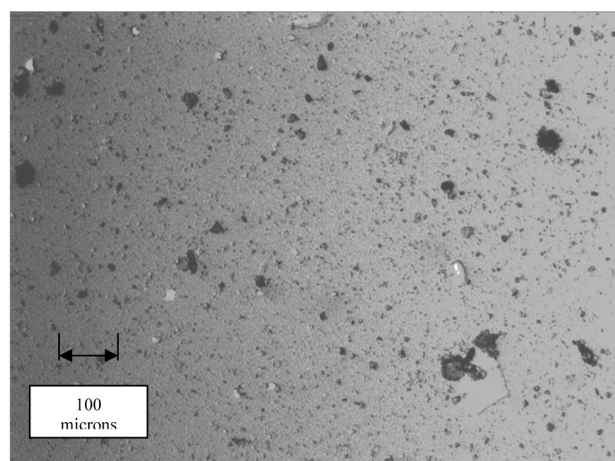
An important observation is non-roundness of the dispersed particles which could be the result of their rubbery and solid states (Figures 1 and 2).



(a)



(b)

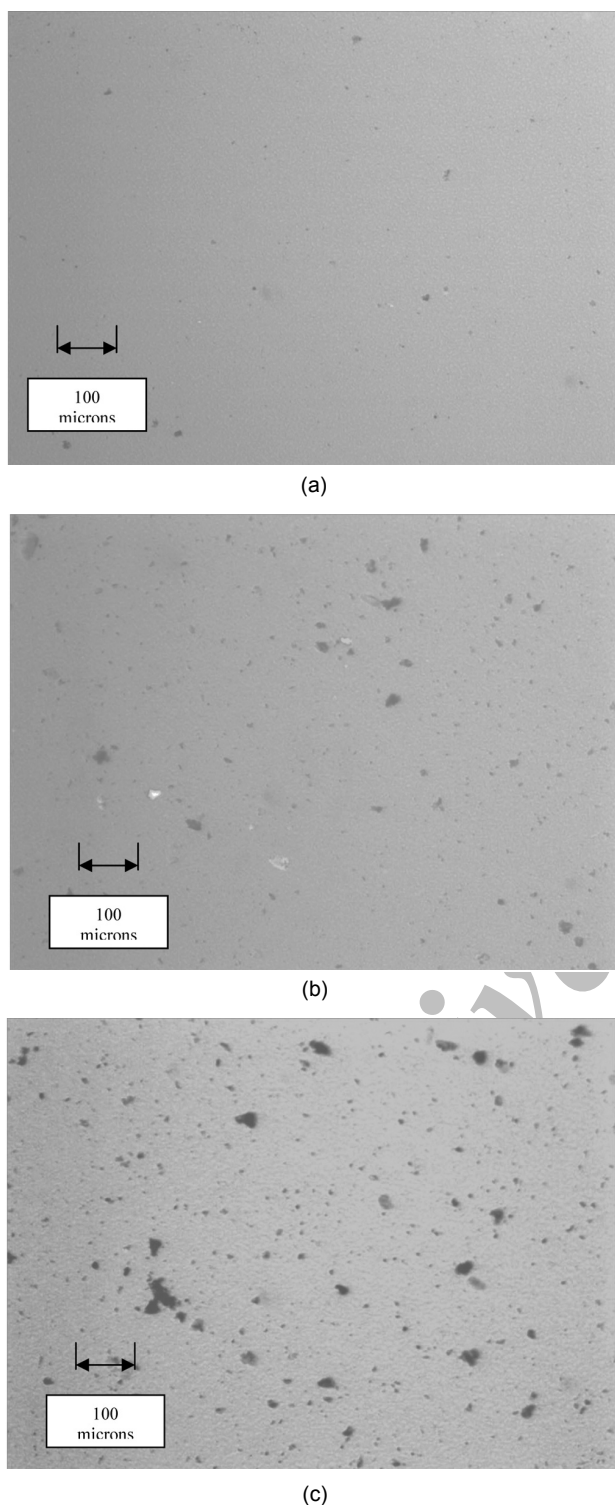


(c)

**Figure 1.** States of the polysulphide (PSP) dispersion in bitumen: (a) 1%, (b) 3% and (c) 5% by weight (magnification, 100×).

### Engineering Properties of the Blends

The blends of bitumen with the PSP and WR were



**Figure 2.** States of the waste residue (WR) dispersion in bitumen: (a) 1%, (b) 3% and (c) 5% by weight (magnification, 100 $\times$ ).

prepared according to formulations in Table 2 and the engineering properties of the resulting blends were

summarized in the same table. According to Table 2, addition of the PSP would cause increments in softening point and decrease in penetration. In case of WR we observed a reverse effect, although, the variation of penetration and softening point temperatures were uniform with increased polymer content. Moreover, a significant increase in the softening point temperature of the PSP-modified bitumen was observed at 5% polymer content. Since, the decreased penetration and the increased softening point temperature indicated an increased hardness of the modified bitumen; the results demonstrated that the PSP-modified bitumen might be less sensitive to permanent deformations. This is expected due to the polymeric structure of the PSP and the non-polymeric structure of the WR.

The penetration index (PI) is used to classify bitumen. PI values can be used to determine the stiffness (modulus) of bitumen at any temperature and loading time. It may also be used to identify a particular type of bituminous materials in a limited extent. Typical values of PI are shown in Table 3 [32]. Polymer modification reduces the temperature susceptibility of the bitumen. Lower values of PI indicate higher temperature susceptibility. Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation [33].

Penetration index results of the prepared modified bitumens are presented in Table 2. It is clearly seen that with increased amount of the PSP in bitumen formulations, the PI is increased (from -0.45 to -0.12). The PI of the bitumens modified with 1-5 wt% PSP is within the range of conventional paving bitumen. However, a less negative PI value upon the addition of PSP is an indication of improved PI. As it is observed in Table 2, the PI value of 5 wt% PSP-modified attains -0.12 which is four times larger than that of the base bitumen. This represents four times slower in bitumen consistency loss. This behaviour stems from the very low temperature susceptibility of the added modifier which has a polymeric nature. This will result in turn in a higher resistance against thermal cracking of the pavement at low temperatures, whereas at high temperatures less permanent (plastic) deformation will appear on the road surface under traffic loadings.

**Table 2.** Blends of the base bitumen with different percentages of the polysulphide polymer (PSP) and waste residue (WR).

Blend	Polysulphide polymer (%)	Waste residue (%)	Penetration (0.1 mm)	T <sub>R&amp;B</sub> (°C)	Penetration index
1	-	-	58.0	50.0	-0.859
2	1	-	45.0	54.2	-0.452
3	3	-	43.4	55.0	-0.357
4	5	-	37.0	57.8	-0.119
5	-	1	55.0	50.0	-0.986
6	-	3	56.1	45.0	-2.289
7	-	5	58.2	34.0	-5.924

**Table 3.** Typical values of the penetration index [32].

Bitumen type	Penetration index
Blown bitumen	>1
Conventional paving bitumen	-1 to +1
Temperature susceptible bitumen (tars)	<-1

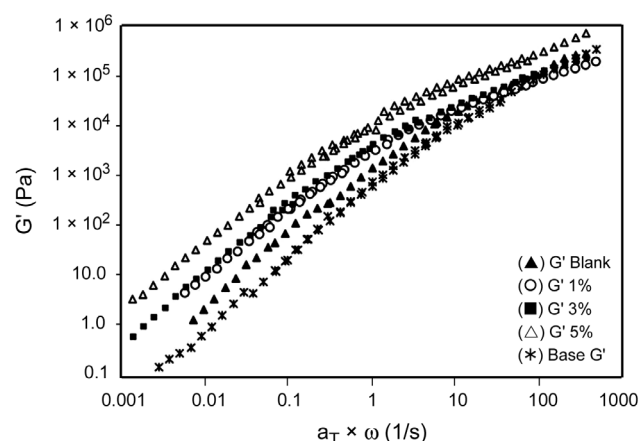
Incorporating 1, 3 and 5 wt% WR into bitumen the PI decreases to -0.986, -2.289 and -5.924, respectively. According to the range provided in Table 3, it can be concluded that the nature of WR-modified bitumens coincides to those of bitumens which are highly temperature susceptible materials such as tars. A decrease in the PI towards negative zone indicates that the bitumen becomes more brittle under frozen conditions. Meanwhile, this similarity in the behaviour of tars confirms the existence of poly-aromatic crystallizable components in WR. The poly-aromatic materials are flat molecules that have a very high tendency towards packing which ultimately leads to crystallization. These crystalline phases are separated from the rest of the bitumen and play the roles of stress concentrators at low temperatures, and promote low-temperature crack initiation and propagation.

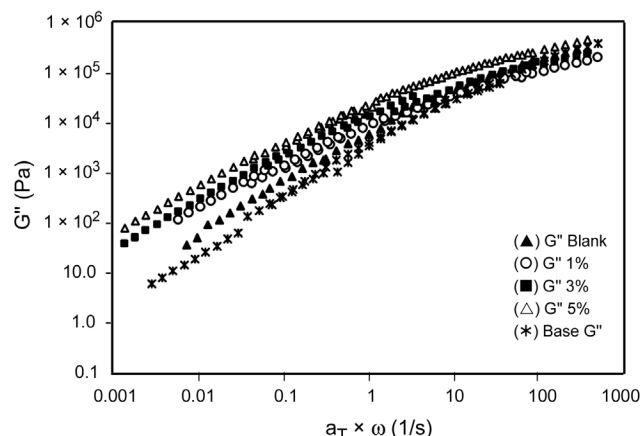
### Rheological Properties

Bitumen compositions and temperature strongly influence the mechanical properties and micro-structure of bitumen. In this sense, rheology has become a useful tool in characterizing bitumen

performance on pavements. At any combination of time and temperature within the linear viscoelastic zone in the mechanical performance, the elasticity is usually characterized by the shear elastic modulus,  $G'$ , which is calculated as the ratio of the maximum shear stress to the maximum shear strain.

To elucidate the effect of PSP on the rheological properties of bitumen samples some mechanical tests were carried out. As it is shown in Figures 3 and 4, addition of the PSP to bitumen leads to an increase in both elastic ( $G'$ ) and loss ( $G''$ ) modulus. The effect of this polymer on bitumen's elasticity is not very different for 1% and 3% by weight polymer modification. The grade of the PSP which was used in this study was not of a high molecular weight and this led to less polymer chain entanglements. Due to this

**Figure 3.** Master curves of  $G'$  for base, blank, 1, 3 and 5 wt% PSP-modified bitumens at 30°C.



**Figure 4.** Master curves of  $G''$  for base, blank, 1, 3 and 5 wt% PSP-modified bitumens at 30°C.

fact, the polymer particles in bitumen matrix are not able to show a very high elasticity. Meanwhile, the low-molecular weight PSP does not show any kind of incompatibility with bitumen, and so no phase segregation is expected. The chains of polysulphide polymer are very flexible and just like other types of rubbers show entropic elasticity. The glass transition temperature ( $T_g$ ) of this polymer is well below 0°C which avoids brittle failures at low temperatures of pavement service life. Meanwhile, due to the rubbery characteristic of the polymer at high enough polymer concentrations in bitumen matrix, the modified bitumen is assumed to resist a permanent deformation. An increase in the elasticity of the 5 wt% modified bitumen supports this conclusion. This has also been observed that the elastic modulus of the bitumen is more sensitive to the polymer content of

the blend. Therefore, a relatively large difference between the 5 wt% modified blend and the base bitumen is observed. As it appears in Figure 1c, the elastic polymer particles dispersed in bitumen matrix, are more populated than those of WR modified bitumen. This may also help to comprehend the differences in the elastic properties of different PSP-modified bitumens. This is an indication for the effective contribution of PSP in rheological elastic response of MB to the induced stresses. Considering the morphology of these blends, it is possible that this polymer is able to form a type of network in bitumen medium.

One interesting observation is that this polymer highly affects the low-frequency (high temperature) response of the blend, whereas its high frequency (low temperature) response of the blend is not very different from the base bitumen. This means that the resulting modified bitumen is resistant to rutting (permanent deformation) at high temperatures, and it is not very different from the base bitumen against thermal cracking.

Another important observation in the time-temperature superposition (TTS) principle holds for these bituminous blends and some conflicts are observed on the master curves which can be considered as an artifact of fitting operation. Normally, the shift factors of TTS principle obey Arrhenius equation and the "flow activation energy" of the blended bitumens increases with the polymer content. This is a direct evidence for increased resistance to rutting at high temperatures. The numerical data are reported in Table 4. The Arrhenius

**Table 4.** The shift factors of different bitumenous blends in master-curve construction.

Blend	Polysulphide polymer (%)	Waste residue (%)	30°C	45°C	60°C	75°C	90°C
1	-	-	1	0.070	0.0185	0.00450	0.002500
2	1	-	1	0.245	0.0200	0.00340	0.000620
3	3	-	1	0.300	0.1000	0.00350	0.000580
4	5	-	1	0.200	0.0030	0.00170	0.000300
5	-	1	1	0.120	0.0016	0.00060	0.000125
6	-	3	1	0.080	0.0008	0.00045	0.000085
7	-	5	1	0.070	0.0015	0.00095	0.000150

**Table 5.** Curve fitting parameters and calculated flow activation energy of the bituminous binders.

Blend	Equation of the fitted line	R-squared value (R <sup>2</sup> )	ΔH (kJ/mol)
Base	y = 8.5972x - 0.5435	0.9560	71.48331
Polysulphide 1 wt%	y = 11.004x + 0.2459	0.9852	91.49518
Polysulphide 3 wt%	y = 10.809x + 0.5312	0.8885	89.87381
Polysulphide 5 wt%	y = 12.485x + 0.0701	0.9891	103.8093
Waste residue 1 wt%	y = 13.829x - 0.0618	0.9949	114.9843
Waste residue 3 wt%	y = 14.289x - 0.2523	0.9862	118.8090
Waste residue 5 wt%	y = 13.005x - 0.3482	0.9842	108.1329

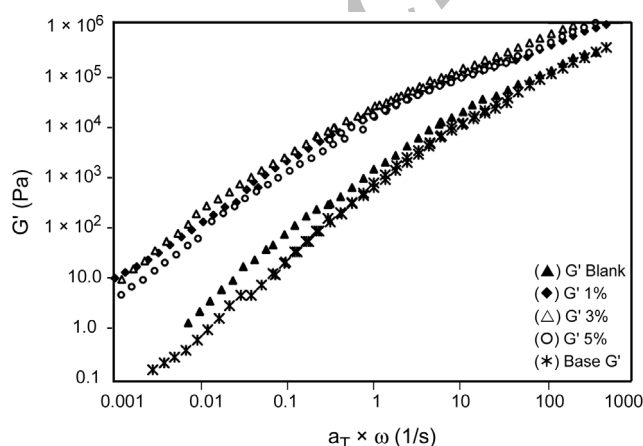
equation, contrary to Williams-Landel-Ferry (WLF) equation, fits to the temperature dependency of the low molecular weight materials and molten polymers far from the T<sub>g</sub> of polymer. This equation reads as follows [34]:

$$a_T = \exp\left(\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \rightarrow \Delta H = R \frac{d(\ln a_T)}{d\left(\frac{1}{T}\right)}$$

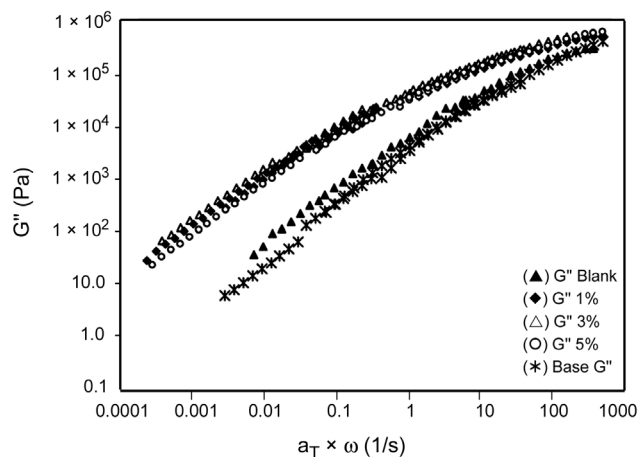
where a<sub>T</sub> stands for shift factor, ΔH the "flow activation energy", R the ideal gas constant, T<sub>ref</sub> the reference and T the test temperatures, respectively. The "flow activation energy" can be calculated as the slope of the trace of Ln(a<sub>T</sub>) against 1/T-1/T<sub>ref</sub>. The list of shift factors used in construction of the master curves is provided in Table 4. The lines fitted in the data are presented in Figure 7 and the corresponding

line equations and R<sup>2</sup> values are reported in Table 5. The calculated flow activation energies are listed in Table 5. As it is clear, the flow activation energy of the blends is systematically 10 to 50 units higher than that of the base bitumen. All these are indicating that the modified bitumen are more resistant to flow and show that less rutting will happen under traffic loads. This result is in agreement with the results of conventional tests. Another important observation is the dramatic change in the slope of the line fitted into the data presented in Figure 7. This is a very clear evidence for changes in bitumen structure after introducing the modifier and altering the bitumen temperature susceptibility.

The dynamic oscillatory measurements of bitumen blends with WR are also reported in Figures 5 and 6. Almost all concentrations of this modifier produce the same rheological properties. This can be



**Figure 5.** Master curves of G' for base, blank, 1, 3 and 5 wt% WR-modified bitumens at 30°C.



**Figure 6.** Master curves of G'' for base, blank, 1, 3 and 5 wt% WR-modified bitumens at 30°C.



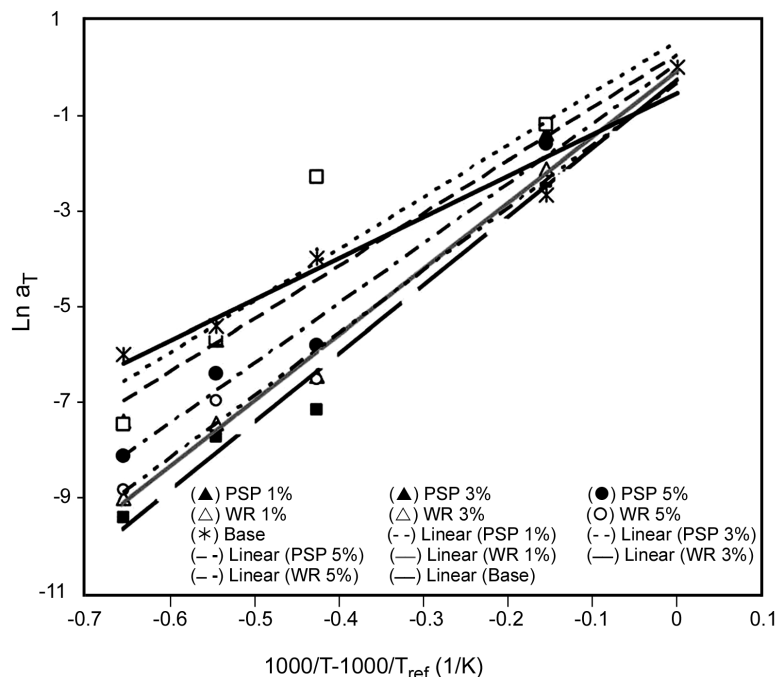


Figure 7. The Arrhenius plot of shift factors used in construction of blends' master curves.

the result of non-polymeric structure of the residue. Some parts of the differences between modified bitumen and the base bitumen come from the physical ageing of bitumen during mechanical mixing process and the other part from the solid nature of WR. However, an interesting phenomenon is clearly observable on the elastic modulus of the modified blends. This witnesses the existence of some dispersed phases in the WR which is able to contribute in the blend elasticity at low frequencies (high temperatures). This ensures a less tendency towards rutting at high temperatures. As it is observed in Figures 5 and 6, the TTS principle pretty well holds for these modified bitumen and these bitumens are not prone to disobey the TTS principle. The shift factors of these blends are summarized in Table 4, and the corresponding information and flow activation energies are reported in Table 5. Very higher flow activation energy of these blends can stem from the high-cohesive energy polyaromatic compounds embedded into the base bitumen.

## CONCLUSION

Environmentally hazardous petrochemical waste can

be safely reused. This paper introduces ways to reuse the above wastes. The properties of bitumens are improved by polysulphide polymer, and waste residue has been used for the first time. This result has been achieved by conventional test methods such as the penetration, softening point and rheology. The addition of different percentages of polymer and waste residue to bitumen, in order to improve its performance, has been studied. The experimental results have shown that for PSP-modified bitumen the softening point increases and penetration decreases. In the case of WR we observe a reverse effect. The PI's PSP-modified bitumen samples confirm that they are suitable for paving application. The WR addition increases the PI value and, consequently, the thermal susceptibility of the binder. The morphology of PSP and WR modified bitumen are similar, and suggests rubbery and solid states of the dispersed particles. The rheology results have shown that these modifiers can form a type of network in bitumen matrix which is resistant to the permanent deformation at high temperatures. The TTS principle holds for both families of the modified bitumens and shows an increase in the "flow activation energy" upon the addition of a modifier. The provided rheology data's are in full agreement with engineering properties of

the bituminous blends.

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