



Polymer Wastes Reinforced the Rheological Properties of Bitumen Composites Pastes



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Abstract

The provision of raw materials is a major challenge for the next generation due to the improvement of living standards and population growth, as well as the expansion of construction and industrial activities, causing unparalleled demands for raw material supplies. Plastic waste and spent lubricants are the most important polymer waste, with a share of 75.5% of the total available municipal waste. The Central Agency for Public Mobilization and Statistics confirmed that the largest solid waste sector is currently unused. The present study included modifying the rheological properties of bitumen by partial substitution using solid waste materials represented by PVA and spent lubricating oils. The transformation process was carried out at a temperature of 180°C in the presence of sulfur again and anhydrous aluminum chloride. The rheological properties of the original and modified bitumen composites were investigated, which included measurement of penetration, softening point and ductility, as well as the calculation of the penetration index. The modified composites were cured with the original asphalt bitumen patches for 12 months, and then rheological properties were re-measured again after one year of aging. This is an actual case study of the replacement of bitumen with solid waste and the positive advantages over its physical properties.

Keywords: Polymer Waste, Bitumen, Sulfur Again and Rheological Properties.

1. Introduction

Plastic poses a huge burden to the environment due to its recalcitrant nature which makes it resistant to biodegradation, as plastic left in the same condition for a longer period is a huge threat to the environment, plant life, and wildlife as well as to people. Elastomers are a group of organic polymers comprising synthetic, semi-synthetic, or natural materials that can be folded and shaped into solid bodies [1-2]. Polymers are large molecular weight synthetic materials made of long chains consisting of carbon and other elements such as hydrogen, chlorine and nitrogen, each unit in the chain is called a (monomer), and it is a chemical substance that is produced from crude oil and gases. The demand for plastic has increased in the global market as an alternative to natural rubber, glass, wood, and other raw materials and metals which may be attributed to the properties that plastics/polymers have, and as a

result of these properties, these materials have many uses in many areas of our daily life needs and as raw materials for different industries. Commercial and economic applications of plastics are a unique "mixture" in terms of low cost, low toxicity, and ease of processing, excellent thermal stability, the balance of physical properties [3-7]. In addition to that, more cars, vans, and trucks on the road in Iraq, an increasing number of used lubricating oils (ULO) are generated. If it is not disposed of properly, the used lubricating oils will threaten the environment and human health [8], especially, the waterways and soil might be polluted if ULO were discharged. Meanwhile, with large-scale highway revamping and maintenance, there has been a high demand for asphalt in road engineering. Because fossil fuel reserve is decreasing around the

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world, seeking alternative asphalt materials is more badly in need of road engineering [9-13].

The issue of obtaining asphalt with rheological properties that is resistant to aging factors is an important and necessary matter to ensure the longest possible period of time for asphalt use in the most important area, which is paving. Asphaltic materials are heterogeneous hydrocarbon materials containing sulfur, nitrogen and oxygen (S, N, and O) and it has produced from direct distillation. In addition, asphalt contains cyclic and non-cyclic compounds [14].

The influence of clay bricks powder on the hydration of gray Portland cement was well studied worldwide. In addition, there are too little works studied the hydration characteristics of white Portland cement. In contrast, there is a lack of knowledge dealing with the role of clay bricks powder on the hydration of white Portland cement. Hence, the aim of this study is to discuss the influence of clay bricks powder on the whiteness reflection (Ry), both physico-mechanical and microstructure features of white cement composites and producing a new cement type may named as dark white evolution (DWE) cement for various construction purposes and reduce the cost of white cement with good chance of solid waste recycling. The rheological modification of asphalt processes using polymeric materials is one of the most important methods that is led to obtaining asphalt with rheological properties that exceed what is found in the original asphalt. The chemical modification process with polymers was preferred over other methods because it leads to obtaining asphalt with compatible properties [15]. When we return to the literature, we see many studies that dealt with this topic. Murshid [16] modifying asphalt materials using SBS rubber, as this study resulted in an increase in the resistance of asphalt to the thermal effect. Maharaj et al., [17] studied the use of low-density polyethylene and polyvinyl alcohol along with spent motor oils at rates of up to 30%. From the process of adding the above materials to the asphalt, it was found that the addition process led to an increase in the stress crack resistance property as well as Decrease in resistance to the formation of canyons in the street. Hussein and Hamdoun [18] were able to modify the rheological properties of asphalt by spent lubricating oils as an additive along with the process of anaerobic oxidation. Al-Azzawi and Hamdoun [19-20]; also modified the rheological properties of asphalt by using a mixture of polyethylene terephthalate and spent lubricating oils. The process gave good results when compared with the original asphalt. In our study Polyvinyl alcohol and spent lubricating oils; were used as a additive for asphaltic materials. The properties of the modified rheological asphalt were measured after the addition, and then they were measured after 12 months to know the extent of resistance of the prepared samples

to the aging factor [18]. This study aims to discuss the physical properties of asphalt incorporate with polymer waste recycling and its positive impact on the environment and health in order to conserve raw material resources. Attention to all success factors and the adequacy of implementation mechanisms to modernize and develop replacement systems with a higher level of replacing plastic waste and spent lubricants to raise the efficiency of construction management, reduce losses resulting from transportation, raising the secondary efficiency of solid waste channels. Also; The importance of training technicians on the operation and maintenance of asphalt systems and making them aware of the advantages of modern and smart building systems. We intend to move towards the use of smart building systems technologies in the world, by producing advanced asphalt at appropriate prices and quantities to be within the reach of all users.

2. Materials and Methods

2.1 Materials Overview

This study included the treatment of asphalt materials with each of Polyvinyl alcohol and spent lubricating oils in different proportions at a temperature of 180 °C and in the presence of 1% by weight of sulfur and at times of (1, 2 and 3) hours. The above reaction was repeated using 0.25% by weight of anhydrous aluminum chloride as a catalyst for this process. The rheological properties of the primary and modified asphalt were measured, which included the measurement of penetration [21], ductility [22] and softening point [23] as well as the calculation of penetration index [24]. The measurements were repeated for all samples after 12 months of curing. In addition, the aging of some asphalt sample was examined using a thin film furnace [25], the marshal was compared with the asphalt sample [26].

2.2 Methods

The AS matrix asphalt was kept at 180°C, treated with a mixture of ethylene-vinyl acetate and spent car lubricating oils, as well as polyvinyl chloride where the PW & ULO in a fixed ratio (1:1:1), with 1% by weight of sul-fur (as an addition) with asphalt at 4000 rpm shear rate for 1h, the temperature was kept at 180°C along the experiment.

3. Results and Discussions

3.1 Rheological Properties

3.1.1 Normal Curing Aging

In this study, two types of additives were used to modify the rheological properties of asphalt. The first is polyvinyl alcohol: this polymer is one of the types of the vinyl polymers using in several areas, the most important of which are pipes. The second additive is the spent lubricating oils. The processes of using

these additives contribute to reducing even a small percentage of environmental pollutants. PVA was used after thermally crushing in order to obtain a polymer with a lower molecular weight as possible.

We also know that the compatibility between asphalt and the additive increases as the molecular weight of the additive decreases. Polyvinyl alcohol was used under the conditions described in the experimental part, Table (1) shows the results obtained.

It is evident from the above table that the use of the PVA as an additive in modifying the rheological Properties of asphalt, as indicated by the literature, is considered a filler material and works to reduce the cracking of asphalt [26]. The treatment of asphalt with this additive led to obtaining modified samples with excellent ductility values, as these values remained constant to the extent of 0.5%, then decreased at a time of 3 hours and for the same ratio. As for the increase in the ratio to 0.75% by weight, the ductility values increased to the time limit of 2 hours, and then they decreased at a time of 3 hours. This applies to the ratio of 1% by weight, since the ductility was decreased and did not reach to 100+ in any case. This percentage was taken in the hope that we will obtain better values than the previous one. While the values of penetration and softening point were decreased and increased, some samples gives a

good value when at compared with the standard samples.

We note from Table (2) that the process of adding anhydrous aluminum chloride as a catalyst for this process led to a deterioration in the rheological properties by increasing the percentages of the additive. In spite of this, samples were obtained with rheological properties similar to those of paving asphalt and that is at 0.125%, as it gave values of Softening point, Penetration and ductility close to the original sample as for higher percentage we do not recommend their use. Lubricants are obtained from petroleum derivatives called reduced petroleum, as the boiling point of compounds in reduced petroleum is very high 315 ° C and cannot be distilled under normal conditions. They are hydrocarbon compounds containing naphthenic and aromatic compounds, and the rings or naphthalene compounds are connected to one or more paraffin side chains of different lengths. The greater the number of these chains, the closer the composition of the oil to the paraffin composition. The reason for choosing the oils as an additive is that they are one of the pollutants for the environment. The composition of both oil and asphalt gives a high degree of compatibility. Tables (3) and (4) explain the results obtained.

Figure (1):- Rheological properties of asphalt treated with PVA at 180°C in the presence of 1% by weight of sulfur at (1,2 and 3) hours

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	--	--	56	38	100+	-0.428
As1	1	0.125	57	40	100+	-0.108
As2	2	0.125	59	30	100+	0.313-
As3	3	0.125	60	25	100+	0.476-
As4	1	0.250	60	29	100+	0.190-
As5	2	0.250	61	25	100+	0.292-
As6	3	0.250	62	23	100+	0.268.-
As7	1	0.500	58	29	100+	0.574-
As8	2	0.500	59	28	100+	0.449-
As9	3	0.500	63	24	70	0.012-
As10	1	0.750	58	28	100+	0.642-
As11	2	0.750	61	26	100+	0.271-
As12	3	0.750	63	23	60	0.092-
As13	1	1.000	60	28	91	0.259-
As14	2	1.000	61	26	88	0.217-
As15	3	1.000	65	22	27	0.166

Table (2):- Rheological properties of asphalt treated with different PVA at 180°C, in the presence of 0.25% of (AICI3) and 1% by weight of sulfur at (1,2 and 3) hours.

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	----	---	56	38	100+	-0.428
As16	1	0.125	56	30	100+	A-0.908
As17	2	0.125	58	29	100+	-0.574
As18	3	0.125	59	26	68	-0.590
As19	1	0.250	55	30	81	-1.115
As20	2	0.250	57	26	59	-0.977
As21	3	0.250	59	25	39	-0.664
As22	1	0.500	57	31	91	-0.642
As23	2	0.500	58	30	50	-0.508

As24	3	0.500	60	25	40	-0.476
As25	1	0.750	60	24	41	-0.552
As26	2	0.750	57	28	86	-0.839
As27	3	0.750	59	25	51	-0.664
As28	1	1.000	58	30	54	-0.508
As29	2	1.000	58	28	42	-0.642
As30	3	1.000	57	26	38	-0.977

Table (3):- Rheological properties of asphalt treated with spent lubricating oils at 180°C in the presence of 1% by weight of sulfur at (1,2 and 3) hours.

Sample No.	Time (Hour)	Spent lubricatiuy oils %	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	--	--	56	38	+100	-0.428
As31	1	4	52	48	+100	-0.805
As32	2	4	54	40	+100	-0.749
As33	3	4	57	36	+100	-0.336
As34	1	5	51	57	+100	-0.643
As35	2	5	55	40	+100	-0.531
As36	3	5	58	35	+100	-0.193
As37	1	6	51	62	+100	-0.433
As38	2	6	52	53	+100	-0.574
As39	3	6	55	38	+100	-0.641
As40	1	7	48	75	+100	-0.725
As41	2	7	49	55	+100	-1.234
As42	3	7	51	43	+100	-1.283
As43	1	8	42	75	+100	-2.544
As44	2	8	47	68	+100	-1.261
As45	3	8	50	40	+100	-1.671

Table (4):- Rheological properties of asphalt treated with spent lubricating oils at 180°C in the presence of (0.25%) of (AlCl₃), and 1% by weight of sulphur at (1,2 and 3) hours.

Sample No.	Time (Hour)	Spent lubricatiuy oils %	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	--	--	56	38	+100	-0.428
As46	1	4	57	56	+100	0.696
As47	2	4	58	50	+100	0.621
As48	3	4	57	46	+100	0.210
As49	1	5	50	49	+100	-1.242
As50	2	5	51	41	+100	-1.382
As51	3	5	53	45	+100	-0.717
As52	1	6	49	49	+100	-1.493
As53	2	6	50	47	85	-1.334
As54	3	6	55	38	94	-0.641
As55	1	7	46	58	+100	-1.921
As56	2	7	48	55	+100	-1.495
As57	3	7	52	44	63	-0.998
As58	1	8	47	66	+100	-1.336
As59	2	8	50	60	60	-0.768
As60	3	8	53	49	89	-0.523

3.1.2 Long Curing Aging

It is evident from both tables that the treatment of asphalt with the spent lubricating oils and in both paths resulted an obtaining asphalt samples with a good to excellent rheological properties with the exception of a few samples in which the ductility values fell below +100. This reinforces what we have said that the interaction between the components of the medium is at a high degree of perfection and homogeneity, because both materials were derived from one substance, which is oil, which led to these excellent results.

The selection process of the samples resistance to its aging conditions is one of the most important things that must be taken into account and that must be studied and determined with regard to asphalt axis. The asphalt suffers from a change in its properties after a period has passed from its exposure to weather factors, as exposure to the asphalt leads to the oxidation reactions, which take place with the mechanism of free radicals, which is leads to an increase in the asphalt hardness. The aging was studied in this study by leaving the asphalt samples for

a period of 12 months and then returning the same measurements that were made on the original asphalt

and the modified asphalt before aging. Tables (5-8) illustrate the results obtained.

Table (5):- Rheological properties of asphalt treated with (PVA) at 180°C in the precede of 1% by weight of sulfur at (1,2 and 3) hours after aging for 12 months.

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	--	--	60	35	100+	0.199
As1	1	0.125	61	38	100+	0.583
As2	2	0.125	62	28	100+	0.146
As3	3	0.125	61	25	100+	-0.217
As4	1	0.250	62	27	100+	0.037
As5	2	0.250	63	28	100+	0.289
As6	3	0.250	60	25	90	-0.476
As7	1	0.500	60	30	94	-0.122
As8	2	0.500	63	30	100+	0.430
As9	3	0.500	60	24	74	0.552-
As10	1	0.750	63	30	100+	0.430
As11	2	0.750	60	25	100+	-0.122
As12	3	0.750	62	25	55	0.112-
As13	1	1.000	65	27	100+	0.564
As14	2	1.000	61	25	94	-0.217
As15	3	1.000	66	20	26	0.156

Table (6):- Rheological proportions of asphalt treated with (PVA) at 180°C in the presence of 0.25% of AlCl₃ and 1% by weight of sulfur at (1,2 and 3) hours after aging for 12 months.

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	--	--	60	35	100+	0.199
As16	1	0.125	58	28	100+	-0.642
As17	2	0.125	60	25	100+	-0.476
As18	3	0.125	60	25	66	-0.476
As19	1	0.250	59	30	61	-0.313
As20	2	0.250	58	28	84	0.642-
As21	3	0.250	60	26	36	-0.476
As22	1	0.500	60	22	91	-0.630
As23	2	0.500	61	30	50	0.065
As24	3	0.500	62	25	52	-0.112
As25	1	0.750	63	25	43	0.065
As26	2	0.750	62	28	90	0.147
As27	3	0.750	61	27	51	-0.144
As28	1	1.000	60	28	56	-0.231
As29	2	1.000	61	25	42	-0.217
As30	3	1.000	69	26	39	-0.476

Table (7):- Rheological properties of asphalt treated with spent lubricaty oils of 180 °C in the presence of 1% by weight of sulfur at (1, 2 and 3) hours after aging for 12 months.

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	0		60	35	100+	0.199
As31	1	4	53	45	100+	-0.717
As32	2	4	56	38	100+	-0.220
As33	3	4	59	35	100+	0.004
As34	1	5	52	55	100+	-0.998
As35	2	5	56	38	100+	-0.220
As36	3	5	60	33	100+	0.073
As37	1	6	53	58	100+	-0.574
As38	2	6	53	50	100+	-0.409
As39	3	6	56	35	100+	-0.601
As40	1	7	51	66	89	-0.433
As41	2	7	51	50	96	0.951-

As42	3	7	53	40	100+	-0.962
As43	1	8	44	70	79	2.140
As44	2	8	50	63	81	-0.768
As45	3	8	51	38	100+	-1.382

Table (8):- Rheological properties of asphalt treated with spent lubricating oils in the precentor (0.25)% of $AlCl_3$ and 1% by weight of sulfur of (1, 2 and 3) hours after aging for 12 months.

Sample No.	Time (Hour)	PVA (Wt.%)	Softening Point (°C)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Penetration Index (PI)
As0	0		60	35	100+	0.199
As46	1	4	60	50	100+	1.028
As47	2	4	60	46	100+	0.823
As48	3	4	60	42	95	0.606
As49	1	5	52	48	100+	-0.805
As50	2	5	52	40	100+	1.200-
As51	3	5	55	42	100+	-0.312
As52	1	6	51	48	100+	-1.045
As53	2	6	52	44	80	-0.998
As54	3	6	56	35	90	-0.601
As55	1	7	49	55	100+	-1.234
As56	2	7	50	52	100+	-1.144
As57	3	7	55	40	60	-0.531
As58	1	8	50	60	100+	-0.768
As59	2	8	52	55	50	-0.487
As60	3	8	55	44	86	-0.269

3.1.3 Synergetic for Long Curing Aging Composites

The aging test was also conducted for some sample using a thin-film furnace, and the test was carried out according to the American standard specifications (ASTM, D1754-97R2002) [22-23]; and as shown in Table (9).

We note from the tables that the degree to which the modified samples are affected with aging and in comparison with the long time is good. This gives us evidence that the resistance of the modified samples to stress is good and that the occurrence of cracks is less and this is due to the fact that the additives used in the modification worked to improve the mechanical properties for asphalt, represented by increasing the durability of samples and reducing thermal cracking [27-28], especially in the case of the spent lubricating oils.

The fact that the asphalt is not affected by weather factors qualifies it for use in the field of paving. In order to know the suitability of asphalt sample for paving purposes, the Marshall Asphalt Paving Examination was carried out. This examination gives an indication of the suitability of asphalt for paving by applying pressure on the sample to be tested, and when the model begins to deform, the stability and flow measurements are taken through certain gradients present in the device. Stability is defined as the ability of the asphalt mixture to resist deformation resulting

from road exposure to repeated loads of different transportation modes, as stability depends on internal friction and cohesion. As for creep, it can be defined as the amount of vertical deformation in the Marshall model now of failure. As the high values of the creep rate give an indication that the asphalt mix is more plastic, which fails in what is known as permanent deformation. As for the low values, they give an indication that the mixture contains few voids that lead to the appearance of primary cracks. In our study, the Marshall's examination of the original sample was conducted, as well as some modified samples that were in conformity with the specifications of the Iraqi Roads and Bridges Authority (S.C.R.B) [29-32].

We note the high stability values of the modified models, and this is a good indication of the ability of the tiling to resist the deformation resulting from the road exposure to the repeated loads of the means of transport. We notice a lower value of flow (Flow) than what it is in the original asphalt, which makes it more resistant and stable to rattle (crawl) when the road is exposed to repeated loads of transportation media, and this gives an indication that the mixture has a small void ratio. Tables (11) illustrate the standard properties for asphalt used in several fields.

Table (9):- Rheological properties of some asphalt before and after subjecting to the furnace test of Thin Asphalt Films (TFOT).

Samples No.	Rheological Properties	Units	Before Examination	After Examination
AS0	Ductility	Cm.25°C	100+	100+
	Softening point	°C	56	59
	Penetration	(100gm.5sec.25°C)	38	36
	Weight loss	%	-----	0.04
AS1	Ductility	Cm.25°C	100+	100+
	Softening point	°C	57	58
	Penetration	(100gm.5sec.25°C)	40	39
	Weight loss	%	-----	0.025
AS16	Ductility	Cm.25°C	100+	100+
	Softening point	°C	56	58
	Penetration	(100gm.5sec.25°C)	30	28
	Weight loss	%	-----	0.03
AS31	Ductility	Cm.25°C	100+	100+
	Softening point	°C	52	54
	Penetration	(100gm.5sec.25°C)	48	46
	Weight loss	%	-----	0.035

Table (10):- Marshall Test records.

Samples No.	Asphalt (%)	Marshall Test		
		Stability (KN)	Flow(mm)	MQ
AS0	4.5	12.3	4.9	2.5
AS1		15.9	3.1	5.1
AS16		16.3	2.8	5.8
AS31		16.5	3.6	4.6
AS46		17.6	3.1	5.7
AS*		7 Minm.	2-4	3.5Minm.

Table (11):- American Standard Specifications (41-D491) ASTM for asphalt used to produce mastic (29).

Rheological measurements	Minimum	Maximum
Softening point(C°)	54	65
Penetration (100 gm mm,5 sec, 25° m)	20	40
Ductility (Cm.25°C)	15	0

3. Conclusion

We conclude from this study the following:

1. Modification of asphalt with polymeric materials is a good process to obtain asphalt with good rheological properties.
2. Spent lubricating oils gave a high-consistency asphalt samples.
3. The modified samples had good firing resistance to aging factor.
4. It was clear that the additives have positive impact on bitumen physical properties, and highly recommended to be used in in countries with high temperatures..

4. Conflict of interest

There is no conflict of interest.

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