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Research Paper

# High Temperature Behavior of Asphalt Mixture with Bitumen Modified by Polyphosphoric Acid Polymers and Rubber Powder

Sajad Chavoshi Najafabadi[1], Mohammad Mehdi Khabiri[2,*], Hamed Khani Sanij[3]

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## Abstract
The main purpose of this study was to determine the effect of adding polyphosphoric acid (PPA) and rubber powder (CR) on the modification of bitumen properties and also to evaluate the asphalt mixture made of modified bitumen. In addition to the usual tests of new bitumen, a variety of standard tests of strength and modulus of elasticity were performed on the asphalt mixture at high temperatures. The results showed that the addition of PPA improved the performance of bitumen at high temperatures and also reduced the effects of aging in the sample and the addition of rubber powder also improved the performance in the entire operating temperature range of bitumen. The combination of these two additives has also succeeded in reducing the bitumen sensitivity to temperature and aging and also increasing the bitumen resistance to common damages at high temperatures. The combination of these two additives was also able to improve the performance grading of bitumen (PG) to 4 categories without having much effect on the performance of bitumen at different temperatures. In order to investigate the microstructural changes in the samples after modification with rubber powder and polyphosphoric acid, the morphology of the samples was performed by scanning electron microscopy and the uniformity and integrity of the modifiers with bitumen was revealed. Marshall Resistance in modified and average samples increased by 15% compared to unmodified samples and also the modulus of resistance in modified samples increased by 24% on average compared to control samples.
**Keywords:** Modified Bitumen, Polyphosphoric Acid, Rubber Powder, High Temperature Behavior, Asphalt Mix

* Corresponding author. E-mail: Mkhabiri@yazd.ac.ir
[1] Master of science., Road and Transportation Eng., Civil Engineering Department, Yazd University, Yazd, Iran
[2] Associate Prof., Road and Transportation Eng., Civil Engineering Department, Yazd University, Yazd, Iran
[3] Associate Prof., Road and Transportation Eng., Civil Engineering Department, Yazd University, Yazd, Iran

# 1. Introduction

One of the important challenges in pavements is a bitumen with optimal performance against different thermal conditions [Erkuş et. al; 2020]. One of the ways to achieve such a bitumen is modifying it using different additives. Although the weight of bitumen occupies a negligent percent of asphalt mixture, it has attracted the attention of considerable number of studies and sources to itself considering its important and effective role. Nowadays, many researchers have accepted that asphalt mixture resistance against fatigue and rutting depend on the properties of the bitumen used in it. For example [Goli,et.al.,2018, Gómez et. al; 2021], cracking out of fatigue usually stars from bitumen and then expanded [Ziari, Ameri, and Khabiri, 2007].

Rubber powder has been widely used in asphalt mixtures in 1975 and then modified bitumen by rubber defined in "American Society for Testing and Materials" (ASTM D8) and then defined in "ASTM D6114-97" and published. Moreover, federal law of the US called "Integrating Efficiency of Transportation Land Systems" was approved (then it was cancelled) when asphalt-rubber technology was popular [Kuennen,2004].

When applying bitumen modifiers was expanded, some of bitumen additives weak points were recognized such as instability against heat and also some polymers being diphasic. Attempts have been made to remove bitumen additives weak points since 1990. Giavarini and colleagues (2016) maintained that adding polyphosphoric acid polymers to bitumen is used to prove it and also it increases bitumen stability for storage [Giavarini, 2016].

Alfaki and Tabatabai (2009) searched for an instruction to modify bitumen exiting in Iran for different weathers, so seven different samples of bitumen have been prepared from different factories and were modified by adding some different additives to them. The results showed that using polyphosphoric acid improves bitumen behavior both at low and medium temperature and at high temperature. Also they mentioned that among all additives which have been used, polyphosphoric acid can reduce lifecycle and increases bitumen stability and durability [Alfaki and Tabatabai , 2019].

Yan and colleagues (2013) investigated the effect of polyphosphoric acid on the physical properties, chemical compounds and morphology of bitumen and they also considered that Poly Phosphoric Acid (PPA) effect on different bitumen depends on the source of crude oil. The samples observed high interaction between bitumen and PPA which increased viscosity and asphaltene in them and reduced resin [Yan et. al., 2013].

Faxina (2015) studied the effect of PPA on different bitumen with different oil sources because they considered PPA effect mechanism highly dependent on bitumen basic compounds. The results showed that adding different values to the samples increases bitumen Performance Grade (PG) at high temperature, but this change depends on crude oil source [Faxina, et.al. 2015].

White (2016) mentioned that bitumen is widely modified by acid especially by PPA in Australia. They used acid to reduce bitumen sensitivity to viscosity due to temporal changes. Also they maintained that the biggest problem in modifying bitumen by PPA is not understanding bitumen chemical modification process [white, 2016].

Varanda (2016) stared studies aimed at investigating the effect of PPA on the chemical properties of bitumen and its effect mechanism on bitumen structure. The samples were evaluated before and after modification by PPA by chemical experiments such as SARA Test, elemental analysis and some other tests and also they were investigated by standard tests like softening point and permeability. SARA Test results showed that generally, modifying bitumen by PPA increases asphaltene effective value and decreases resins and bitumen saturated oils which these changes improve bitumen performance properties such as permeability index which is demonstrative of bitumen compounds thermal stability modified by PPA [Varanda, et. al., 2016].

Lio and colleagues (2016) conducted a study aimed at investigating the rheological and morphological properties of warm mix asphalt containing PPA and so they used superpave test and also microscopic tests to measure PPA effect on warm mix asphalt. Four different levels of PPA (0.5%, 1.0%, 1.5% and 2.0%) added to it to modify bitumen behavior and its effect was studied. The experiments showed that adding PPA to bitumen increases viscosity at all temperatures and the results of temperature sweep test showed that bitumen containing PPA has better performance rather than the unmodified bitumen and increasing PPA also increases complex module (G*) and also decreases phase angle (δ), bitumen containing 1.5% PPA had the best performance. Also the effect of crude oil source and also aggregates needs more investigation [Lio et. al., 2016].

Huang and colleagues (2016) considering the fact that adding PPA hardens bitumen studied its effect on the process of bitumen aging. So 1.0% PPA added to bitumen and then aging process conducted on them as well as control bitumen during different times in Pressure Aging Vessel (PAV) and they were evaluated after each stage. Oxygen and carbonyl were less in the sample containing PPA rather than control sample after aging process, this shows that PPA in bitumen not only does not accelerate aging process, but also it seems that it decelerates oxidation. Also bitumen modified by PPA had more value and less hardness compared with control bitumen at low temperature which shows that modified bitumen is more flexible at low temperature and will be less exposed to cracking. Also the results related to modified recycled bitumen showed that they can be used as antiaging factor to naturally reduce using rejuvenating [Huong et.al. 2016].

Khodadadi and colleagues (2017) investigated the effect of adding PPA on the strength of asphalt pavement against rutting. Improved resistance against rutting tested based on super pave instructions and PPA added to bitumen at three levels (0.5%, 1.0% and 1.5%). Investigating rutting ration compared with modified bitumen showed that all modified samples have become resistant against rutting. Although PPA is considered an expensive polymer, considering that a little value of it is needed to modify bitumen, using it is economical [Khodadadi et. al.2017].

Lio and colleagues (2018) evaluated PPA as a very useful additive which represents good compatibility with asphalt and also it has a proven effect on the rheological properties of bitumen and asphalt mixture. In this study also the effect of PPA has been investigated on properties and reaction to creeping in basic bitumen and also bitumen containing Styrene-Butadiene Rubber (SBR) and Styrene-Butadiene Styrene (SBS) and also asphalt mixtures at different temperatures by several tests. The results showed that adding PPA to all samples reduces creep hardness slightly which means bitumen flexibility increase at low temperatures but this process is reverse after aging process. Also PPA at medium temperatures increases resistance against cracking and improved samples viscoelastic properties. Therefore, adding PPA may influence negatively bitumen performance at low temperatures slightly but its effect besides SBR and SBS polymers evaluated very useful [Lio et.al. 2018].

Valentin and colleagues (2014) investigated the effect of different rubber powder production methods and also the size of particles on the performance of bitumen. Between 10% and 20% of rubber powder which has been achieved through different methods added to bitumen with and without additives and evaluated by normal and also performance tests. The results showed that all rubber powder with every characteristics improve the performance of bitumen. Generally, modifying bitumen by rubber powder mainly depends on the size of particles and how it is produced does not matter. Rubber particles larger than 0.5 mm represent their elasticity and resistance against rutting well but they are produced with difficulty. Fine particles smaller than 0.5 mm have less viscosity at very high temperature (150°C) rather than coarser ones and this is important for the process. The main problem with rubber powder instability in storage that none of the additives which have been used in this study had no effect on improving it [Valentin et.al.2014)].

Xiao and colleagues (2014) studied rheological properties of bitumen modified by four types of polymer which were investigated once with adding 0.5% PPA and another time without PPA. These four polymers consisted of: SBS, oxidized polyethylene, propylene-maleic anhydride and rubber powder (mesh size 40). In addition to bitumen performance normal tests, Linear Amplitude Sweep (LAS) test, creep and creep recovery and rest spectrum. The results showed that among the above compounds, the most level of viscosity related to rubber powder compound as well as PPA and it showed that adding 0.5 PPA may decrease the use of polymers to 1.0%. Also the effect of polymers and PPA was described based on $G^*/\sin\delta$ value dependent on bitumen basic crude oil compounds [Xiao et. al., 2014]

Zhou and colleagues (2016) compared some types of polymer added to rubber bitumen with each other and understood that PPA influenced better and it showed better elasticity and rheological properties rather than other additives regardless of the type of basic bitumen. This study is conducted by combining five types of polymer with modified bitumen by 7.0%rubber powder that three type of basic bitumen have been used for that and oxidized polyethylene, propylene-maleic anhydride, PPA, ethylene butyl acrylate glycidyl methacrylate terpolymer and butadiene styrene are polymers used in this study. This study showed that rubber bitumen combined with PPA has larger complex shear module rather than other additives. Also PPA reduced phase angle and shows more elasticity properties. Results have been estimated equal for both laboratory and field compounds in this study [Zhou et.al. 2016].

Waqua and colleagues (2016) experimented a set of modified and simple bitumen to achieve bitumen with very high hardness and to produce asphalt mixture with High Modulus Asphalt Concrete (HMAC). It consisted of very hard bitumen with low permeability and PPA (30/45+1.0%PPA) and its combination with rubber powder (30/45+15%CR+1.0%PPA) were among researchers' options and they evaluated samples' hardness, sensitivity against moisture and also complex shear module. They understood that it is possible to use PPA compound as well as rubber powder to produce multi-grade binder. The results demonstrate that all samples enjoy high elastic rebound and also MSCR test results showed that the best bitumen sample contains PPA, especially when it has been combined with rubber powder. Results out of DSR device were also similar that bitumen containing PPA had the best performance, especially when it is combined with rubber powder [Waqua et.al.2016].

Behnoud and Oulek (2017) studied bitumen rheological properties as a result of adding three types of different bitumen modifiers including: PPA, rubber powder and SBS. It has been observed that all three additives improved bitumen high temperatures properties and also they increased hardness and elasticity property in basic bitumen. PPA and rubber powder did not influence bitumen properties at medium temperatures and no significant effect observed on bitumen at low temperature although PPA increases "m-value" in BBR and SBS test, so SBS performance is evaluated negative at low temperature. But rubber powder influenced bitumen properties significantly at low temperature. Main curves in this study showed that these three additives generally could increase bitumen hardness and meanwhile decreases bitumen fragility [Behnoud, Oulek, 2017].

Huang and Zhou (2017) conducted a study aimed at measuring Binder Bond Strength (BBS) considering that contacting with moisture is one of the most common problems in asphalt mixtures and stability between bitumen and aggregate is considered as vital factor for resistance against moisture. Therefore, the performance of some bitumen modifiers including SBS, rubber powder, polyethylene with high density, PPA, gilsonite, Ethylene-Bis Stearamide wax (EBS) on bitumen bond strength was measured. The results showed that gilsonite, heavy polyethylene and PPA could increase bitumen bond, SBS did not effect this matter positively but they reduced bitumen bond in low values and other additives influence this matter negatively and also PPA optimal vale has been announced 0.4% to improve bond strength [Huang , Zhou 201)].

Lio and colleagues (2018) investigated the effect of some polymers and PPA on bitumen resistance against ageing. Therefore, two basic bitumen, three types of polymer (oxidized polyethylene, propylene maleic-anhydride and SBS), 10% rubber powder and 0.5% PPA selected as bitumen modifier. One group of samples were only modified by 3.0% of polymers and another group by 2.0% polymer as well as 0.5% PPA aimed at replacing 1.0% polymer with 0.5% PPA that the results showed the possibility of this matter. $G^*.\sin\delta$ values related to samples showed that PPA can improve bitumen performance against fatigue as a result of Pressure Aging Vessel (PAV) but basic bitumen compounds effect on this process must not be ignored. Samples containing 0.5% PPA showed more elasticity properties rather than those which were modified only by 3.0% polymer and polymer and PPA combination represent very good elasticity properties. Also adding 0.5% PPA may improve bitumen performance slightly at low temperature and also it has been said that it is possible to use PPA as an alternative for SBS in specific values [Lio et.al. 2018].

Considering the effect of PPA on bitumen, scientists soon understood that combing polymer with PPA causes synergy on expected mechanical properties and improve them specifically [Orange, et.al. 2018].

Synergy is systems is defined as when two or some factors are interacted or reacted with each other, an effect is usually made, now if this effect be more than all effects that each of them could be made separately, synergy has been happened. Using rubber powder and PPA seem a good option to achieve considered properties in pavement. The combination of these two additives has been studied limitedly in some studies that they have been referred to in studies. The results showed that investigating the effects of these two additives on bitumen more accurately and comprehensively is valuable and so the effects of each of additives was measured on bitumen and then the combination of these two additives was investigated dynamically by different tests. Finally, representing an applied model to use additive optimally and identifying their effect on pavement experimental performance are among the most important objectives of his study in pavement industry. The objective of this paper is to article and discuss how PPA affects high temperature behavior of asphalt mixture performance. The principal aim of the present research was to explore the influence of Rubber Powder and PPA additives, on the high temperature behavior of asphalt samples.

## 2. Materials and Methods

### 2.1. Bitumen

Bitumen (85-100) PG 58-22 which has been produced in Jey Oil Refining Company used in this study. The basis to choose bitumen with high permeability (lower viscosity) was to modify bitumen with lower quality rather than common ones. Although there is no difference in bitumen cost in Iran, over time and with the increase of exporting this product, the economical use of substituent materials (such as a combination of bitumen + vacuum batuum 1) as well as additives to modify it will be obvious. Table 1 shows the physical characteristics of bitumen used in this study.

## 2.2. Rubber Powder

Rubber powder used in this study prepared by Yazd Rubber Industry Association. The gradation size has been recognized mesh 40# considering the previous national and international studies and also previous experiments of Jey Oil Refining Company. According to the mentioned studies, four levels (6%, 12%, 18% and 24%) selected to add to bitumen. At 24% rubber powder, mixing has not been conducted correctly, even increasing mixing device ability (up to 5000 rpm) and mixing temperature more than 190°C this matter didn’t happen and investigating the sample showed that the lion’s share is rubber powder and the sample has been agglomerated, therefore, three 6%, 12% and 18% values used for that and 24% removed from this study.

**Table 1. The physical characteristics of bitumen used in this study**

| Bitumen tests | Standards | | Bitumen PG 58-22 | Unit of measurement |
|---|---|---|---|---|
| | ASTM | National | | |
| Relative density | D75 | 3873 | 1.0179 | - |
| Penetration grade | D5 | 2950 | 90 | 0.1 Millimeter |
| Softening Point | D36 | 3868 | 45.8 | Celsius |
| RV rotational viscosity | D4402 | 15434 | 0.245 | Pa.s to 135 Celsius |
| Flash point | D92 | 12860 | 332 | Celsius |
| Solubility in Trichlorethylene | D2042 | 2953 | 99.7 | Percentage |

## 2.3. Poly Phosphoric Acid (PPA)

PPA used in this study produced in Merck Company of Germany and purchased from a commercial company which prepares and distributes different chemicals. The manufacturing company has mentioned that due to specific melting range, it may be represented to the consumer in solid, liquid and or melting semi-solid. Table 3 shows the characteristics represented by the manufacturer of this product. Also figure 1 shows product packaging and its appearance.

**Table 2. The physical characteristics of rubber powder used in this study**

| Characteristics | amount | Unit |
|---|---|---|
| Moisture | 0.15 | Percentage |
| Special Weight | 0.33 | g/cm$^3$ |
| Contaminants | 0.07 | Percentage |
| Abrasion Resistance | Excellent | (ASTM D1630-06) |
| Compression Capability | Excellent | (ASTM D395-14) |


**Figure 1. Poly Phosphoric Acid (PPA)**

According to the previous studies and most researchers focusing on that the reaction of this additive is strongly dependent on crude oil source from which bitumen has been obtained and the different percentages of this additive which have been used in different studies, this study used four 0.5%, 1.0%, 1.5% and 2.0% PPA levels to modify bitumen, the reason for not using higher percentages of polymer is to avoid increasing the cost and excessive hardness of the bitumen. At the first stage, additives added to bitumen solitarily and considering the results of tests and the limitations to do experiments, PPA 0.5% was removed from combining with rubber powder regarding negligent effects on bitumen. At the second stage, two 1.5% PPA and 18% PPA selected as basis considering the better performance they represented and they were combined with other additives and were tested. Table 4 shows different levels of additives used in this study as well as their acronyms.

**Table 3. The characteristics of PPA used in this study**

| | |
|---|---|
| **Product Name** | Polyphosphoric acid |
| **Abbreviation** | PPA |
| **chemical formula** | HO[P(OH)(O)O](n)H |
| **Boiling point** | 530°C |
| **melting point** | -20°C |
| **Density (at 20 ° C)** | 2/06 g/cm$^3$ |

**Table 4. Different levels of additive used in this study**

| CR (%) / PPA (%) | 0 | 6 | 12 | 18 |
|---|---|---|---|---|
| 0 | Control | 6cr | 12cr | 18cr |
| 0.5 | 0.5 ppa | × | × | × |
| 1.0 | 1.0 ppa | × | × | 18cr+1 ppa |
| 1.5 | 1.5 ppa | 6cr+1.5 ppa | 12cr+1.5 ppa | 18cr+1.5 ppa |
| 2.0 | 2.0 ppa | × | × | 18cr+2ppa |

## 2.4. Aggregates

Broken aggregates have been used to build asphalt samples in this study, considering that gradation number 4 (known as binder 19) is the most common gradation in Iran to build asphalt pavements, this type of gradation was decided to be used for asphalt samples mix design. Table 5 shows physical characteristics of aggregates used in this study.

**Table 5. The physical characteristics of aggregates used in this**

| | | AASHTO | ASTM | |
|---|---|---|---|---|
| Maximum Abrasion by Los Angeles method (percentage) | 25 | T96 | C131 | 17 |
| Maximum water absorption of fine-grained materials | 2.0 | T84 | C128 | 1.4 |
| Maximum water absorption of coarse aggregates | 2.0 | T85 | C127 | 0.6 |
| Minimum percentage of breakage in one side (left on sieve #4) | - | - | D5821 | 100 |
| Minimum percentage of breakage in two side (left on sieve #4) | 90 | - | D5821 | 97 |
| Percentage of Lamination of aggregates | 15 | - | D4791 | 11 |
| Percentage of Elongation of aggregates | 15 | - | D4791 | 9 |

## 2.5. Preparing Bitumen and Asphalt Mixture Samples

Previous studies around the world and also experiments gained in the laboratory of Jey Oil Company [Amini, 2015] well showed that mixing duration and its temperature influence the rubber powder dissolution and consequently the performance of the ultimate product at high and low temperature significantly. Therefore, the process of bitumen modification by rubber powder was selected as; first bitumen temperature increased to 150° C and rubber powder added with 2500 rpm speed to bitumen. Then the temperature of bitumen containing rubber powder increased to 180°C and mixing operations done at 3500 rpm speed. All mixes conducted in the laboratory of Jey Oil Company and by high shear mixer.

Also investigations showed that temperature between 120°C to 140°C is the best temperature to add PPA to bitumen and 60 minutes is needed to mix PPA with bitumen. Since few studies have been conducted to investigate the effect of PPA on bitumen rather than other additives, it seems possible to propose the effect of mixing duration and also mixing temperature of PPA with bitumen measuring the performance characteristics of bitumen as a research topic.

Samples containing PPA and rubber powder heated up to 130°C and PPA added to the sample. Then temperature increased gradually and rubber powder added to the sample at 150°C and mixed for 15 minutes. Then temperature increased to 180° C and mixing took 120 minutes, the reason for choosing temperatures higher than 150°C for mixing is to provide the right flow for the two base materials. Two additives mixed at high temperature because no recommendation neither positive nor negative have been mentioned for PPA mixing conditions (neither from manufacturing company nor from the conducted studies) and no limitation found for that. It is worth mentioning that the modified bitumen used to build asphalt samples was [reared in the laboratory of Jey Oil Company and then it was transferred to pavement laboratory of Yazd University and asphalt samples were built there (Figure 2).

**Figure 2. Mixing additive and bitumen**

4.5%, 5.0%, 5.5% and 6.0% selected in this study for basic bitumen (unmodified) and three samples built for every bitumen percent. Also 4.5%, 5.0%, 5.5%, 6.0% and 6.5% selected for modified bitumen and asphalt samples were prepared. Marshall Method has been used in different studies to measure the effect of polymeric and containing additives bitumen and this accepted scientifically. Also due to the accessibility of Marshall method and also removing mixing and density conditions variables from the experiment it was decided that all samples including modified and basic ones be built under equal conditions and be measured and evaluated in similar conditions.

The most famous indicator to introduce pure bitumen in Iran National Standard is naming them based on bitumen permeability grade. This test has been conducted according to Iran National Standard code 2950 (ASTM D5–AASHTO T49) aimed at measuring the consistency of bitumen, so higher permeability shows bitumen lower consistency. This is done by measuring the length of standard needle (based on mm) which permeates into the bitumen perpendicularly in specific loading, temperature and time conditions. Also in order to use pure bitumen in pavement, its

characteristics and limits determined by Iran National Standard code 12505-1 (ASTM D946 – BS EN 12591) [ Tafti, Khabiri, Sanij, 2016].
Experiments done on Marshall Samples includes: apparent specific gravity according to AASHTO T 166 or ASTM D 2726, Marshall Stability Test which measure Marshal Strength and flow according to ASTM D1559. All preparation stages of asphalt samples through Marshall Method mentioned in Iranian National Standard code 21076. Also determining Marshall Strength and flow of asphalt mixtures we all we test method are mentioned in Iranian Standard code 21075. How the real specific weight of condensed asphalt mixtures is determined by paraffin coated samples is described in Iranian standard 10868. Although the usual method to determine real specific weight which is common in laboratories has not been standardized. Also modulus of resilience or modulus of elasticity is obtained from periodic loading with small strains through indirect elasticity and it is considered as one of the common ways to determine stress-strain curve to evaluate the elasticity properties of materials. Most materials used in pavement were not elastic and will be deformed plastically or irreversibly but if the exerted force be reduced to be negligent rather than materials strength and instead the number of load repetition periods increased, the created strain is reversible in every loading cycle and in such a state the materials can be considered elastic.
Asphalt sample built in laboratory and or field sample is loaded diametrically in this experiment which is based on standard ASTM D4123 which has been usually repeated between 100 and 200 times and its curve is depicted for every loading cycle. This is nondestructive experiment and the similar sample can be evaluated under different environmental and experimental conditions.

# 3. The Results of Bitumen and Asphalt Mixture Tests

## 3.1. The Results of Classic Tests related to Bitumen

Bitumen permeability grade test shows bitumen sample viscosity and is not able to recognize the presence of additives such as elastomers in bitumen and when bitumen viscosity is high, the standard needle is less able to permeate into bitumen sample. Figure 3 shows the changes process of permeability grade based on additives changes of this study. Combining two additives increases hardness and viscosity of bitumen and the most increase is related to sample containing 18% rubber powder as well as 1.0% PPA.
Ring and ball test determines bitumen softening point and it is the point where bitumen turns into flow from solid state and the higher is that temperature, the less sensitive is the sample to thermal changes. Figure 4 shows that adding these additives increases this temperature and PPA and rubber powder combination reduces basic bitumen thermal sensitivity doubly.
Figure 5 shows that increasing additives in this study influence bitumen performance process positively and this positive effect continues after combining these two additives.

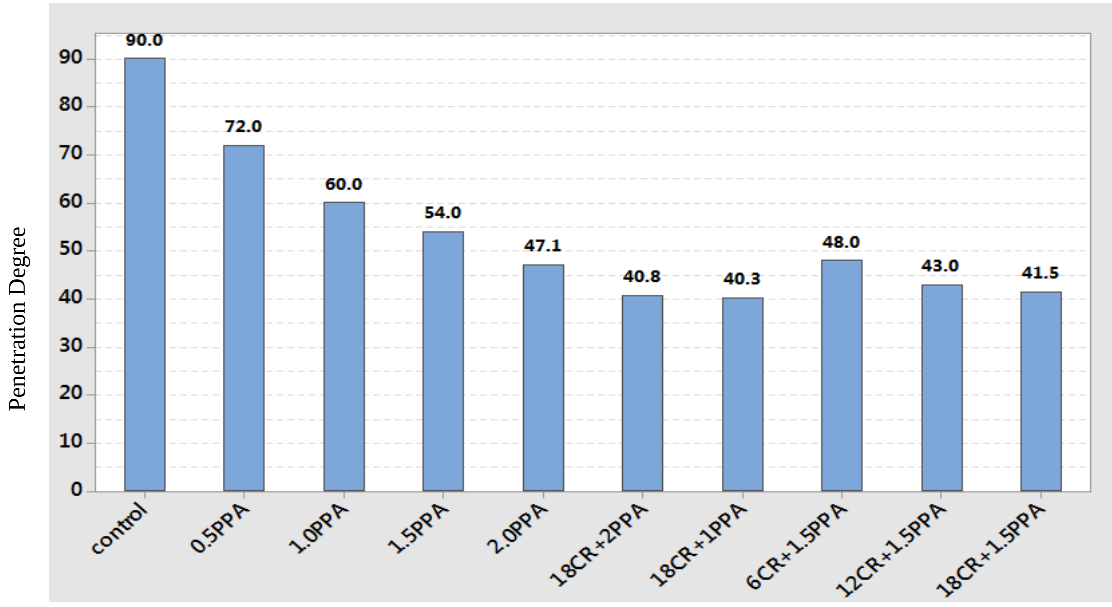



**Figure 3. Changes process of bitumen penetration grade based on different levels of additives**

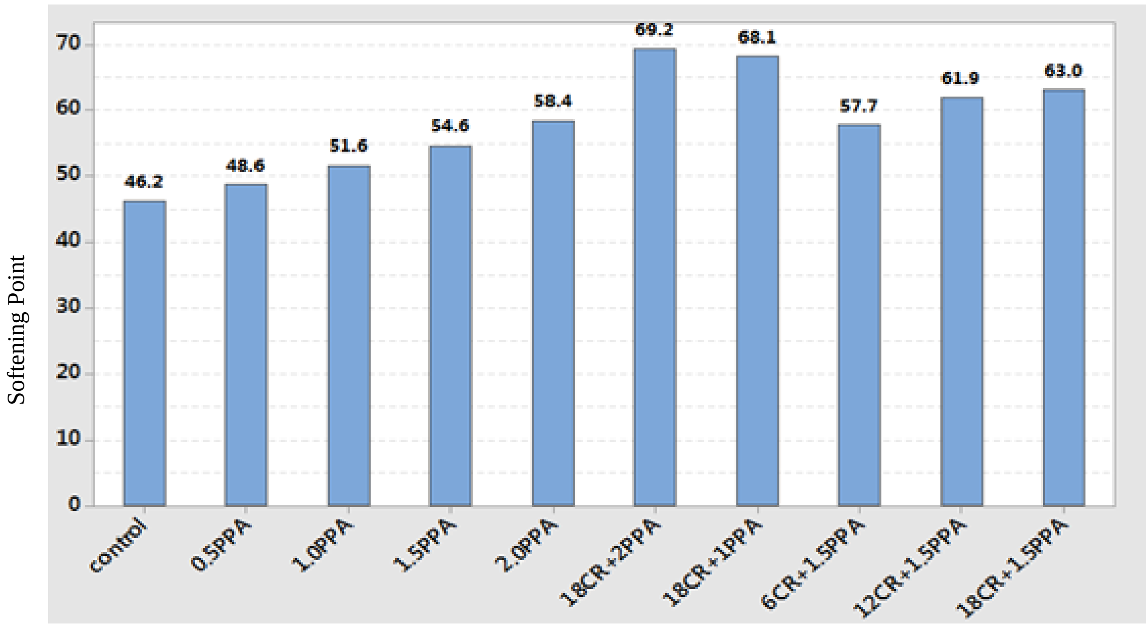



**Figure 4. Changes process of softening point based on different levels of additives**

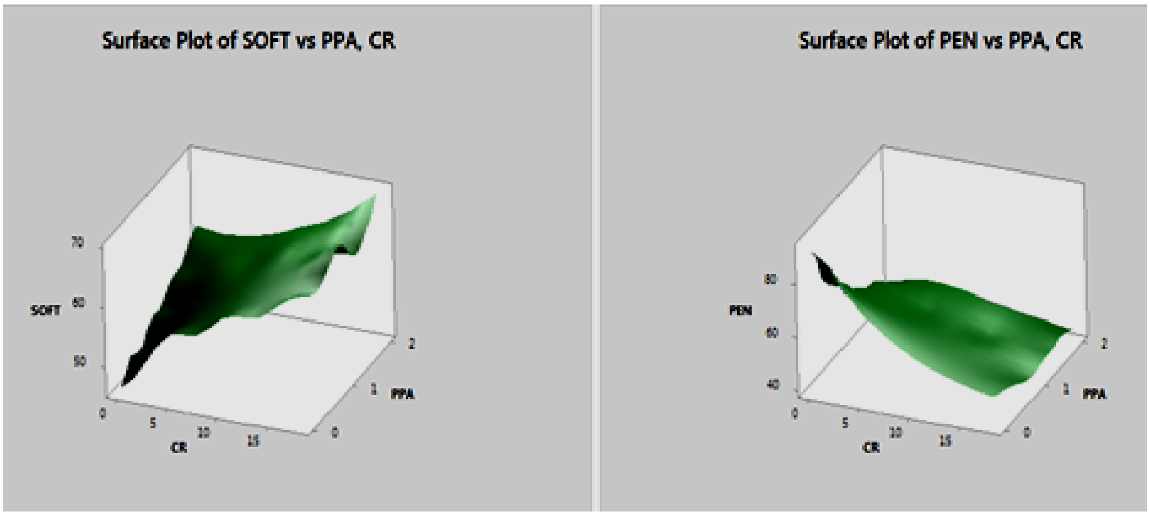



**Figure 5. Changes process of softening point and bitumen permeability grade based on additives changes**

## 3.2. Investigating the Morphological Characteristics of Modified Bitumen

Chemical mechanism during modifying bitumen by PPA still needs more research and study to be fully comprehended. Similarly new chemical mechanism and changes in the structure of bitumen are expected in combining PPA with other materials such as rubber powder to modify bitumen. Therefore, samples were considered by Scanning Electron Microscope (SEM) aiming at better studying microstructural changes of bitumen after modification. These images prepared by electron microscope (TESCAN VEGA 3) existing in the laboratory of Physics College and with 2000 times magnification. Figure 6 shows these images.

600 µ was the biggest size related to rubber powder particles used in this study and also slightly less than 75µ was the smallest size for particles which includes low percent of particles. There is no effect observed from rubber powder particles which are agglomerated in the modified samples and consistent and homogenous samples are observed. Totally, there is no problem to combine rubber powder and PPA to modify bitumen from bitumen structure perspective. Although more samples need to be evaluated to conclude

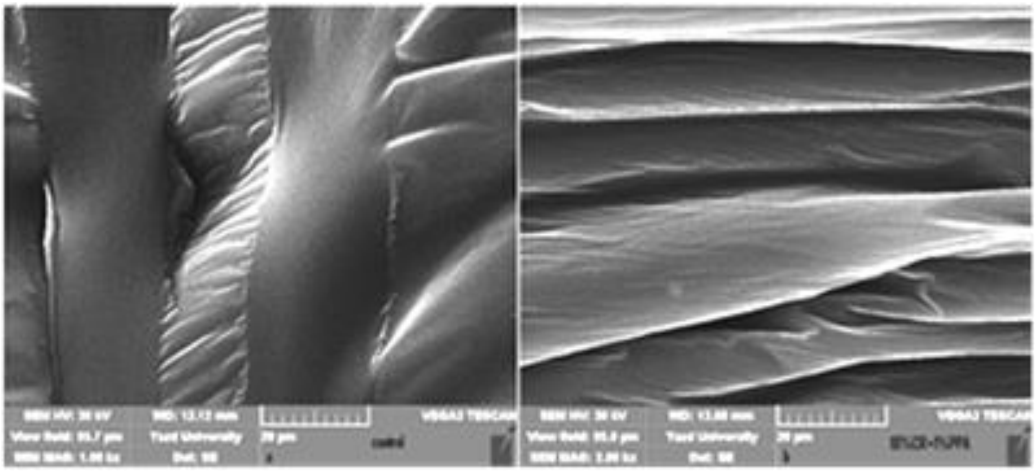


**Figure 6. SEM images from unmodified sample (left) and modified one**

### 3.3. Determining Bitumen Performance Grade at High Temperature

Bitumen rheological characteristics evaluated by DSR to determine bitumen high temperature performance grade and G*/sinδ parameter is the criterion to measure bitumen behavior at high temperature. The dynamic shear rheometer (DSR) is used to characterize the viscous and elastic performance of bitumen at standard to high temperatures. This characterization is used in the Superpave PG bitumen requirement (AASHTO T 315). As with other Superpave bitumen tests, the real temperatures estimated in the area where the bitumen will be placed control the test temperatures used. According to super pave instruction (ASTM D6373) this parameter has to be bigger than 1.0Kpa for young and old bitumen and it has to be bigger than 2.2 Kpa for bitumen samples after short-term ageing (RTFO). Figure 7 shows information related to samples and temperature which were qualified for test conditions.The important point is the effect of ageing process on samples. Basic bitumen samples and those modified by rubber powder lost performance grade a little after RTFO but samples containing PPA experienced performance improvement in some cases. Also adding PPA to rubber bitumen improves samples performance after RTFO and PPA also reduces negative effects resulted from ageing process.

Considering all results related to bitumen tests, it was recognized that bitumen containing 18% rubber powder we all as 1.0% PPA has shown good performance at all temperatures. Besides improving basic bitumen performance significantly at high temperature, this combination has not influenced basic bitumen behavior at low temperature at all. In addition to what has been mentioned, regarding the relatively high cost of PPA, its economic explanation must be considered in selecting optimal additive level. So the modified sample (18%CR+1.0%PPA) selected to build asphalt samples and comparing it with basic bitumen.

In general, the results of experiments on bitumen show that these additives improve the rheological and mechanical behavior of bitumen, which is consistent with the previous research results [Hajikarimi et al; 2019, Samieadel, & Fini; 2020].

### 3.4. Tests Results Related to Asphalt Mixtures

#### 3.4.1. Determining Asphalt Mixtures Optimal Bitumen

Marshall Mix Design used to determine optimal bitumen of asphalt mixtures and samples were built at four bitumen percent levels for unmodified bitumen and at five bitumen percent level for modified samples and they were,

Tested. Principally, increasing bitumen viscosity increases needed optimal bitumen. Although Marshall Mix Design designed for unmodified bitumen, researchers showed that [Anwar; 2014] using it for modified samples also show acceptable results. According to the results, optimal bitumen for Marshall Mix Design and for unmodified bitumen equals to 5.27% and for selected modified bitumen is 5.34%. Figure 8 shows diagrams related to two mixdesigns.

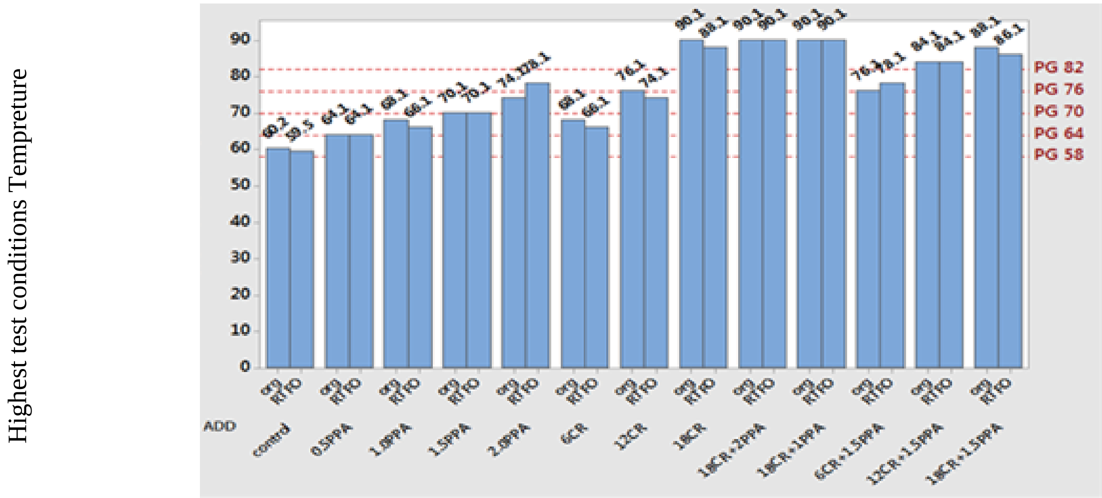



**Figure 7. The degree of performance of the samples at high temperatures**

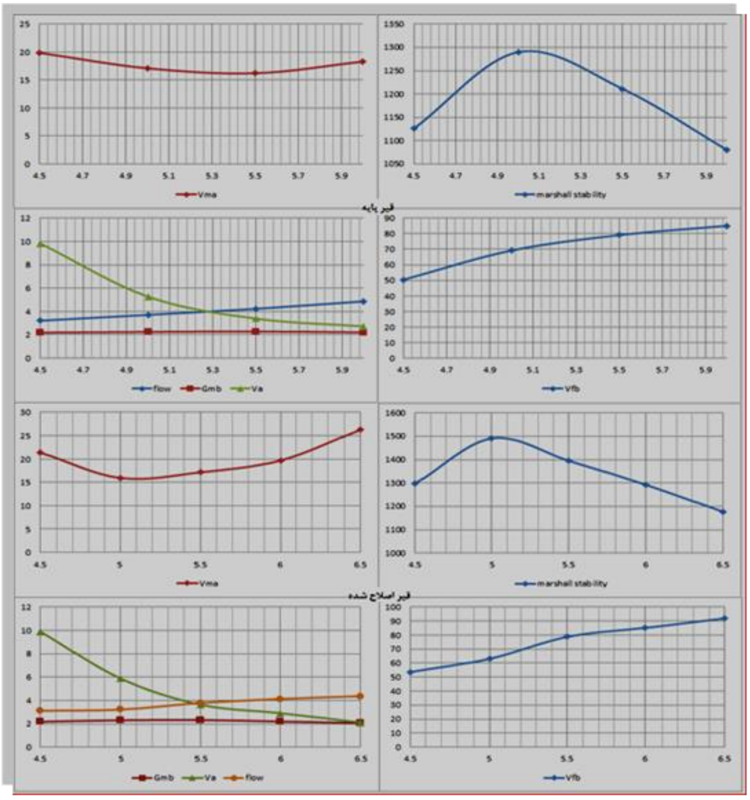



**Figure 8. Marshall mixing scheme diagrams, related to base bitumen, modified bitumen**

### 3.4.2. Marshall Stability and Strength

Compressive strength or Marshall compressive tolerance is the maximum load that sample tolerates under Marshall Experiment without permanent deformation. Marshall Strength does not suffice solely to measure asphalt sample stability and flow parameter has to be considered. Flow means asphalt sample dissolution under loading. In other words, the more is flow parameter, the more sample sensitivity increases to loading. Comparing both parameters of Marshall stability and flow related to modified and basic samples showed that modified bitumen behavior was significantly better than control sample and asphalt mixture performance has been improved at all bitumen levels. All test conditions related to samples are equal and the only influential variable is the presence of additives in sample and this improvement in behavior is due to bitumen modification.

#### 3.4.3. Results related to Asphalt Samples Modulus of Resilience (MR)

In order to measure asphalt mixtures modulus of resilience, UTM-14 device in the bitumen and asphalt laboratory of Yazd University was used. Besides measuring the effect of bitumen modification on MR in this study, the changes percent of bitumen used in samples measured on MR changes. Investigations show that all modified samples experienced MR increase regardless of the bitumen level used in them. Figure 9 shows this changes process.

Observing variables simultaneous effects diagram (figure 10) shows that modified bitumen has influenced samples MR changes process significantly (P-value=0.00). The bitumen percent used in these samples did not influence MR parameter significantly (P-value=0.269). But the process of these changes seems considerable and needs more number of samples and studies.

In general, the results of experiments show that bitumen modified with this additive improves the properties of asphalt, which is consistent with the results previous investigations [Khodadadi et al; 2017, Ma et. al 2021].

#### 3.4.4. Developing Statistical Model

Dependent variable normal distribution is one of main hypotheses of many statistical tests. Various tests such as Kolmogorov-Simonov test can be used to investigate data distribution normality and compares the distribution observed in population with hypothetical distribution. Data related to MR parameter enjoys normal distribution and figure 11 shows data normality test. Therefore, a statistical model built to predict different variables effect on dependent variable (MR). Error remained in the model also enjoys acceptable level. Although due to few number of samples, square coefficient R has been placed in medium range. Figure 12 shows diagnostic report and also model prediction strength.

Even though MR parameter changes depends on bitumen percent changes negligibly, the changes effects of this variable on response parameter has been considered in the ultimate model. Linear regression equation has been used to predict MR changes process which seems that changes process is not complicated and changes linearly. However, more experimental observation are needed to conclude more accurately and comprehensively. Figure 14 shows report related to finding optimal points and also report related to building model and finding changes process.

MR has been considered dependent variable (response) in statistical modeling that its maximum value is the most optimal state. So statistical model-which is bitumen percent used in sample and the type of mixture including modified or unmodified- tries to represent a model to identify variables effect on response and through which the most optimal method is selected. Considering the obtained model, modified models showed better performance and the best behavior has been related to sample containing 4.5% bitumen.

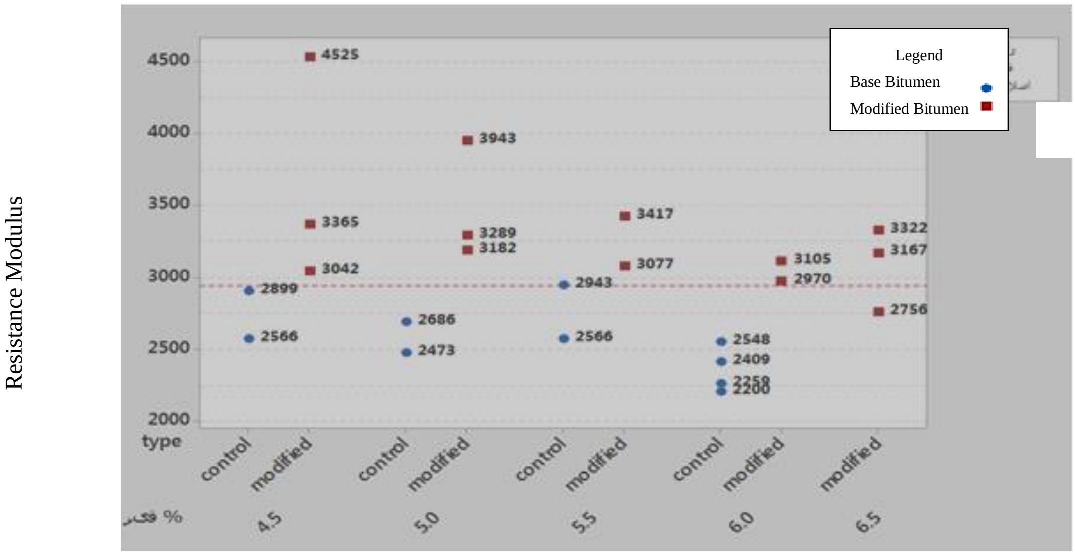



**Figure 9. Modulus of resilience (MR) values for control samples and modified samples**

Interactions for modulus of resilience

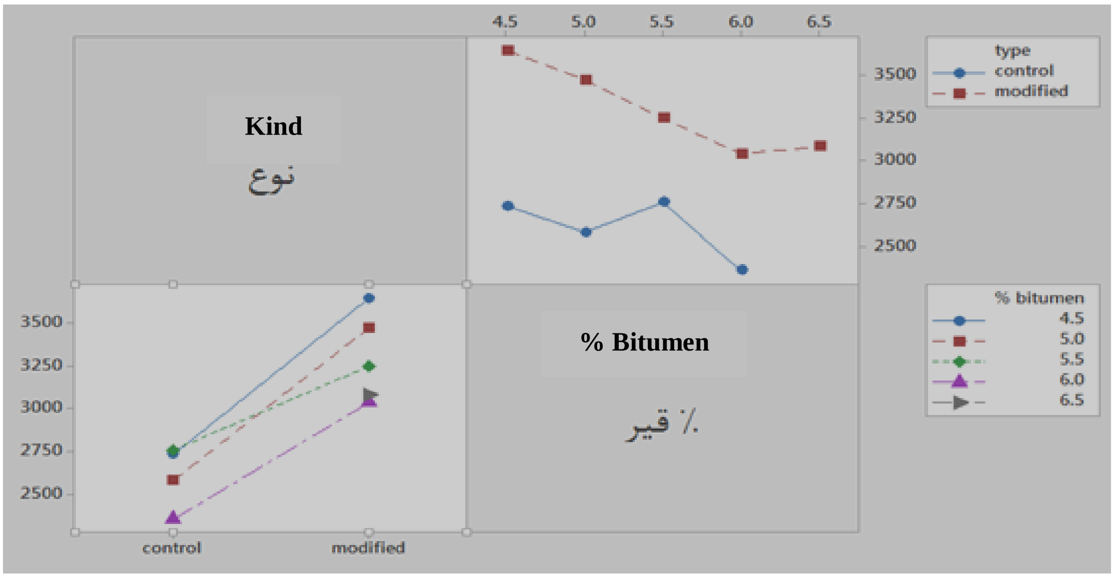



**Figure 10. Diagram of effects related to Mr parameter and test variables**

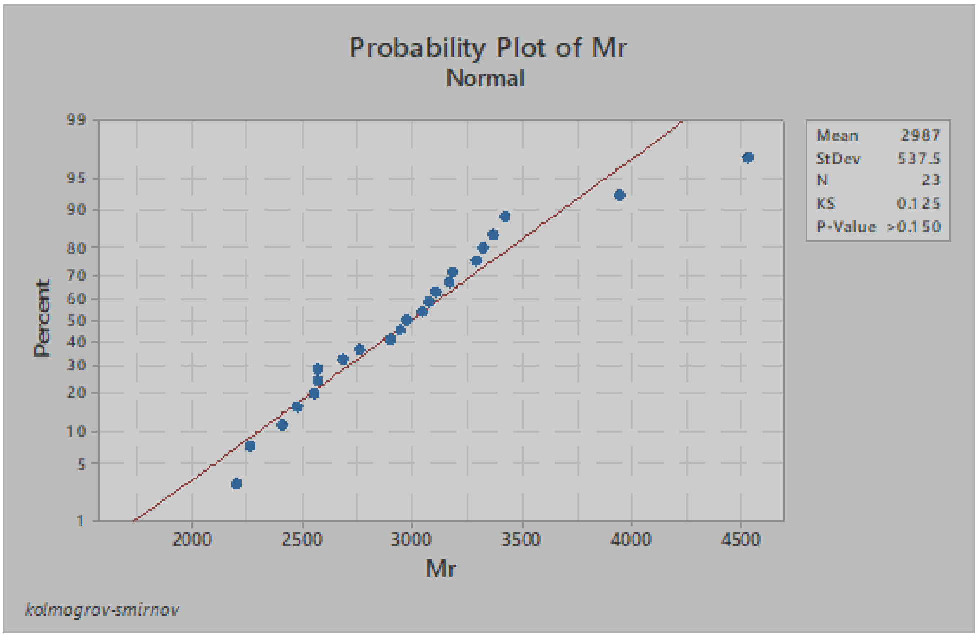



**Figure 11. Test the normality of the modulus distribution data**

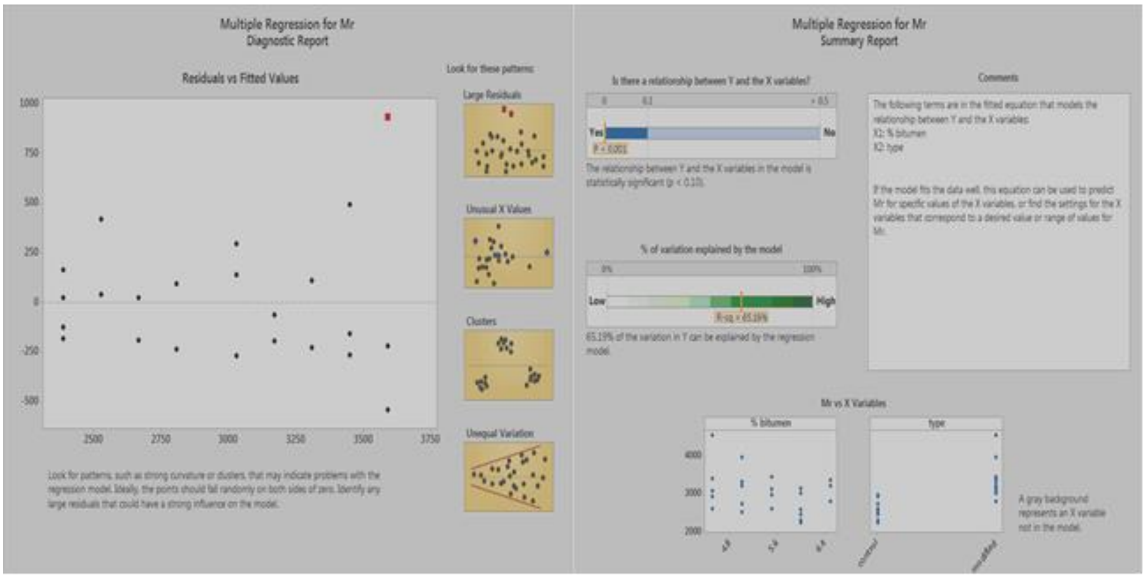



**Figure 12. Diagnostic report and report summary related to building model based on MR parameter**

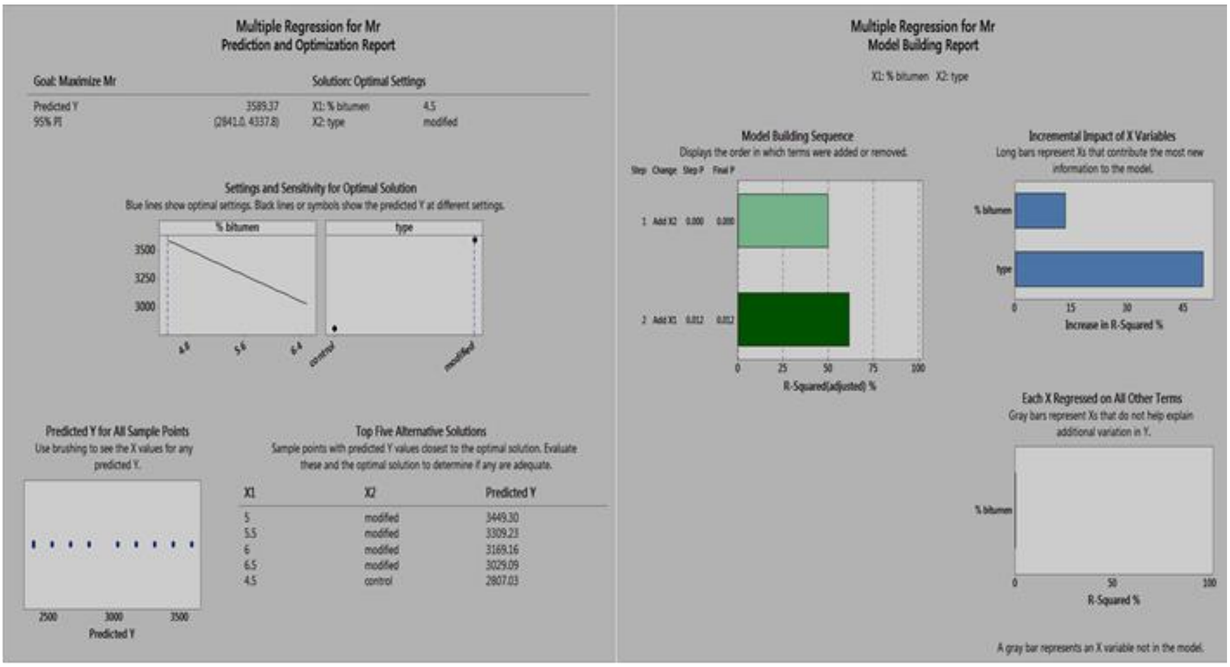
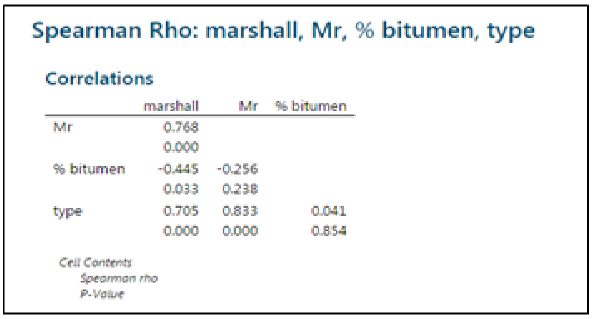



**Figure 13. Report related to optimal points and report related to building model based on MR parameter**

Also the correlation of all MR test variables measured by Marshall Stability parameter. Investigations showed that there is a significant relationship between bitumen percent changes and Marshall Stability parameter changes (P-value=0.033); However, there is a significant correlation between Marshall strength parameters and MR and increasing Marshall strength has increased MR. the type of bitumen used in the samples is the most influential parameter of this test that modifying bitumen has definitely increased MR and also Marshall strength (P-value=0.00). Figure 12 shows Spearman's rank correlation coefficient results between variables.


Spearman Rho: marshall, Mr, % bitumen, type

Correlations

| | marshall | Mr | % bitumen |
|---|---|---|---|
| Mr | 0.768 | | |
| | 0.000 | | |
| % bitumen | -0.445 | -0.256 | |
| | 0.033 | 0.238 | |
| type | 0.705 | 0.833 | 0.041 |
| | 0.000 | 0.000 | 0.854 |

Cell Contents
Spearman rho
P-Value

**Figure 14. Correlation test between some variables of asphalt samples assessment**

## 5. Conclusion

This study first investigated the effect of each of research additives on bitumen structure. The results showed that PPA and rubber powder enjoy acceptable ability to modify bitumen structure. Also combining these two additives have not influenced each other negatively and in some pints they improved bitumen performance doubly and had synergy.

1- Using rubber powder at the highest possible level (18% in this study) is permissible in bitumen sample and no negative effect observed from this additive. The determining condition for its maximum level is sample integration and proper mix.

2- Both additives of rubber powder and PPA increase bitumen softening point significantly. Both additives of this study have succeeded to reduce bitumen sensitivity to temperature and ageing and combining these two increases basic bitumen performance rate at high temperature to rate four.

3- Results related to asphalt tests showed that Marshall Stability in modified samples has increased 15% in average. Also Modulus of Resilience (MR) of modified samples has increased 24% in average compared with control samples. Combining PPA and rubber powder not only reduced asphalt mixture flow, but also increased sample strength against permanent deformation and has decreased asphalt mixtures sensitivity against temporal changes.

Recommendations such as investigating correlation between Marshall Strength and MR and representing model to determine mixed optimal bitumen or using rubber powder as a part of aggregates in asphalt mixture and modifying bitumen by PPA are represented for future studies.

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