İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF EFFECT OF BITUMEN CHEMICAL COMPOSITION, POLYMER AND WARM MIX ASPHALT ADDITIVES ON THE PROPERTIES OF BITUMEN BY USING RESPONSE SURFACE METHOD

M.Sc. THESIS

Emel BAŞKENT

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(515131008)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BİTÜM KİMYASAL İÇERİĞİ, POLİMER VE ILIK KARIŞIM ASFALT KATKILARININ BİTÜM ÖZELLİKLERİ ÜZERİNE ETKİSİNİN TEPKİ YÜZEYİ YÖNTEMİYLE İNCELENMESİ

YÜKSEK LİSANS TEZİ

Emel BAŞKENT
(515131008)

Polimer Bilimi ve Teknolojisi Ana Bilim Dalı

Polimer Bilimi ve Teknolojisi Yüksek Lisans Programı

Tez Danışmanı: Prof. Dr. Mustafa Hulusi ÖZKUL

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Emel BAŞKENT, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 515131008, successfully defended the thesis/dissertation entitled "INVESTIGATION OF EFFECT OF BITUMEN CHEMICAL COMPOSITION, POLYMER AND WARM MIX ASPHALT ADDITIVES ON THE PROPERTIES OF BITUMEN BY USING RESPONSE SURFACE METHOD", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Mustafa Hulusi ÖZKUL** İstanbul Technical University	....
Jury Members :	**Prof. Dr. Nurseli UYANIK** İstanbul Technical University	....
	Prof. Dr. Turan ÖZTURAN Boğaziçi University	....

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To my family and fiance,

FOREWORD

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Emel BAŞKENT
(Chemical Engineer)

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ABBREVIATIONS

SBS	: Styrene-Butadiene-Styrene
SARA	: Saturates-Aromatics-Resins-Asphaltenes
TLC-FID	: Thin Layer Choromatography-Flame Ionization Dedector
TS	: Turkish Standards
EN	: European Standards
ASSHTO	: American Association of State Highway and Transportation Officials
RTFOT	: Rolling Thin-Film Oven Test
DSR	: Dynamic Shear Rheometer
PAV	: Pressure Aging Vessel
BBR	: Bending Beam Rheometer
DTT	: Direct Tension Test
PMB	: Polymer Modified Bıtumen
PMA	: Polymer Modified Asphalt
HMA	: Hot Mix Asphalt
WMA	: Warm Mix Asphalt
AP	: Asphalt Pavement
Super Pave	: Superior Performance Pavement
PG	: Performance Grade
SHRP	: Strategic Highway Research Program
CCD	: Central Composite Design
RSM	: Response Surface Method

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SYMBOLS

%	: Percent
^oC	: Degree Celcius
G*	: Complex Module
MPa	: MegaPascal
cP	: CentiPoise
S	: Creep Stiffness

INVESTIGATION OF EFFECT OF BITUMEN CHEMICAL COMPOSITION, POLYMER AND WARM MIX ASPHALT ADDITIVES ON THE PROPERTIES OF BITUMEN BY USING RESPONSE SURFACE METHOD

SUMMARY

Bitumen, a binder material used in asphalt applications, is one of the important components that affects the service-life of asphalt. Bitumen chemistry, and amounts of Saturate, Aromatic, Resin, Asphaltene (SARA) fractions within the bitumen, affect the properties of both base and modified bitumen.

The desired properties of bitumen change with varying content of bitumen and purpose of application. To improve the properties and the performance while using in the asphalt mixtures usually the polymer addition is utilized. While thermoplastic elastomers are mostly preferred, plastomers such as polypropylene, ethylene vinyl acetate, and natural / synthetic rubber can also be used for the modification of bitumen. The addition of materials like Styrene-Butadien-Styrene (SBS) copolymer can simultaneously develop the durability and flexibility at high temperatures by containing the both soft and hard segments in its structure.

In addition, hot mix asphalt additives can be used to prepare bitumen-aggregate mixtures at lower temperatures in order to improve the application conditions. For this purpose, organic or chemical additives included into the bitumen, as well as processes with the foaming techniques can be used for lowering the mixing and layout temperatures.

Influence of all these additives on the properties of bitumen changes with the type and amount of additive and bitumen chemistry. An additive applied to improve the some properties of bitumen may adversely affect another feature of the bitumen and consequently asphalt. Especially when the addition of these additives together and variety in the bitumen chemistry are taken into consideration, the desired properties may not be obtained in the final product. Therefore, understanding the simultaneous effect of the variation of bitumen composition, amount of polymer and warm mix additive on the bitumen properties is aimed in this study. Experimental statistical methods were used for this purpose and the effects of independent parameters on the response functions individually and simultaneously were investigated by using Response Surface Method.

The composition of bitumen and the amount of polymer and warm mix asphalt additives were defined as independent variables in this study. Dynamic shear rheometer (DSR), Bending beam rheometer (BBR), Elastic recovery and Viscosity were determined as response functions of this system. The effects of these independent variables on the response functions were investigated by the full factorial analysis initially and then the response surface method.

In the experimental study, SARA analysis was performed on the bitumens which are in the same penetration grade and obtained from Izmit, İzmir and Batman refineries.

Furthermore, Fourier Transform Infrared Spectroscopy (FTIR), Simulated Distillation Gas Chromatography (GC-SimDis), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were performed for detailed characterization of the bitumens. Styrene-Butadiene-Styrene (SBS) tri-block copolymer and a commercial paraffin wax were used as warm mix asphalt additives for the modifications of the bitumens. FTIR, DSC and TGA analysis were carried out to determine whether these additives can be used in bitumen blends.

When the results of characterization tests and chemistry of bitumen were considered together, it can be seen that the same penetration grade bitumens may have different chemical properties and when the performance grade was determined according to TS EN 14023 standardization it may be also found different. This result shows that it cannot be achieved same performance grade by applying the same modifications to the same penetration grade bitumens which have different chemical compositions. Moreover the difference of SARA fractions in the three bitumens could not be seen in the FTIR analysis. The reason for the lower initial boiling point observed in GC-Simdis and the low temperatures at which loss of mass starts for Batman bitumen in TGA analysis are due to the light fractions of the Batman bitumen rather than the amount of saturated content. On the other hand, the high amount of aromatic and saturated structures in the bitumen decreased the glass transition temperature of Izmit bitumen.

For the characterization analysis of the additives, it has been proved that the properties of the additives are the same as those of the commercially available common ones having without extra features.

The Gaestel index (GI), one of the independent parameters, was used to define the bitumen chemistry in a single variable and examine the effect of bitumen chemistry on the response functions. The GI values of İzmit, İzmir and Batman bitumens were calculated by using the determined SARA fractions as 0.487, 0.622 and 0.988, respectively. In the experimental design matrix, 3 discrete values (0.487, 0.622, 0.988) were defined for the GI as discrete numeric variable, and 2-5%, 1-3% upper and lower limit values for the SBS and Wax, respectively, which were defined as continuous variables. Within these limits, bitumen modifications were made according to the experimental matrix designed by JMP® software and DSR, Viscosity, Elastic recovery and BBR tests which were determined as response functions of system, were carried out. Model equations were constructed with response functions of independent variables by using the data obtained from the measurements and the response surface method. Three-dimensional response surfaces and two-dimensional interaction curves are plotted by using the model data that indicates the effect of each parameter on the properties of bitumen.

For the individual analysis, all independent variables were found as significant in different degrees for DSR and BBR response functions. The increasing amount of SBS promotes the value of DSR and creep stiffness exponentially. However this increasing trend affects the creep stiffness negatively since it has the upper limit in the standard. Furthermore the bitumen composition which was defined as GI in the analysis, was an effective term on the all response functions especially for elastic recovery, viscosity and DSR properties which improve rapidly with the increasing value of GI. The higher amount of asphaltene and saturates or lower amount of resins and aromatics enhance the higher value of GI.

On the other hand, the amount of wax were determined as insignificant on the viscosity and elastic recovery properties of bitumen despite the fact that the wax is known as an organic additive for viscosity decreasing in the asphalt mixtures. This may be the result of the fact that the viscosity decreasing effect of Wax is very small, comparing with the increasing effect of the SBS and GI.

Finally, the optimum values of variables were determined by performing the simultaneous analysis of independent variables with the four response functions together within the desired performance limits. The optimization analysis showed that all variables have effects on the response functions in different degrees.

When the result of simultaneous analysis of response functions were compared to the individual analysis, there were terms added or eliminated from the model expression. Especially the GI*GI term which is important for the effect of bitumen composition on the response function was found as insignificant for DSR, Viscosity and Elastic recovery responses in simultaneous analysis. The reason for this was shown as the given limitation for the maximization of DSR and Elastic recovery and the minimization of viscosity. The optimum variable values within the given response limits are GI: 0.988, SBS: 3.2% and Wax: 3%. Tests within the scope of EN 14023 standard and asphalt tests were carried out on modified bitumen prepared in optimum values to investigate the improvement on the performance on both bitumen and asphalt properties. The performance grade of neat Batman bitumen was found to be PG 70-22 while it was determined as PG 82-16 after the modification at optimum conditions. As a result of the modification, while the high temperature performance of bitumen improves as two performance grade, the low temperature performance was affected negatively. The reason maybe that all the modified bitumen samples has the result on BBR as -16 since the addition of SBS increases the creep stiffness and although the amount of SBS is minimum (%2), the performance criterion was not achieved on -22.

As a result of the Marshall asphalt design for determining the asphalt properties, aggregate-bitumen blends had 4.8% of the unmodified bitumen, whereas it was necessary to use 6.2% of the modified bitumen. Asphalt samples prepared by using the amounts of bitumen found in design and tested on the wheel tracking test machine. The amount of rutting were found as 13% for unmodified bitumen, while in the modified bitumen this value was improved by 50% to 6.7%. Thus, the DSR, viscosity, elastic recovery and creep stiffness properties of the bitumen have been successfully modelled based on the bitumen content, amount of polymer and warm mix asphalt additives and optimum mixing ratios have been successfully determined by using the "Response Surface Method". The widespread use of experimental design methods will provide a scientific and realistic basis for the preparation of asphalt mixture formulations instead of personal experience as well as the prevention of waste of time.

BİTÜM KİMYASAL İÇERİĞİ, POLİMER VE ILIK KARIŞIM ASFALT KATKILARININ BİTÜM ÖZELLİKLERİ ÜZERİNE ETKİSİNİN TEPKİ YÜZEYİ YÖNTEMİYLE İNCELENMESİ

ÖZET

Bitüm, asfalt karışımlarında bağlayıcı olarak kullanılan ve asfaltın içeriğinde sadece %4-7 arasında değişen oranlarda kullanılmasına rağmen, asfalt karayolu performansını ve ömrünü etkileyen en önemli bileşenlerinden biridir. Bu nedenle bitümün özelliklerini etkileyen parametrelerin belirlenmesi daha uzun ömürlü karayolu kaplamaları oluşturulması ve yol yapım, bakım-onarım vb. işlemlerin maliyetlerinin düşürülmesi açısından büyük önem taşımaktadır. Bitümün bileşimi özelliğini etkileyen parametrelerin başında gelmektedir. Ancak bitüm içeriğindeki yapıların çeşitleri ve miktarları bitümün elde edildiği ham petrol çeşidi ve üretildiği süreç dahil birçok etkene bağlı olarak değişebilmektedir. Bitüm kimyasını oluşturan bu yapılar Doymuş-Aromatik-Reçine-Asfalten (DARA) olarak sınıflandırılmıştır.

Doymuşlar; genellikle (-70) ^oC civarında camsı geçiş sıcaklığına sahip oldukları için oda sıcaklığında sıvı halde bulunmaktadırlar. Hidrojen/karbon mol oranı 2'ye yakındır ve sayıca ortalama molekül ağırlıkları 600 g/mol civarındadır.

Aromatik bileşikler ise bitümün yaklaşık % 30-45'ini oluştururlar ve doymuş fraksiyonlar gibi camsı geçiş sıcaklıkları (-20) ^oC civarında olduğu için oda sıcaklığında sıvı halde bulunurlar. Aromatik halkalarla birlikte alifatik bir karbon iskeletine sahiptirler. Sayıca ortalama molekül ağırlıkları 800 g/mol civarındadır.

Oda sıcaklığında siyah katı halde olan reçine fraksiyonları ise bitüm içerisinde yaklaşık %30-45 oranında bulunurlar. 1100 g/mol sayıca ortalama molekül ağırlığına sahiptirler. Asfaltenlere oranla daha polar bir yapıya sahip olmalarına rağmen daha az yoğunlukta aromatik halka bulundurmaktadırlar.

Bitişik aromatik halkalar ve yan zincirlerden oluşan, içerisinde kükürt, oksijen, azot gibi heteroatomlar ve ağır metaller barındıran, n-alkan çözücülerde çözünmeyen asfalten fraksiyonu bitüm ağırlığının yaklaşık % 5-20'sini oluşturmaktadır. İşlenen ham petrolün özelliğine göre yapısı değişmekle beraber ağır hampetrollerden elde elde edilen bitümlerin yapısında daha fazla asfalten bulunmaktadır. Bitüme viskoz yapısını veren düşük çözünürlüğe sahip fraksiyon olarak bilinen asfaltenler oda sıcaklığında siyah toz şeklindedirler ve 200 ^oC'ye kadar herhangi bir termal geçişleri gözlemlenmemektedir. Asfaltenlerin sayıca ortalama molekül ağırlıkları ise 800-3500 g/mol civarındadır.

Değişen bitüm içeriği ve kullanım amaçlarına göre bitüm performansında aranan özellikler değişiklik göstermektedir. Bitüm özelliklerinin iyileştirilmesi ve asfalt kullanımlarındaki performansının arttırılması için ise polimer katkısı bitüm modifikasyonlarında en çok tercih edilen yöntemlerdendir. Ağırlıklı olarak termoplastik elastomerler tercih edilmekle beraber, polipropilen, etilen vinil asetat gibi plastomerler ve doğal/sentetik kauçuk malzemelerin de kullanılabildiği görülmektedir. Stiren-butadien-stiren gibi yapısındaki sert-yumuşak segmentleri birarada barındıran

polimerler bitümde istenen yüksek sıcaklıklardaki dayanıklık ve elastikiyet özelliğini eş zamanlı geliştirebilir.

Ayrıca bitümün agrega ile karıştırılması ile elde edilen sıcak karışım asfaltlarda uygulama şartlarının iyileştirilmesi amacıyla, daha düşük sıcaklıklarda bitüm-agrega karışımları hazırlanmasını sağlayan ılık karışım asfalt katkıları da kullanılabilir. Bu amaç için bitüm içeriğine eklenen organik veya kimyasal katkılar kullanılabildiği gibi, köpürtme tekniği ile de karıştırma ve serme sıcaklığını düşürmeye yönelik işlemler yapılabilir.

Tüm bu katkıların bitüm özelliklerine etkileri ise bitüm kimyasının yanında katkı maddesinin tipine ve miktarına göre değişebilir. Bir amaca yönelik uygulanan katkı maddesi bitümde ve buna bağlı olarak asfaltta başka bir özelliği olumsuz etkileyebilir. Özellikle bu katkıların bir arada kullanımı ve değişen bitüm çeşidi göz önüne alındığında elde edilen son üründe istenen özellikler bulunmayabilir. Bu sebeple, bu çalışmada bitüm bileşimindeki değişimin, polimer ve ılık karışım katkılarının bitüm özelliklerine olan etkisinin eş zamanlı olarak incelenmesi amaçlanmıştır. Bu çalışma için deneysel istatistik yöntemlerinden faydalanılmış, bağımsız parametreler ve tepki fonksiyonlarının belirlenmesi ile Tepki Yüzeyi Yöntemi kullanılarak tekli ve eşzamanlı olarak bağımsız parametrelerin tepki fonksiyonları üzerinde etkileri incelenmiştir.

Bu çalışmada bitüm kompozisyonu, polimer ve ılık karışım asfalt katkısı miktarları bağımsız değişkenler olarak tanımlanmıştır. Bitümlerin yüksek sıcaklık duyarlılığını gösteren dinamik kayma reometresi, düşük sıcaklık direncini gösteren eğme kiriş reometresi, süneklik davranışı hakkında bilgi veren elastik geri dönme miktarı ve işlenebilirliğini gösteren viskozite özellikleri de tepki fonksiyonları olarak belirlenmiştir. Bu bağımsız değişkenlerin tepki fonksiyonları üzerindeki etkileri ise öncelikle tam faktöriyel daha sonra tepki yüzeyi yöntemi ile araştırılmıştır.

Deneysel çalışmada öncelikle İzmit, İzmir ve Batman rafinerilerinden temin edilen aynı penetrasyon sınıfındaki bitümlere DARA analizi yapılmıştır. Ayrıca bitümlerin detaylı karakterizasyonu için Fourier Dönüşümlü Infrared Spektroskopisi (FTIR), Simule Distilasyon Gaz Kromatografisi (GC-SimDis), Diferansiyel Taramalı Kalorimetri (DSC) ve Termal Gravimetrik Analiz (TGA) yapılmıştır. Bitümlerin modifikasyonlarında ise Stiren-Butadien-Stiren (SBS) tri-blok kopolimer ve ılık karışım asfalt katkısı olarak yararlanılan ticari parafin wax kullanılmıştır. Bu katkı maddelerinin karakterizasyonu ve ısıl özellikleri bakımından bitüm karışımlarında kullanılabilir olduğunun belirlenebilmesi için FTIR, DSC ve TGA analizleri yapılmıştır.

Bitüm kimyası ve karakterizasyon testlerinin sonuçları bir arada değerlendirildiğinde, aynı penetrasyon sınıfı bitümlerin farklı kimyasal özellikler taşıyabileceği ve TS EN 14023 standardı kapsamında da performans sınıfı belirlendiğinde ise farklı performans sınıfında olabildiği görülmüştür. Batman bitümünün asfalten miktarının yüksek olması ile yüksek sıcaklık deformasyonuna karşı direncinin diğer bitümlere göre daha yüksek olabileceği ve buna bağlı olarak performans sınıfının da yüksek olabileceği sonucu çıkarılmıştır. Bu sonuç aynı penetrasyon sınıfında olsa da farklı kimyasal içerikteki bitümlere aynı modifikasyonlar uygulanması ile aynı performans özelliklerine ulaşılamayacağını göstermiştir. Buna ek olarak bitümlerin içeriğindeki fraksiyonların miktarlarının farklı olması FTIR analizinde görülemeyen bir parametre olarak karşımıza çıkmıştır. GC-Simdis ve TGA analizlerinde görülen ilk kaynama noktası ve kütle kaybının başladığı sıcaklıkların Batman bitümünde düşük görülmesinin sebebi içeriğinde doymuşların miktarı ile değil bu fraksiyonun taşıdığı yapıların daha kısa zincirli ve hafif yapılar olması ile ilişkilendirilmiştir. DSC analizinde görülen camsı geçiş sıcaklıklarındaki farklılık ise doymuş ve aromatik yapılarının miktarı ile ilişkilendirilmiştir. Aromatik ve doymuş yapılarının bitümde artışı camsı geçiş sıcaklığını düşürmektedir ve beklenen bu sonuç aromatik ve doymuş fraksiyonu en yüksek olan İzmit bitümünde en düşük camsı geçiş sıcaklığı olarak karşımıza çıkmıştır.

Katkı maddelerinin karakterizasyon analizlerinde ise literatür çalışmalarına konu olan aynı malzemelerin özellikleri ile kıyaslanmış, katkıların ekstra özelliklerinin bulunmadığı, ticari olarak temin edilebilir genel özelliklerdeki örnekleri ile aynı özellikte olduğu görülmüştür. Ayrıca ısıl analizler sonucunda bitüm karışımları sırasında yüksek sıcaklık ortamında malzemelerde buharlaşma veya bozunma vb. görünmeden malzemenin özelliklerini koruyarak karışımlar hazırlanabileceği belirlenmiştir.

Bağımsız değişkenlerden biri olarak tanımlanan bitüm kimyasının, bitümü oluşturan 4 fraksiyonun, tek bir değişken ile tanımlanabilmesi ve etkilerinin incelenebilmesi için Gaestel İndeks kullanılmıştır. Bulunan DARA analizi sonuçlarına göre İzmit, İzmir ve Batman bitümleri için GI değerleri sırasıyla 0.487, 0.622 ve 0.988 olarak hesaplanmıştır. Deneysel istatistik açısından oluşturulan deney tasarımı matrisinde kesikli numerik değişken olarak GI için 3 kesikli değer (0.487, 0.622, 0.988) tanımlanmış, devamlı değişkenler olan SBS miktarı ve Wax miktarı için de sırasıyla %2-5, %1-3 alt ve üst sınır değerleri tanımlanmıştır. Bu sınırlar içinde JMP® yazılımı yardımıyla tasarlanan deney matrisine göre bitüm modifikasyonları gerçekleştirilmiş, modifiye bitümlerin tepki fonksiyonları olarak belirlenen dinamik kayma reometresi, viskozite, elastik geri dönme ve eğme kiriş reometresi ölçümleri yapılmıştır. Ölçümler sonucunda elde edilen veriler ile tepki yüzeyi yöntemi kullanılarak bağımsız değişkenlerin tepki fonksiyonlarıyla model denklemleri oluşturulmuştur. Elde edilen tahmin ifadeleriyle oluşturulan 3 boyutlu tepki yüzeyleri ve 2 boyutlu eştepki eğrileri ile her parametrenin bitüm özellikleri üzerinde etkisi eşzamanlı olarak belirlenmiştir.

Bitümün yüksek sıcaklık altında uygulanan yüke karşı direncini ifade eden DSR analizinde belirlenen bağımsız değişkenlerin doğrusal etkileri olduğu görülmüştür. Buna ek olarak GI değeri ve SBS miktarının artışına bağlı olarak bitümün bu özelliğinin üstel bir şekilde iyileştirilebileceği belirlenmiştir. Diğer bir deyişle bitüm içeriğindeki asfalten ve doymuş fraksiyonlarının artışı ya da aromatik ve reçine fraksiyonlarını azalması DSR değerinin yükselmesini sağlamaktadır. 0.98 düzeltilmiş R-Kare değeri ile elde edilen model verisi ile yapılan doğrulama analizinde ise tahmin sonuçları ile ölçülen değerler oldukça yakın ve tutarlı bulunmuştur.

Viskozite ölçümlerinin sonucunda elde edilen tepki yüzeyinde ise beklenenin aksine viskozite düşürme amacıyla tercih edilen ılık karışım asfalt katkısı Wax'ın etkili olmadığı sonucu bulunmuştur. Bu çıktı aslında tepki yüzeyi yönteminin değişken parametrelerin tepki fonksiyonuna etkisini eşzamanlı olarak incelemesinin bir sonucu olarak görülmüştür. Wax teriminin viskozite fonksiyonunu düşürme etkisinin SBS ve GI değerinin viskoziteyi arttırma etkisinin yanında oldukça küçük kalması sebebiyle Wax önemli terimler arasında görülmediği sonucu çıkarılmıştır. Diğer yandan SBS ve GI değerlerinin de kendi etkileri yanı sıra etkileşimlerinin de viskozite sonucu için önemli bir parametre olduğu görülmüştür. Değişen bitüm içeriği ve SBS miktarı ile farklı viskozitelerde modifiye bitümler elde edilebileceği anlaşılmıştır.

Bitümün önemli bir özelliği olan elastik geri dönme miktarını etkileyen parametrelere bakıldığında ise viskozite ile benzer şekilde Wax miktarındaki değişimin bu özelliği değiştirmediği görülmüştür. Bitüm kimyasının ise oldukça önemli olduğu, asfalten ve doymuş oranı yüksek veya reçine ve aromatik oranı düşük bitümler kullanılarak yüksek elastik geri dönme miktarı elde edilebileceği anlaşılmıştır. Ayrıca bitüm içeriği ve SBS miktarının tek başına elastik geri dönme miktarına olan katkısının yanında bu iki değişkenin birbiri ile etkileşiminin de bu özellik üzerinde etkisi olduğu belirlenmiştir.

Sünme rijitliği ve bu özellikteki değişimin belirlendiği BBR analizinde ise denenen değişken parametrelerin tümünün etkili olduğu belirlenmiştir. Ancak sünme rijitliği değerinin bitümü düşük sıcaklık performansı için ölçüm yapılan sıcaklıkta 300 MPa sınırı bulunmaktadır. Bu sınır göz önüne alındığında sünme rijitliğini bu değerin üstüne çıkarabilecek bitüm kimyası, SBS veya Wax miktarı kullanılamamaktadır. Özellikle SBS etkisinin 2. Dereceden doğrusal olmayan bir terim ile sünme rijitliğini etkilediği düşünüldüğünde yüksek miktarlarda SBS kullanımı bu özellik için mümkün olmayabilmektedir.

Değişken parametrelerin etkisinin dört tepki fonksiyonu birlikte ve istenen bitüm performans limitleri içerisinde eşzamanlı analizi yapılarak optimum değişken değerleri belirlenmiştir. Tepki fonksiyonlarının ayrı ayrı analizlerine göre bir arada değerlendirilmesi sonuçlarında eklenen veya çıkan terimler olmuştur. Özellikle $GI^{*}GI$ terimi DSR, Elastik geri dönme ve Viskozite fonksiyonları için ayrı ayrı analizlerde önemli bulunurken optimizasyon analizinde bu fonksiyonlar bir arada değerlendirildiğinde önemli bulunmamıştır. Bunun sebebi olarak ise analiz için tanımlanan tepki limitlerinde DSR ve Elastik geri dönme özellikleri için maksimizasyon istenirken, Viskozite değeri için minimizasyon istenmesi olarak görülmüştür. Verilen tepki limitleri içerisinde bulunan optimum değişken değerleri ise GI:0.988, SBS: %3.2 ve Wax:%3'tür. Bu değerlerde hazırlanan modifiye bitümün EN 14023 standardı kapsamındaki testleri ve asfalt çalışmaları yapılarak hem bitümde hem de asfalt özelliklerinde sağlanan performans artışı araştırılmıştır. Optimum koşullarda hazırlanan modifiye bitümün katkısız haldeyken performans sınıfı PG 70-22 iken modifikasyon sonrası PG 82-16 olarak bulunmuştur. Modifikasyon sonucunda bitümde yüksek sıcaklık performansı iki sınıf yukarı çekilirken, düşük sıcaklık performansı olumsuz yönde etkilenmiştir. Bunun sebebi BBR test sonuçlarında modifikasyon yapılan bitüm örneklerinin tamamının -22 sınıfında olmamasıdır. SBS katkısının sünme rijitliğini arttırması ve buna bağlı olarak m-değerinin gerekli kriteri sağlayamaması sebebiyle modifiye bitümlerde minimum (%2) dahi olsa düşük sıcaklık performansını bir sınıf aşağı çekmiştir. Asfalt özelliklerinin belirlenmesi için yapılan Marshall asfalt dizaynı sonucunda agrega-bitüm karışımlarında katkısız bitümden %4.8 kullanılırken, modifiye bitümden %6.2 oranında kullanılması gerekliliği sonucu çıkmıştır. Bu miktarlara göre hazırlanan ve tekerlek izinde oturma testi yapılan asfalt numunelerinde katkısız bitümde %13 bulunurken, modifiye bitümde bu değer %50 civarında iyileştirilerek %6.7 bulunmuştur.

Sonuç olarak modifiye bitümlerin DSR, viskozite, elastik geri dönme ve sünme rijitliği özelliklerinin bitüm içeriği, polimer ve ılık karışım asfalt katkıları miktarı parametrelerine bağlı olarak modellenmesi ve optimum karışım oranlarının bulunmasında "Tepki Yüzeyi Yöntemi" ile başarılı sonuçlar elde edilmiştir. Deneysel tasarım yöntemlerinin yaygın olarak kullanılmasıyla zaman kaybının önlenmesinin yanında kişisel tecrübelere dayanan asfalt karışım formulasyonlarının hazırlanması bilimsel ve gerçekçi bir temele oturtulabilecektir.

1. INTRODUCTION

Petroleum products are used for operations that require energy in many areas of our lives. Refining processes has been developed for this purpose that aimed to convert the crude oil to the more valuable products such as LPG, kerosene, gasoline, diesel etc. After the fractional distillation at 30-350 ^{o}C, both atmospheric and vacuum conditions of crude oil, residue has been obtained is called as “bitumen”.

Bitumen is the heaviest petroleum product of crude oil which is a mainly consist of hydrocarbon structure including some heteroatoms and heavy metals such as nitrogen, sulfur, nickel, vanadium etc. In some regions the term of “asphalt” pointed out also the bitumen, however, in this study, asphalt wording will be used for only the mixture of bitumen and aggregate.

1.1 Literature About Materials

1.1.1 Bitumen

1.1.1.1 Definition and production of bitumen

Bitumen (CAS No. 8052-42-4) is defined as the dark brown to black residuum, cement-like semisolid or solid or viscous liquid, produced by the non-destructive distillation of crude oil during petroleum refining by the US National Institute for Occupational Safety and Health (NIOSH) [1]. The term “bitumen” is also referred as a generic material composed of long hydrocarbon backbones and pointed out the binder material of the asphalt mixtures.

There are a wide range of refining processes to produce different types of bitumen and these methods gives a chance the manufacturer to produce bitumen having special properties. The common processes to produce bıtumen are distillation and solvent de-asphalting methods [2]. In the refineries, crude oils are blended in some ratios to produce consistent, high-quality products, also specific characteristics bıtumen. General bitumen production processes shown in Figure 1.1.

The most preferred refining process is the sequential atmospheric and vacuum distillation to get the bıtumen fraction from crude oil. The light components in the crude oil, having low boiling temperatures between 30-350 ^{o}C at atmospheric conditions, are separated by the atmospheric distillation column and the bottom residue is still contains the fuel products. To remove this latest fuels, distillation conditions are made more difficult. By using the vacuum pressure, the boiling point of heavy fuel fractions is decreasing and the second distillation process is applied. crude oil, having low boiling temperatures between 30-350 ^{o}C at atmospheric conditions, are separated by the atmospheric distillation column and the bottom residue is still contains the fuel products. To remove this latest fuels, distillation conditions are made more difficult. By using the vacuum pressure, the boiling point of heavy fuel fractions is decreasing and the second distillation process is applied. While atmospheric residue become distillation in vacuum conditions, the unwanted thermal cracking of hydrocarbon molecules is not observed.

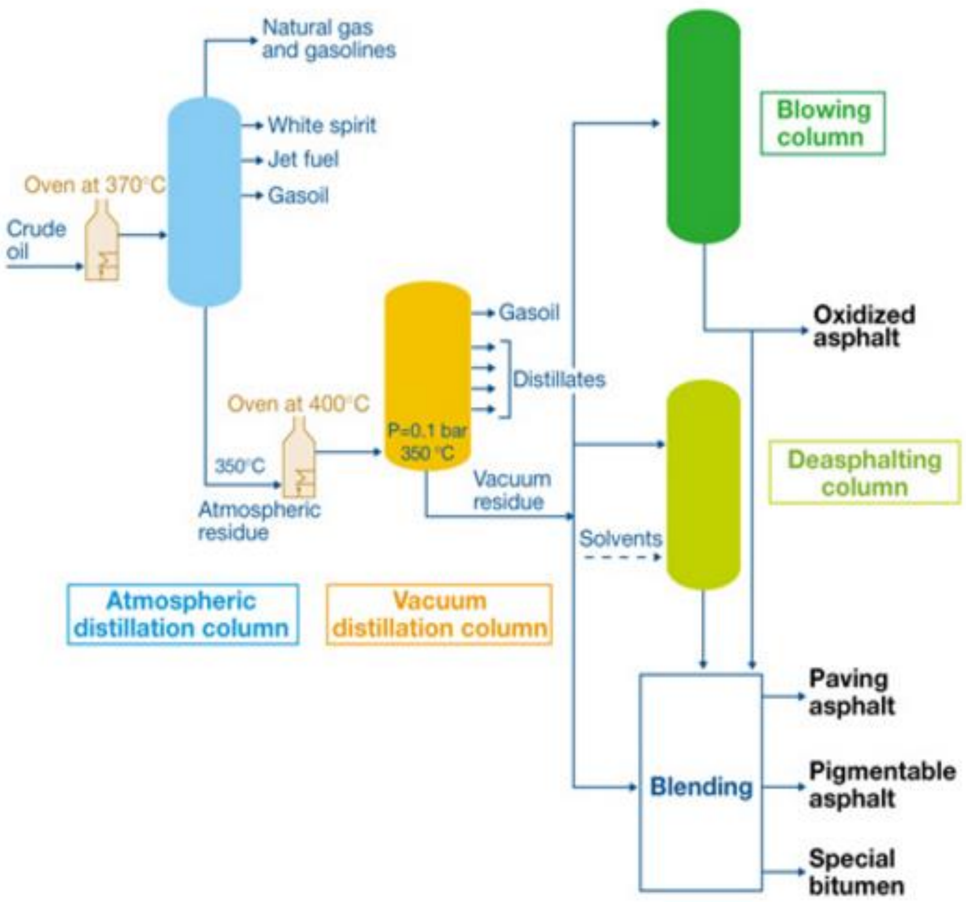

Figure 1.1 : Typical Bitumen Production Process [3].

Fıgure 1.1. shows that the vacuum residue can be obtained as either bıtumen or feed for solvent de-asphalting process which has a solvent system to separate the lube oils and bitumen components of vacuum residue. Propane or butane can be used for de-asphalting extraction as a solvent and the chemical structure of bıtumen is not changed after this process except physical properties. The different penetration types of bıtumen can be obtained by both vacuum distillation and solvent de-asphalting processes.

Another process is the oxidation for the production of bıtumen with desired properties which is called as “oxidized bitumen”. Blowing column is used to produce this type of bitumen that is accessed by the air blowing at temperatures 280 ^oC on average. This type of bitumen has specific properties such as stiffness and softening point varying the oxidation reaction time. Oxidized bitumen is usually used in roofing applications due to the strength properties.

To get the desired properties in final product according to the purpose of use, the bıtumen comes from the all process can be mixed in a blending or storage tank. In the blending, different types and properties of bıtumen can be obtained by the type of additives with or without additional process. Cutback bitumen can be obtained by blending of penetration bitumen with solvent such as kerosene or polymer modified bitumen with the mixtures of conventional bıtumen and polymers such as thermoplastics or elastomers [4].

1.1.1.2 Chemical and physical properties of bitumen

Bıtumen is a complex hydrocarbon mixture with high molecular weight fractions. The colloidal system of bitumen is defined as asphaltene micelles dispersed or dissolved in a maltenes. When the asphaltene micelles were fully dispersed is called as sol-type bitumen while the interconnecting asphaltene micelles presence is gel-type bitumen. Sol and gel type structures exist together within a bitumen as shown in Figure 1.2 [5]. This is because hydrocarbon mixture is classified as polar and apolar fractions that are asphaltenes and maltenes, respectively [6]. These fractions are soluble in different solvents. While maltenes are soluble in both toluene and n-heptane, asphaltene fractions are defined as n-heptane insoluble part of the bitumen [7].

Also, maltenes are formed from three groups that are saturates, aromatics and resins. Figure 1.3. indicates the molecular structures of the bitumen SARA (Saturate, Aromatic, Resin, Asphaltene) fractions. These fractions can be separated from the bitumen by using chromatographic methods standardized as in ASTM D 4124 [8]. A classical experimental setup for the determination of SARA fractions in the bitumen or crude oil sample is Thin Layer Chomatography – Flame Ionization Dedector (IATROSCAN) [9].

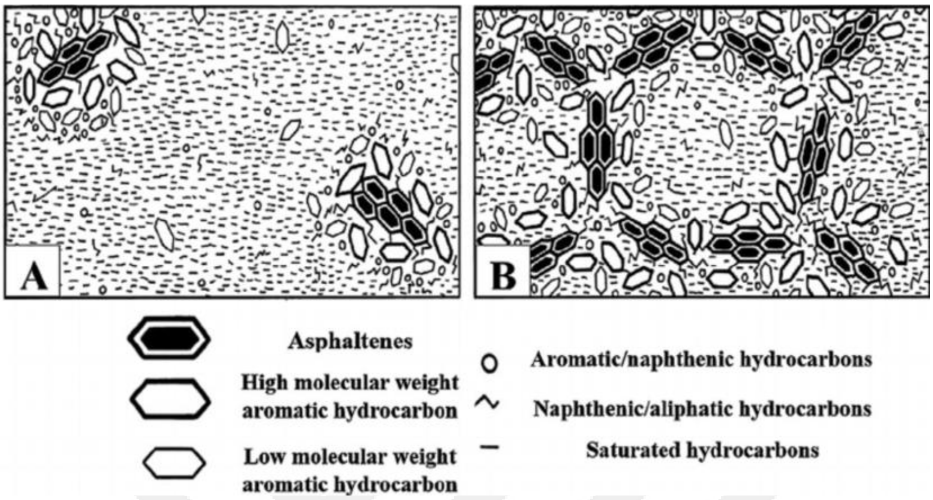

Figure 1.2 : The Colloidal Structure of Bitumen (A) Sol and (B) Gel type bitumen [10].

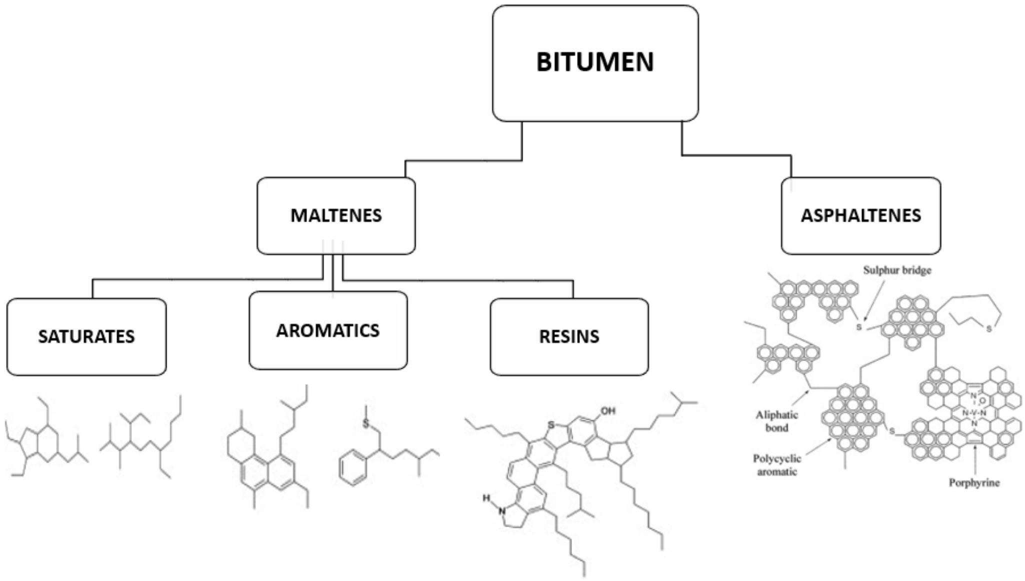

Figure 1.3 : Bıtumen SARA Fractions: Saturates, Aromatics, Resins, Asphaltenes [11].

The amount of saturates in the bitumen is approximately 5-15 wt.% and the glass transition temperatures are so low such as -70 ^{o}C [12]. The result of elemental analysis of saturates gives the H/C ratio which is close to 2 because of the absence of heteroatoms [13]. Unlike the high molecular weight of bitumen, saturates have number average molecular weight around 600 g/mol [14].

Aromatics, yellow to red liquid fractions at room temperatures, are approximately 30-45 wt.% constituents of total bitumen [10]. The temperature to pass glassy to rubbery regions for aromatic fractions is around -20 ºC [13,15]. The number-average molecular weight is around 800 g/mol [16].

The heaviest fraction of the maltenes of the bitumen is resins called as polar aromatics have around 1100 g/mol number-average molecular weight [12]. These fraction can presence 30-45 wt.% in the bitumen. Since the resins have heteroatoms in the structure such as oxygen, sulfur, nitrogen etc., hydrogen to carbon ratio is found as lower than 2 [17].

Asphaltenes, the key fraction of the bitumen, represent between 5-20 wt.% of a bitumen. It has a role in the behavior and the physical properties of bitumen. The range of molecular weight of asphaltenes are very wide between 800-3500 g/mol [18]. Asphaltenes are in the black powder form and it has not any transition temperatures up to 200 ºC [13].

Since the bitumen is a mixture, it has a specific properties such as penetration, softening point etc. European standards cover the specifications of all grade of bitumen and bituminous binders [19]. Figure 1.4 represents the standards for different types of bitumens.

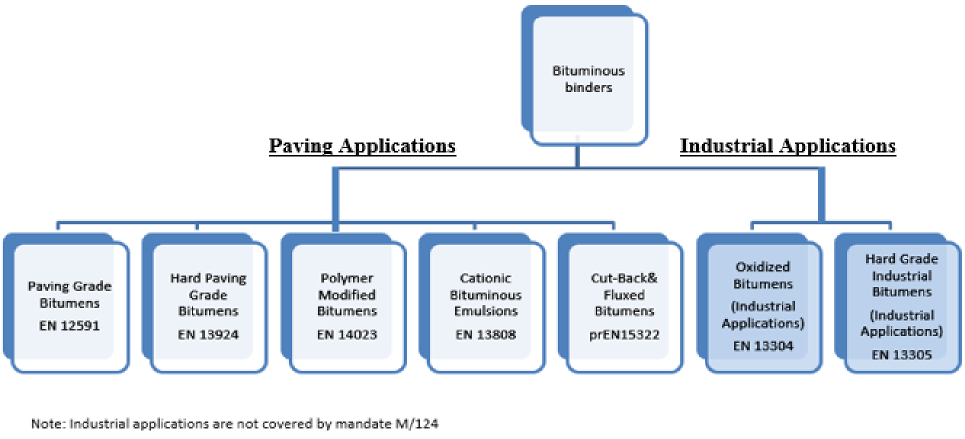

Figure 1.4 : European Standards for Bitumen [19].

For the base bitumen that is not processed or mixed any additive, EN 12591 standard is used and the mainly physical properties of bitumen is listed with the related tests. The list of the standard is given in the Table 1.1. The analysis of bitumen divided into two categories as before and after short term aging (hardening) process is called as Rolling Thin Film Oven Test (RT-FOT). Paving grade bitumen is also named as penetration grade bitumen and it classified as penetration value which represents the hardness or consistency of bituminous material. Additionally, the softening point of penetration grade bitumen is another criteria of the standard. The physical meaning of the softening point is the temperature susceptibility of bitumen.

Penetration test aims to assess the suitability of bitumen for use under different climatic conditions and various types of construction. It is the vertical distance penetrated by the point of a standard 100 gr weighed needle into the bituminous material under specific conditions of load, time (5 seconds) and temperature at 25 ^oC. This distance is measured in one tenths of a millimeter [20].

The determination of softening point helps to know the temperature up to which a bituminous binder should be heated for various road use applications. The test is perform with a rig and ball setup. Softening point is the temperature in ºC at which a standard ball passes through a sample of bitumen in a mould and falls through a height of 2.5 cm, when heated under water or glycerine at specified conditions of test. The binder should have sufficient fluidity before its applications in road uses [21].

Table 1.1 : Paving Grade Bitumen Specifications For Grades From 20 x 0,1 mm to 220 x 0,1 mm Penetration- TS EN 12591 [19].

Property	Test Method	Unit	Penetration Grade							
			20/30	30/45	35/50	40/60	50/70	70/100	100/150	160/220
Penetration at 25 ^oC	EN 1426	0,1 mm	20-30	30-45	35-50	40-60	50-70	70-100	100-150	160-220
Softening point	EN 1427	^oC	55-63	52-60	50-58	48-56	46-54	43-51	39-47	35-43
Resistance to hardening at 163 ^oC										
Retained penetration		%	≥55	≥53	≥53	≥50	≥50	≥46	≥43	≥37
Increase in softenin point, - Severity 1	EN 12607-1	^oC	≤8	≤8	≤8	≤9	≤9	≤9	≤10	≤11
or			or	or	or	or	or	or	or	or
Increase in softenin point,- Severity 2[a]		^oC	≤10	≤11	≤11	≤11	≤11	≤11	≤12	≤12
Change of mass [b] (absolute value)		%	≤0,5	≤0,5	≤0,5	≤0,5	≤0,5	≤0,8	≤0,8	≤1
Flash point	EN ISO 2592	^oC	≥240	≥240	≥240	≥230	≥230	≥230	≥230	≥220
Solubility	EN 12592	%	≥99,0	≥99,0	≥99,0	≥99,0	≥99,0	≥99,0	≥99,0	≥99,0

[a] When Severity 2 is selected It shall be associated with the requirement for Fraass breaking point or penetration index or both measured on the unaged binder

Although many different factors contribute to bitumen aging, the key component of concern is the loss of volatiles. The RTFO test also provides a quantitative measure of the volatiles lost during the aging process. The Rolling Thin-Film Oven test (RTFOT) simulates short term aged bitumınous binder for physical property testing. Material is exposed to elevated temperatures to simulate manufacturing and placement aging. During the test, unaged bitumen is placed in a cylindrical jar, which is then placed in a carousel inside a specially designed oven. The oven is heated to 163°C and the carrousel is rotated at 15 rpm for 85 minutes. The carousel rotation continuously exposes new asphalt binder to the heat and air flow and slowly mixes each sample [22,23].

Bituminous material leave out volatiles at high temperatures depending upon their grade. These volatile vapors catch fire causing a flash. The flash point is the lowest temperature at which flash occurs due to ignition of volatile vapors when a small flame is brought in contact with the vapors of a bituminous product, gradually heated under standardized condition [23, 24].

Finally, solubility test checks whether the binder contains any solid contamination. A bitumen sample is dissolved in the solvent and filtered through a layer of glass powder in a sintered crucible. Undissolved material from bitumen is washed, dried and weighed. Then, the result of the solubility test is calculated, expressed as the percentage mass of the dissolved bitumen fraction relative to the mass of the entire sample [% m/m] [25, 26].

1.1.1.3 Application areas

Bıtumen is a material can be used in a wide range of application. World usage of bitumen is estimated as approximately 102 Million tonnes/year. The main industries using bituminous materials are paving and roofing. According to the bitumen industry, 85 percent of all bitumen used world-wide is used in asphalt pavements, 10 percent is used for roofing, and the remaining 5 percent is used in other ways-Figure 1.5 [27].

Typically 4-6 wt.% bitumen used in the asphalt pavement and about 95 wt.% mineral aggregates is mixed with the bitumen which binds the aggregates in a cohesive mix. Every asphalt pavement mix is designed for a specific pavement application, varying its composition accordingly [28].

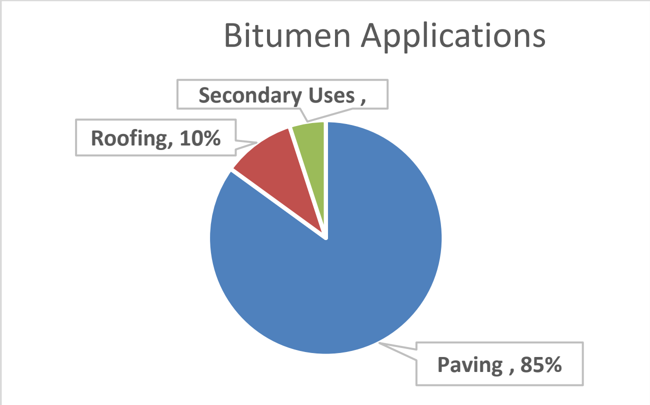

Figure 1.5 : Application Areas of Bitumen [27].

Approximately ten million metric tons bitumen is consumed in roofing industry. “Oxidized bitumen” and “roofing bitumen” can be used synonymously. Bitumen can used in a form of shingles, built-up roofing, bitumen membranes and underlayments or polymer modified bitumen roofing [29].

1.1.2 Polymer modified bitumen

As mentioned in Section 1.1.1.3, bitumen is a material widely used in paving and roofing industries. However the behavior of bitumen may vary depending on the environmental conditions. Due to the some characteristics of the bitumen, it can brittle or soft at low and high temperatures. Therefore, bitumen properties are qualified to use in a wide range of temperature with some additives such as polymer, carbon, emulsifier etc. The most popular method is the making polymer-bitumen blend is called as Polymer Modified Bitumen (PMB) [30]. Polymer addition improves the rheological properties of bitumen mainly against to high temperature deformations. Polymers can have both viscous and elastic properties together. Bitumen deforms at high temperatures under the traffic load and this deformation can permanent. Polymer viscolelastic structure provides thigher creep resistance and recovery chance to bitumen [31].

1.1.2.1 Polymer types used in bitumen

Polymer modification concept is based on the many years ago. But the first known examples of PMB was established after the synthetic polymers were invented at the end of World War II. After that PMB was began to searched and applied increasingly in North America in 1950s [32]. With the increasing of number of vehicles and traffic load, conventional bitumen is inadequate for long service-life. For this reason, the use of polymer modified bitumen on the road has increased over the years. In these days, mainly four groups of polymer is preferred to modify the bitumen properties: Plastomers, Thermoplastics, Elastomers, Reactive Terpolymers, Natural and Synthetic Rubbers [33]. Each of these polymers has their own associated physical properties and has both advantages and disadvantages while used in the bitumen listed in Table 1.2.

Table 1.2 : Category of Some Polymers Used to Modify Bitumen [32].

Category	Examples	Advantages	Disadvantages
Plastomers	Polyethylene (PE)	-Good high temperature properties	-Limited improvement in elasticity
	Polypropylene (PP)	-Relatively low-cost	-Phase separation problems
	Ethylene-vinyl acetate (EVA)	-Relatively good storage stability	-Limited improvement in elastic recovery
	Ethylene-butyl acrylate (EBA)	-High resistance to rutting	-Limited enhancement in low-temperature properties
Thermoplastic Elastomers	Styrene-butadiene-styrene (SBS)	-Increased stiffness	-Compatibility problems in some bitumen
	Styrene-ısoprene-styrene (SIS)	-Reduced temperature sensitivity -Improved elastic response	-Low resistance to heat, oxidation and UV -Relatively high cost
	Styrene-ethylene/butylene-styrene (SEBS)	-High resistance to heat, oxidation and UV	-Storage instability problems -Relatively reduced elasticity -High cost
Reactive Polymers [33]	Reactive ethylene terpolymer (RET)	-Reactivity -Increased polarity	-High cost - The risk of gelation
Natural And Synthetic Rubbers [34]	Reclaimed Tire Rubber	-Rubber Disposal -Low material cost -Fatigue resistance improvement -Longer rutting resistance -Reduce reflective cracking	-Lower physical resistance if used as an extender. -It needs high T and long digestion times -Separation problems
	Natural Rubber	-Better rutting resistance -Higher ductility -Higher elasticity	-Sensitive to decomposition and oxygen absorption.

The most popular polymer is the styrene-butadine-styrene (SBS) copolymer among the PMB industry. Even if SBS addition decreases the bitumen aging resistance, it still the most suitable polymer through both economic and technical aspects of advantages [34].

SBS is a triblock copolymer having polystyrene and polybutadiene blocks in the structure which provides the important properties to the polymer. Figure 1.6 shows the molecular structure of SBS polymer in which soft and hard segments coexists.

Polystyrene end-blocks form domains that enhance the physical crosslinking in the structure. By the help of crosslinking, copolymer has both strength and elasticity in a three dimensional network. Strength and elasticity comes from the polystyrene and polybutadiene blocks, respectively. The effectiveness of these cross-links diminishes rapidly above the glass transition temperature of polystyrene (approximately 100 ^oC), although the polystyrene domains will reform on cooling restoring the strength and elasticity of the copolymer [35].

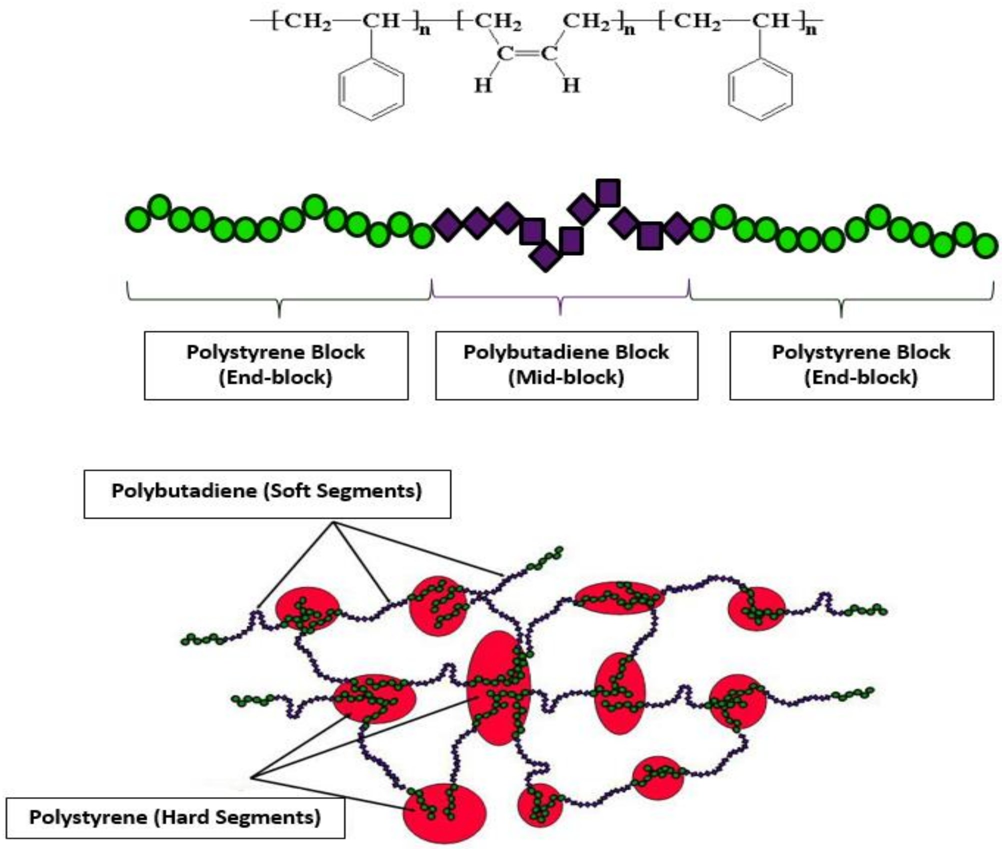

Figure 1.6 : Molecular Structure of Linear SBS Copolymer [35].

1.1.2.2 Polymer-bitumen compatibility

Bitumen is used for lots of applications in road construction and its polymer blends have some instability problems. Polymer dispersed in a bitumen medium after the polymer and bitumen are blended. However, polymer may not be compatible with bitumen and can be seen phase separation during the PMB transport and storage period (Figure 1.7). This phenomena has been studied for decades and different modelling and simulation techniques have been proposed to explain the reasons of this problem [36-40]. The most know study about this subject was reported by Gaestel et al. [39]

and the equation about the fractions of bitumen and polymer compatibility were given in equation 1.1.

$$Gaestel\ Stability\ Index = \frac{Saturates + Asphaltenes}{Aromatics + Resins} \tag{1.1}$$

Bitumen-polymer matrix are obtained with the absorption of maltene fractions by the polymer copolymer matrix. This absorption process can get up to nine times the volume of the SBS by the swelling. The expected morphology of PMB is the formation of single phase with blending polymer and bitumen internal structures with the called as "phase inversion" step. Herein almost all of bitumen modifier polymers are not formed a chemical bonding with reaction. Only physical network is obtained by the mixing of polymer and bitumen and this provides the conservation of polymer properties. When viewed from bitumen, the amount of maltenes in the bitumen medıum affects the amount of polymer that modifies the properties of PMB. However the bitumen and polymer characteristics such as density and composition affect the interaction between two phases, not be first reason of instability but could speed up the process [35,36,41].

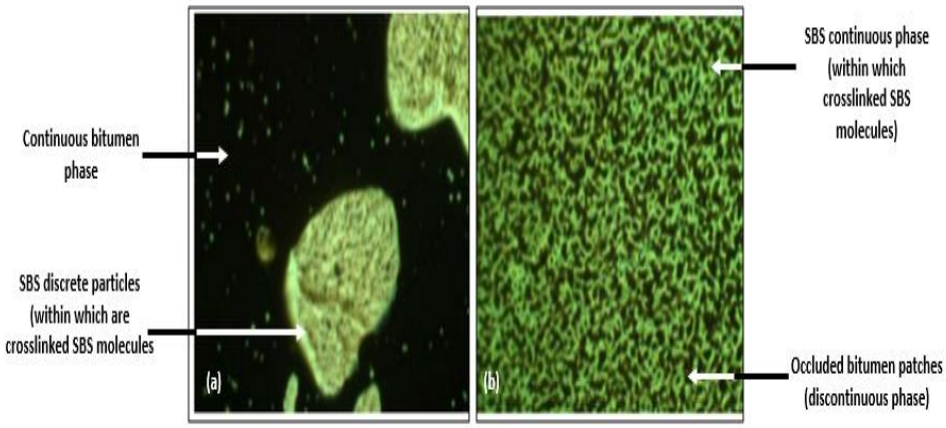

Figure 1.7 : SBS Modified Bitumen Phase Separation with Cooling (a) Binder Cooled Rapidly From 120 °C-Bitumen Dominant Phase (b) Same Binder Cooled Rapidly From 200 °C- Polymer Phase Dominant [33].

Compatibility can be defined as the state of dispersion between two dissimilar components. Figure 1.8 represents the phase diagram of SBS modified bitumen that the critical point for one phase PMB at which different polymer concentrations are needed. With the increasing of temperature and polymer content, the polymer and bitumen rich phases competes in a mixture. At low concentrations of polymer, usually

5-7% by mass, one phase PMB is formed with the continuous polymer network that shows an amazing improvement in the properties of bitumen [42,43].

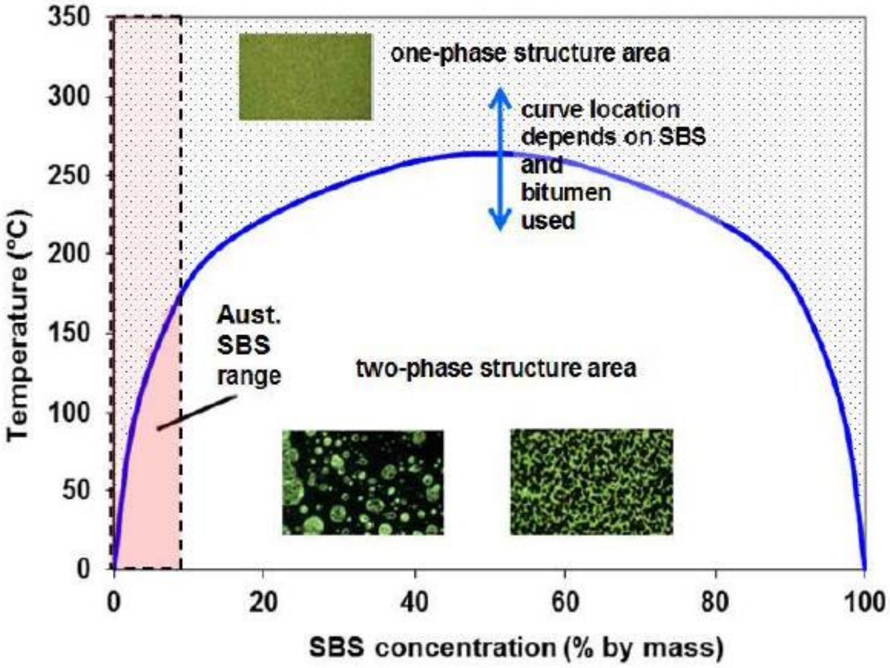

Figure 1.8 : SBS Modified Bitumen Phase Diagram [43].

SBS, a thermoplastic rubber, may have molecular weights close or higher than that of asphaltene molecules at which the competition of solvent effect starts with between maltene and polymer phases. Insufficient maltene fraction in bitumen promoted the phase stability. This phase separation can be prevented by the addition aromatic oil. However, too high an aromatic content in the blend will dissolve the polystyrene blocks and damage the advantages of the SBS copolymer [42].

Low compatibility between the bitumen and polymer may result in poor storage stability. Also, the degree of SBS dispersion in bitumen influenced storage stability and the rheological properties of modified binders. The factors which can be bitumen composition, polymer characteristics, polymer content and mixing conditions affect the compatibility of bitumen-polymer mixtures simultaneously. Storage temperature is another factor influenced the stability of PMB mixture. Figure 1.9 shows the microstructures of different bitumen compatibilities at temperatures from 200 °C to 100 °C. Although good compatibility can be achieved in mixture storage temperatures can be destroy this structure lower than 140 °C [43,44].

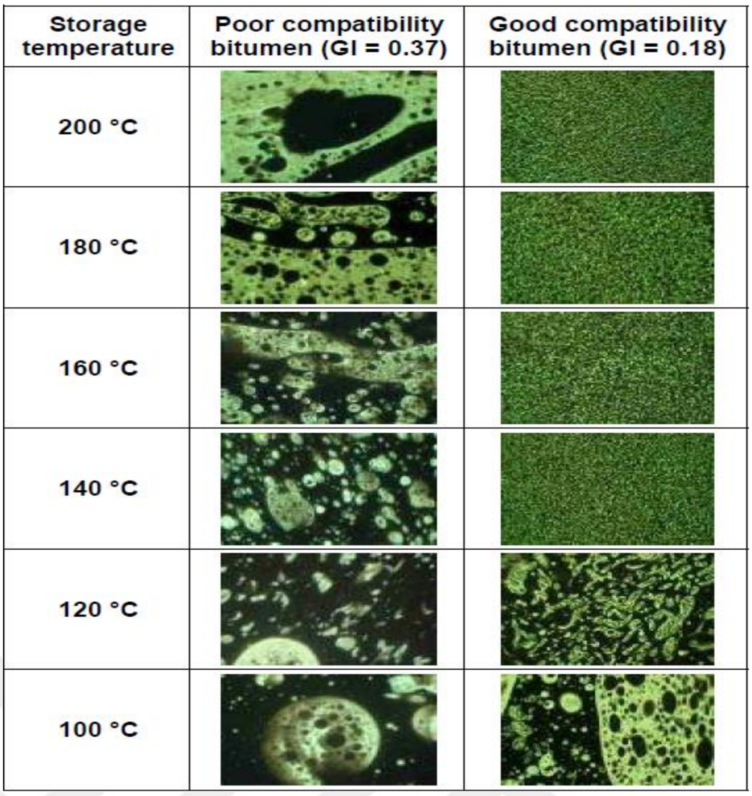

Figure 1.9 : Fluorescent Images of Stored SBS Modified Bitumen at Different Temperatures [43].

1.1.2.3 Properties of polymer modified bitumen (pmb)

Bitumen modifications can be performed by using some groups of polymers which are into four groups listed in the Table 1.2 Binary systems or multicomponent blends can improves the final properties of polymer modified bitumen, providing higher quality materials than the pure bitumen by itself would not perform appropriately. Polymer modification with some kind of polymer can provide greater rigidity, water resistance and durability and also better resistance to permanent deformation, much higher durability and higher resistance to spreading cracks. Every polymer used in modification shows a specific effect and alters properties within an asphalt mixture. Thermoplastic elastomers such as SBS provide good elasticity in a modified binder, while plastomers and reactive polymers improve rigidity and reduce deformation under load [45,46]. Neat bitumen classification is carried out by the penetration grading system that is TS EN 12591-Bitumen and Bituminous Binders Specifications for paving grade bitumens. This specification shows only hardness of binder within the penetration range rather than the durability or performance behavior. Table 1.1 represents the EN 12591 standard tests with the classification of penetration grade bitumen.

SuperPave (Superior Performance Pavement), Performance Grading (PG), is developed by Strategic Highway Research Program (SHRP) in U.S.A. instead of penetration (paving) grade of bitumen. It is the result of a necessity for new tests and specification to characterize the asphalt binder more accurately. Those tests are specifically designed to address asphalt mixture pavement performance parameters such as rutting, fatigue cracking and thermal cracking. Performance grading system provides a temperature range through which the asphalt must meet certain physical properties to resist rutting and cracking. It also includes conditioning procedures to simulate changes in asphalt properties due to aging in the field due to aging in the field.

Superpave performance grading is reported using two numbers; First number is the average seven-day maximum pavement temperature (°C), Second number is the minimum pavement design temperature likely to be experienced (°C). Thus, a PG 64-22 is intended for use where the average seven-day maximum pavement temperature is 64°C and the expected minimum pavement temperature is -22°C.

Low Temperature, °C \ High Temperature, °C	52	58	64	70	76	82
-16	52-16	58-16	64-16	70-16	76-16	82-16
-22	52-22	58-22	64-22	70-22	76-22	82-22
-28	52-28	58-28	64-28	70-28	76-28	82-28
-34	52-34	58-34	64-34	70-34	76-34	82-34
-40	52-40	58-40	64-40	70-40	76-40	82-40

Figure 1.10 : Performance Grades (PG) of Bitumen for Different Minimum and Maximum Pavement Temperatures [47].

Figure 1.10 shows the performance grades of bitumen with three class of color. The pink region can be satisfied with high quality binder, and polymer modification is a requirement to obtain a PG grade bitumen located at blue region.

Performance graded binder is superior to penetration grading system and it results in higher quality binders with appropriate grade of binder for specific location based upon air and pavement temperature, loading conditions and traffic speed. The tests for the performance grading is regulated with the AASHTO MP1a and EN 14023 standards. Three performance-based test methods, DSR,BBR and DTT given below. are used to grade the asphalt binders [47].

The dynamic shear rheometer (DSR) is used to characterize the viscous and elastic behavior of asphalt binders at medium to high temperatures. DSR test measures the high temperature shear stiffness and phase angle of a sample of bıtumen with a thickness of 1-to 2 mm in which between two parallel circular plates with diameter of 8 or 25 mm. The plate located at the bottom remains constant and the plate located at top oscillates back and forth through the sample at 10 rad/sec to load a shearing stress. DSR tests are conducted on unaged, RTFO aged and PAV aged asphalt binder samples.

The Bending beam rheometer (BBR) is used to determine the creep stiffness behvior of bitumen specimen at low temperature. It measures the creep stiffness and determines the slope of logarithm of stiffness and logarithm of time curve. A mold with a dimensions of 125x12.5x6.25 mm is filled with asphalt binder and cooled to obtain test specimen. While applying a force to the centerr of bitumen specimen, beam, the deflection versus time observed on the beam is recorded. Creep stiffness is determined by using the plot of recorded deflection profile. BBR tests are applied on pressure aging vessel aged asphalt binder samples.

The Direct Tension Test (DTT) is used to determine the failure stress on an asphalt binder at low temperatures. A dogbone-shaped specimen is tested at a constant rate of elongation of 1.0 mm/min at a specified temperature +0.2°C until it fractures.

Since the DSR and BBR tests were performed during this research study, the details of tests were given in the Section 2-Experimental Study.

All the performance grades (PG) of an neat or polymer modified asphalt binder sample can be determined with the help of Table 1.3 (AASHTO MP1) [48] after the measurement of performance tests which are listed in the standards.

In a special case for Turkey, Table 1.4 (TS EN 14023) [49] uses for the classification of modified bitumen according to General Directorate of Highway. It is a combination of AASHTO MP1 and EN 12591 specifications with the determination of both penetration and performance tests such as penetration, softening point, dynamic shear rheometer and bending beam rheometer etc.

1.1.3 Asphalt mixtures

Asphalt refers to the mixture of aggregates, binder and filler with the desired properties for constructing and maintaining of all kind of roads. Aggregates for this purpose could be different size of crushed rocks, stones, sand, clay or fines. The most commonly used binder to bind the aggregates is bıtumen which is generally the top layer of different unbounded layers of road. The pavement layers are generally divided into three layers that are surface course, Base course and Subbase course. Figure 1.11 shows the layers of a road construction and the bituminous-bounded layers [50].

Surface course is composed of high performance materials because of it has direct contact with the traffic and climate conditions. This layer provides characteristics such as friction, smoothness, noise control, rut and shoving resistance, and drainage. The base course is the intermaediate layer and its aim is to distribute traffic loads so that stresses transmitted to the pavement foundation will not result in permanent deformation of that layer. The bottom layer, Subbase layer, has the function of support of pavement structure [51].

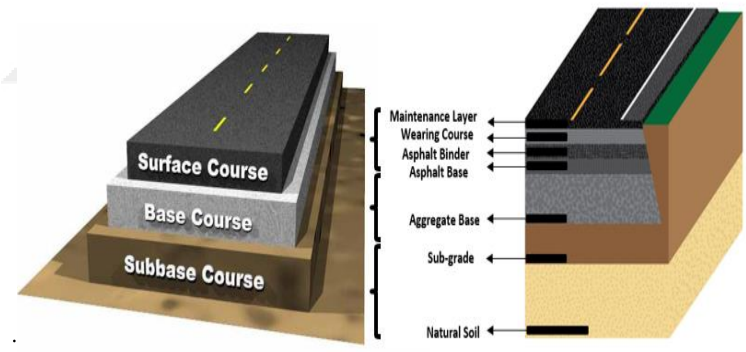

Figure 1.11 : The Sections of Typical Asphalt Pavement Hot Mix Asphalts [51].

Asphalt mixtures are usually prepared at high temperatures which is necessary for the workability of bitumen and completely coverage of the aggregates with binder. Thus the Hot Mix Asphalt (HMA) is the generic name of asphalt mixtures that is produced between 150-200 ^{o}C. Figure 1.12 represents the temperatures for mixing of asphalt pavements. HMA is also known as Asphalt Concrete (AC) or Asphalt Concrete Pavement (ACP). For the applications of different traffic and climate conditions, HMA pavements have three categories which are Open-Graded Friction Courses (OGFC), Stone Matrix Asphalt (SMA), and Dense-Graded mixes [52,53].

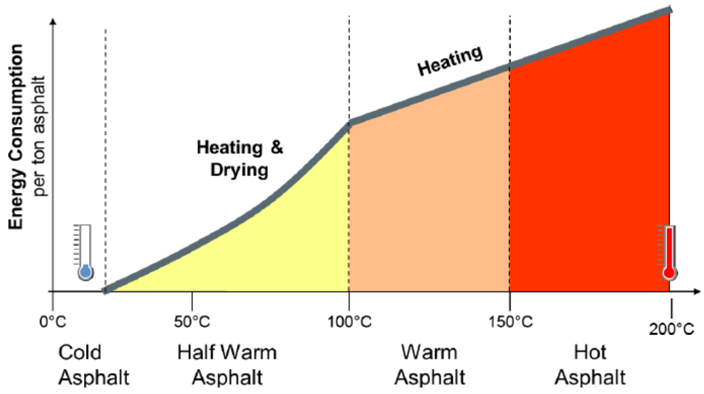

Figure 1.12 : Temperature Ranges for Asphalt Mixtures [54].

Another technology for asphalt mixtures is called as Warm Mix Asphalt-WMA which allows to produce the asphalt mixtures at lower temperatures. The 20-40 ^{o}C reductions on the mixing temperatures during the asphalt production is possible with the chemical additives, foaming admixtures or plant modifications. The details of this technology is given in the following subsection.

1.1.3.1 Warm mix asphalt technology

Environmental concerns are one of the important issues in the asphalt industry as it is in every industrial activities. Especially for the emission of greenhouse gases, the main source of the air pollution, is related to transportation infrastructures, resides in the manufacturing, spreading and conservation of asphalt mixes. A recent technology is one of the green technologies of asphalt manufacturing is called as Warm Mix Asphalt (WMA). It has advantages on the gas emissions due to the 20-40 ^{o}C reduction of mixing temperature of asphalt [55].Typical expected reductions are [56];

- 30 to 40 % for CO_2 and sulfur dioxide (SO_2),
- 50 % for volatile organic compounds (VOC),
- 10 to 30 % for carbon monoxide (CO),
- 60 to 70 % for nitrous oxides (NO_x),
- 20 to 25 % for dust.

Besides the environmental advantages, Reduction of asphalt mixing temperature has also some benefits that [56,57,58];

- Low energy consumption
- Reduction of energy costs of 10 -30 %

Table 1.3 : Performance-Graded Asphalt Binder Specification-AASHTO MP1[48].

PERFORMANCE GRADE	PG 46-			PG 52-							PG 58-					PG 64-						PG 70-						PG 76-					PG 82-				
Average 7-day Maximum Pavement Design Temperature, °C [a]	34	40	46	10	16	22	28	34	40	46	16	22	28	34	40	10	16	22	28	34	40	10	16	22	28	34	40	10	16	22	28	34	10	16	22	28	34
Minimum Pavement Design Temperature, °C [a]	>-34	>-40	>-46	>-10	>-16	>-22	>-28	>-34	>-40	>-46	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-10	>-16	>-22	>-28	>-34
ORIGINAL BINDER																																					
Flash Point Temperature, T48: Minimum °C	230																																				
Viscosity, ASTM D4402 [b]	135																																				
Dynamic Shear, TP5:[c] G*/sinδ, Minimum, 1.00 kPa Test Temp@10 rad/s, °C	46			52							58					64						70						76					82				
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN RESIDUE (T179)																																					
Mass Loss, Max., %	1.00																																				
Dynamic Shear, TP5: G*/sinδ, Minimum, 2.20 kPa Test Temp@10 rad/s, °C	46			52							58					64						70						76					82				
PRESSURE AGING VESSEL RESIDUE (PP1)																																					
PAV Aging Temp., °C[d]	90			90							100					100						100(110)						100(110)					100(110)				
Dynamic Shear, TP5: G*/sinδ, Minimum, 5000 kPa Test Temp@10 rad/s, °C	10	7	4	25	22	19	16	13	10	7	25	22	19	16	13	31	28	25	22	19	16	34	31	28	25	22	19	37	34	31	28	25	40	37	34	31	28
Physical Hardening[c]	Report																																				
Creep Stiffness, TP1:[f] S, Max., 300 MPa, m-value, Min.,0.300 Test Temp@60 s, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24
Direct Tension, TP3:[f] Failure Strain, Min., 1.0% Test temp@ 1.0 mm/min, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24

[a] Pavement temperatures are estimated from air temperatures using an algorithm contained in the Superpave software program, may be provided by the specifying agency, or by following the procedures as outlined in PPX.

[b] This requirement may be waived at the discretion of the specifying agency if the supplier warrants that the asphalt binder can be adequately pumped and mixed at temperatures that meet all applicable safety standards.

[c] For quality control of unmodified asphalt cement production, measurement of the viscosity of the original asphalt cement may be substituted for dynamic shear measurements of G'/sin_ at test temperatures where the asphalt is a Newtouian fluid. Any suitable standard means of viscosity measurement may be used, including capillary or rotational viscometry (AASHTO T201 or "1"202).

[d] The PAV aging temperature is based on simulated climatic conditions and is one of three temperatures 90°C, 100°C or ll0°C. The PAV aging temperature is 100°C for PG 58- and above, except in desert climates, where it is 110°C.

[e] Physical Hardening -- TPI is performed on a set of asphalt beams according to Section 13.1, except the conditioning time is extended to 24 hrs + 10 minutes at 10°C above the inlnirnum performance temperature. The 24-hour stiffness and m-value are reported for information purposes only.

[f] If the creep stiffness is below 300 MPa, the direct tension test is not required. If the creep stiffness is between 300 and 600 MPa the direct tension failure strain requirement can be used in lieu of the creep stiffness requirement. The m-value requirement must be satisfied in both cases.

Table 1.4 : Performance-Graded Asphalt Binder Specification-TS EN 14023[49].

#	TEST NAME	Standard	Unit	PMB 58-28	PMB 64-28	PMB 70-16	PMB 70-22	PMB 70-28	PMB 76-16	PMB 76-22	PMB 76-28	PMB 82-16	PMB 82-22
1	Penetration (25 ^{o}C, 150g, 5sn)	TS EN 1426	0.1 mm	90-150 (8)	40-100 (5)	45-80 (4)	45-80 (4)	45-80 (4)	25-55 (3)	25-55 (3)	25-55 (3)	25-55 (3)	25-55 (3)
2	Softening Point	TS EN 1427	^{o}C	≥45 (8)	≥50 (8)	≥60 (6)	≥60 (6)	≥55 (7)	≥65 (5)	≥65 (5)	≥60 (6)	≥70 (4)	≥70 (4)
3	Force Ductility[a] (25 ^{o}C, 5 cm/dk)	TS EN 13589	J	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)	≥0.5 (11)
4	Elastic Recovery[b] (25 ^{o}C)	TS EN 13398	%	≥80 (2)	≥80 (2)	≥60 (4)	≥70 (3)	≥80 (2)	≥60 (4)	≥70 (3)	≥80 (2)	≥60 (4)	≥70 (3)
5	Flash Point	TS EN 2592	^{o}C	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)	≥220 (4)
6	Specific Gravity	TS EN 15326	g/cm^{3}	1.0-1.1									
7	Dynamic Shear Rheometer (DSR) (G*/sinδ>1 kPa)	TS EN 14770	^{o}C	≥58	≥64	≥70	≥70	≥70	≥76	≥76	≥76	≥82	≥82
8	Storage Stability[c]	TS EN 13399											
8.1	Softening Point Difference	TS EN 1427	^{o}C	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)	≤5(2)
8.2	Penetration Difference	TS EN 1426	0.1 mm	≤13(3)	≤13(3)	≤13(3)	≤13(3)	≤13(3)	≤9(2)	≤9(2)	≤9(2)	≤9(2)	≤9(2)
9	Rolling Thin Film Oven Test (RTFOT)[d]	TS EN 12607-1											
9.1	Change of Mass		%	≤1(5)	≤1(5)	≤1(5)	≤1(5)	≤1(5)	≤0.8(4)	≤0.8(4)	≤0.8(4)	≤0.5(3)	≤0.5(3)
9.2	Increasing in Softening Point	TS EN 1427	^{o}C	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)	≤8(2)
9.3	Decreasing in Softening Point	TS EN 1427	^{o}C	≤5(3)	≤5(3)	≤5(3)	≤5(3)	≤5(3)	≤5(3)	≤5(3)	≤5(3)	≤2(2)	≤2(2)
9.4	Retained Penetration	TS EN 1426	%	≥50(5)	≥50(5)	≥50(5)	≥50(5)	≥50(5)	≥45(4)	≥45(4)	≥45(4)	≥40(3)	≥40(3)
9.5	Dynamic Shear Rheometer (DSR) (G*/sinδ>2.2 kPa)	TS EN 14770	^{o}C	≥58	≥64	≥70	≥70	≥70	≥76	≥76	≥76	≥82	≥82
10	Tests For RTFOT and Pressure Aging Vessel (PAV) Aged Bitumen	TS EN 14769											
10.1	(DSR) (G*/sinδ<5000 kPa)	TS EN 14770	^{o}C	≤19	≤22	≤31	≤28	≤25	≤34	≤31	≤28	≤37	≤34
10.2	Bending Beam Rheometer (BBR) Creep Stiffness (S≤3000 MPa, m≥0.300)	TS EN 14771	^{o}C	≤-18	≤-18	≤-6	≤-12	≤-18	≤-6	≤-12	≤-18	≤-6	≤-12

[a] This specification were checked if it is needed.

[b] only for elastomeric additives

[c] If the modified bitumen were not stored before usage, the test is not mandatory.

[d] RFTO test can be applied above the 163 ^{o}C (up to 180 ^{o}C) for high viscosity modified bitumens.

- Minimize fumes, emissions, and odors
- Cooler working conditions
- Reduction of workers exposure to fumes at the plant and paving site
- potential lower oxidation/improved fatigue life
- Potential for longer haul distances
- extended time available for compaction/workability
- Pave in cool weather and still obtain density
- Extension of paving season
- Earlier opening for traffic

Temperature reduction in asphalt mixture is succeeded with the reduction of the effective viscosity of bitumen which allows complete coverage of aggregates and subsequent field compaction at lower temperatures. Viscosity reducing can be enhanced by using the three techniques are organic additives, foaming techniques and chemical additives. Usually waxes or fatty amides are used as the organic additives. Foaming technique is a process that requires additional systems with the help of water.

Organic Additives

Generally paraffin waxes or fatty amides are used in asphalt mixtures as an organic additives that show a reduction in viscosity above the melting point of wax/amide. There is a controversy about the low temperature behavior of WMA containing wax. The assumption is that the melting of waxes at high temperatures reduces the resistance to rutting and the crystallization of wax at low temperatures contributes the cracking of asphalt pavement [59]. It is also considered that the usage of wax in asphalt improves the performance and quality of mixture especially the rutting resistance of asphalt if the service temperature is lower than the melting point of wax [60-61].

Wax additives used in WMA can be classified in three categories that are [62];

- Synthetic waxes derived from the Fischer–Tropsch process;
- Montan waxes and modified Montan waxes;
- Functionalized waxes

The common commercial examples of three types of waxes were listed in Table 1.5. The most applicable and preferred type of wax listed in the Table 1.6 is Sasobit that is a long chain of aliphatic hydrocarbon with 40-120 carbon chain, product of Sasol Wax in South Africa. It is produced with the coal gasification process by using Fisher-

Tropsch method which is the treating of coal or coke with a blast of steam. Sasobit can be added to asphalt binder or directly into the asphalt mixture with aggregates. During the mixing procedure of Sasobit into either bıtumen or asphalt mixture is not required the additional shear mixing apparatus. The recommended dosage of Sasobit is 0.8-4% by mass of binder. The amount to be added more than the maximum recommended percentage has a negative impact on the performance of asphalt pavement in cold weathers [63,64,65,66,67].

Sasobit was also used in this research study and the effect of the different amount of waxes into the bıtumen was investigated with the interaction of two parameters which are polymer and bitumen SARA fractions.

Table 1.5 : Organic Additives for Addition Into the Binder or Mixture [56].

Additive	Company	Asphalt Production Temperature (at plant) °C	Use Reported In	Approximate Total Tonnage Produced To Date
Sasobit (Fischer- Tropsch wax)	Sasol	Varies, 20–30 C° (36–54 F°) drop from HMA. German guideline recommends 130–170 °C (266 to 338 °F),	Germany and 20 other countries	>10 million tons worldwide
Asphaltan-B (Montan wax)	Romonta	Varies, 20–30 C° (36–54 F°) drop from HMA. German guideline recommends 130–170	Germany	Unknown
Licomont BS 100 (additive) or Sübit (binder)	Clariant	Varies, 20–30 C° (36–54 F°) drop from HMA. German guideline recommends 130–170 °C	Germany	>322,500 square meters since 1994
3E LT or Ecoflex (proprietary)	Colas	Varies, 30–40 C° (54–72 F°) drop from HMA	France	Unknown

Foaming Techniques

One of the traditional methods for the reduction of asphalt processing temperatures is the foaming technology by using the small amount of water or zeolites. When the water is introduced to the hot asphalt mixture via hydrophilic materials or foaming nozzles, the coating of aggregates can be done successfully with the result of volume expansion and large volume of foam. This phenomena consequently leads to the possibility of reducing mixing temperatures. Foaming can be formed by using directly water or water-containing materials as indirect way. Water is directly injected into the hot binder flow usually with a special nozzle in the water-based technology and Figure

1.13 is an example of a foaming technology mechanical system by using water injection [55,56].

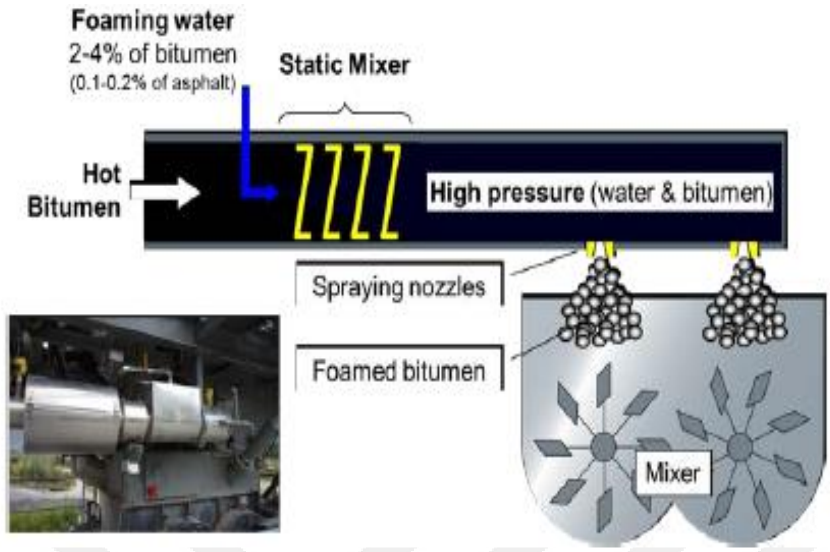

Figure 1.13 : Water-Based Mechanical System For Foaming Technique [57].

Water-containing foaming systems use synthetic zeolites that contain controlled amount of water. Zeolite gives the water in which the structure at high temperatures due to the crystallization step. This causes a microfoaming effect in the asphalt mix [65, 66, 68].

Chemical Additives

Main principle for the chemical additives used in WMA technology is the working at interface of aggregates and bitumen. Thus it works such a kind of lubricant between the aggregate particles. The additives used for WMA purposed is mainly known as surfactants which reduce the surface tension and regulate the frictional forces at interface to lower the required temperature range for mixing and compaction of asphalt pavement. This kind of additives also have a properties as a function of anti-stripping [56,57]. Some examples for the chemical additives are Evotherm (MWV), Iterlow T (Iterchimica), Double-Barrel Green (Astec) etc. Also the fuel consumption in the asphalt mix can be reduced by %35 with using surfactants in the mixture. Similar with the organic additives, chemical additives do not have a negative effect on the mechanical properties of pavement [69].

1.2 Background of Experimental Statistics

1.2.1 Strategy of experimentation and statistics

Science and engineering is inconceivable without the experimental methods. Convenient results of well understood situations that are known as scientific phenomena from the past to present contains mathematical models can be developed directly by applying these well-understood scientific situations. The models that is developed by using the physical phenomena are called as mechanistic models. There are lots of examples for this type of models some familiar ones are Ohm's (E=IR) and Newton's Law (F=m.A). However the situation for the engineering problems is a bit different. To explain an engineering problem, the observation of system or process at work and experimentation is required. The performance of model created by using the experimentation results is affected from the design of experiments and such experimentally determined models are called empirical models [70,71,72].

The flow diagram for the engineering problem solving is given in the Figure 1.14. The vital point in the problem solving is the ıdentification step and the collection of data.

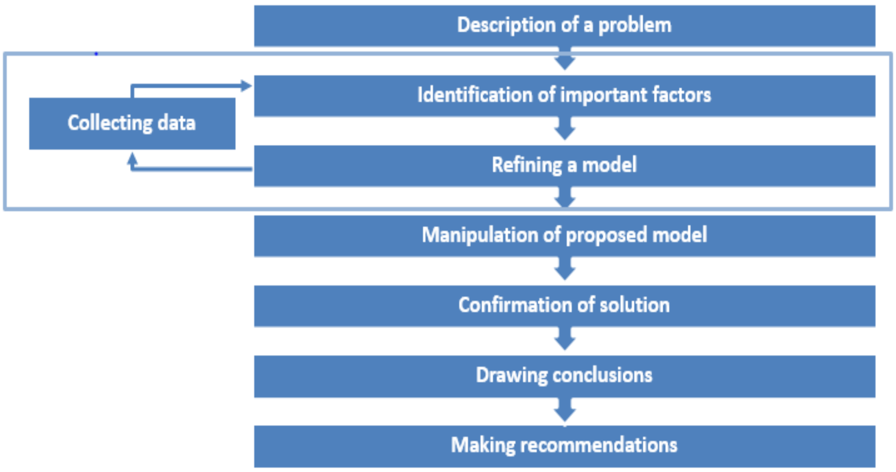

Figure 1.14 : Flow diagram of the Engineering Problem Solving Method [71].

The first step to solve an engineering problem is the description of problem and determination of the borders of this problem that is the system with the input and output parameters including controllable and uncontrollable factors affects the system shown in Figure 1.15.

Controllable factors are the main inputs of a process which can be modified in an experiment and varies systematically among the treatment conditions. Another input of a process is the parameters that cannot be changed and causes variability under same operating conditions called as *uncontrollable factors.* The relationship between the response factors, y, and inputs can be written as a function of independent variables given in the equation 1.2 The additional term, ε**,** represents the uncontrollable input variables also refers to statistical errors.

$$y = f(x_1, x_2, x_3, \dots, x_k) + \varepsilon \tag{1.2}$$

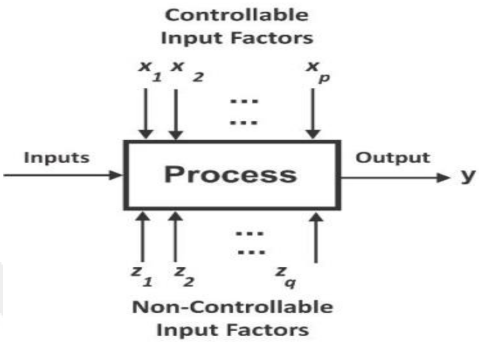

Figure 1.15 : Representation of Process with The System Parameters [72].

Conceptually three ways can be used to collect an engineering data which are the historical data, observational study and designed experiments [71].

Designed experiments are differ from both observational and retrospective studies cause that the different combinations of the factors of interest are applied randomly to a set of experimental units results in the establishing of cause-and-effect relationships. For the experimental study of several factors of interest situations, factorial experiments is a way to test the all varied factors with the all possible combinations of factor levels. The details of the factorial designs are mentioned in 1.2.1.1 and 1.2.1.2 sections [71,72,73].

1.2.1.1 2^k factorial design

Factorial design is a general method to examine the effects of more than one factor on a response variable including main effects and interactions. The key point of the factorial design at which each k factors of interests has only two levels. Thus this type of design has 2^k experimental trials for each independent parameters. Also, 2^k Factorial design is applied for the response surface method in three ways;

-For the screening experiments at the beginning of response surface, 2^k factorial design can be applied to identify the important parameters in the process.

-To fit a first order response surface model and to get the information required for steepest ascent

-To start with a basic point for other developed response surface designs such as central composite design etc.

Experimentally starting point is the considering all factors and the combinations that is *full factorial design* at which all main effects, interactions and at least one replication of center or design points have been done. Full factorial design with a k factor of interest have number of k main effects $(x_1, x_2, x_3, \dots x_k)$, $\binom{k}{2}$ two factor interactions $(x_1.x_2, x_1.x_3, x_2.x_3, \dots . x_j.x_k)$ and $\binom{k}{k}$ k factor interactions $(x_1.x_2.x_3.x_4.x_5.x_6 \dots . x_k)$ [71-77].

Main disadvantage of full factorial design is that the number of runs grow exponentially with the number of factors. Thus the designs with the high number of factors may not be practically applicable.

1.2.1.2 2^3 factorial design

Full factorial design for the case of only three factors having two levels is called as 2^3 Factorial design that comprises in eight experiments without the replication or center point runs. Suppose that x_1, x_2 and x_3 are the factors affect the response and are placed into the corners of a cubic structure given in the Figure 1.16.

Design matrix for three-factor full factorial design can be listed by using coded parameters (-,+) for low and high levels as shown in Table 1.6 Such a design provides the limited information about the unknown physical mechanism.

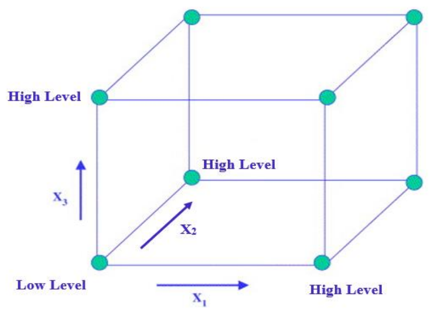

Figure 1.16 : Three-Factor Full Factorial Design without Center Point [78].

To get a practical application of experimental data requires developing an empirical model. For example there can be a linear relationship between the response, y, and the factors x_1, x_2 , x_3 . Equation 1.3 is obtained the *multiple linear regression model* with three independent variables in such case. β_0 fixes the intercept of three-axial geometric view. $\beta_1, \beta_2, \beta_3$ are the *partial regression coefficients* of main effects of independent parameters in the equation. $\beta_{12}, \beta_{13}, \beta_{23}$ and β_{123} are the coefficients of two factor and three-factor interactions, respectively. ε is the random error comes from the uncontrollable variables given in the equation (1.2) [70-79].

The model can be fitted by adding the data with replications of runs or center points but the analysis of variance and checking of the model adequacy must be done.

Table 1.6 : Design Matrix for 2^3 Factorial Design.

# of runs	Factors X1	Factors X2	Factors X3	Effect	Degrees Of Freedom
1	-	-	-	Intercept	1
2	+	-	-	X1	1
3	-	+	-	X2	1
4	+	+	-	X1.X2	1
5	-	-	+	X3	1
6	+	-	+	X1.X3	1
7	-	+	+	X2.X3	1
8	+	+	+	X1.X2.X3	1

$$y = \beta_0 + \beta_1.x_1 + \beta_2.x_2 + \beta_3.x_3 + \beta_{12}.x_1.x_2 + \beta_{13}.x_1.x_3 + \beta_{23}.x_2.x_3$$
$$+\beta_{123}.x_1.x_2.x_3 + \varepsilon \qquad (1.3)$$

1.2.1.3 Response surface methods and designs

As a common definition in almost all resources, Myers and Montgomery [70] define the Response surface methodology (RSM) is a collection of mathematical and statistical techniques which is convenient for modeling and investigation in applications where a response of interest is influenced by a number of variables and also optimize the examined responses. After the factor screening study and the characterization of how a factor affects the response variables within the experimental region, response surface methodology is the following study to determine the setting of independent variables to get the desired value of response variables.

If the means of independent variables for the responses is unknown at the beginning of RSM analysis, the important step is to find the suitable approximation for the true functional relationship between y and the set of independent variables. If there is a linear relationship between the response and the independent variables, the *first order model*, equation 1.4, approximation is obtained. If response surface of system has curvature or saddle, the *second order* equations 1.5 or higher polynomial orders is suitable approximations to get a true functional relationship [74-79].

$$y = \beta_0 + \beta_1 . x_1 + \beta_2 . x_2 + \cdots + \beta_k . x_k + \varepsilon \tag{1.4}$$

$$y = \beta_0 + \sum_{i=1}^{k} B_i \, . \, x_i + \sum_{i=1}^{k} B_{ii} \, . \, {x_i}^2 + \sum_{i<j}^{k} B_{ii} \, . \, x_i . x_j + \varepsilon \tag{1.5}$$

Although a first order model involving main effects and interactions are appropriate to define a response surface of a process, there should be a quadratic or cubic model to understand the whole behavior of process. Equation 1.6, 1.7 and 1.8 represents the linear, quadratic and cubic models for three factor example [80]. Also, Figure 1.17 shows the graphical and response surfaces examples of model orders.

$$y = \beta_0 + \beta_1 . x_1 + \beta_2 . x_2 + \beta_3 . x_3 + \varepsilon \tag{1.6}$$

$$y = \beta_0 + \beta_1 . x_1 + \beta_2 . x_2 + \beta_3 . x_3 + \beta_{12} . x_1 . x_2 + \beta_{13} . x_1 . x_3 + \beta_{23} . x_2 . x_3 + \beta_{11} . x_1^2 + \beta_{22} . x_2^2 + \beta_{33} . x_3^2 + \varepsilon \tag{1.7}$$

$$y = \beta_0 + \beta_1 . x_1 + \beta_2 . x_2 + \beta_3 . x_3 + \beta_{12} . x_1 . x_2 + \beta_{13} . x_1 . x_3 + \beta_{23} . x_2 . x_3 + \beta_{11} . x_1^2 + \beta_{22} . x_2^2 + \beta_{33} . x_3^2 + \beta_{123} . x_1 . x_2 . x_3 + \beta_{112} . x_1^2 . x_2 + \beta_{113} . x_1^2 . x_3 + \beta_{122} . x_1 . x_2^2 + \beta_{133} . x_1 . x_3^2 + \beta_{233} . x_2 . x_3^2 + \beta_{111} . x_1^3 + \beta_{222} . x_2^3 + \beta_{333} . x_3^3 + \varepsilon \tag{1.8}$$

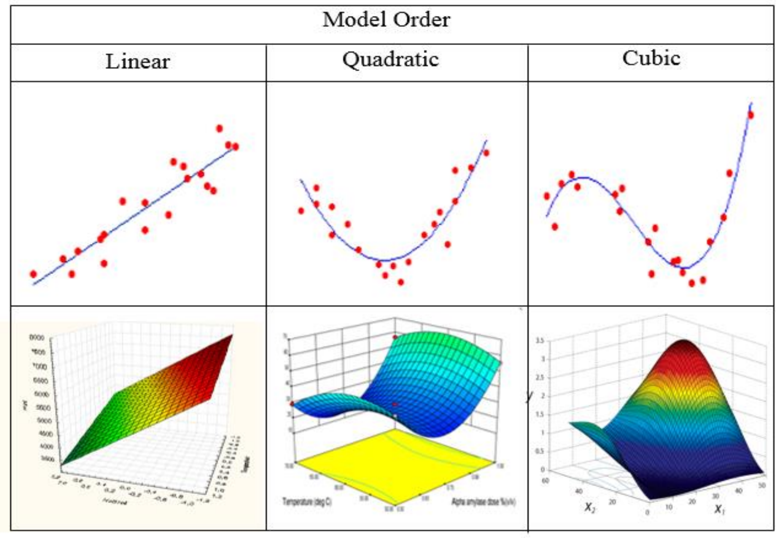

Figure 1.17 : Higher Order Polynomial Models and Response Surface Examples.

The operating conditions of any system may have a little curvature throughout the small limits and the first order model may be shown appropriate but the objective here is to arrive the optimum point with rapid and the most efficient way. The sequential nature of RSM consists of three phases for this type of systems;

Phase 0- Screening Experiment: Eliminating the unimportant factors

Phase 1- Steepest ascent/descent: Determination of where the collected data lie relative to an ideal response and possible setting of independent variables to approach the optimum

Phase 2- Response Surface Study: Fitting a model to estimate accurately approximate the true response function around the optimum point. Since the true response surface usually consists curvature near the optimum, second or higher order model is applied to find the optimum after once an appropriate approximating model has been obtained [82] .

Central Composite Design (CCD) or Box-Behnken Design are used to obtain a second order model for response surface study. There are three types of CCD; Central Composite Circumscribed (CCC), Central Composite Inscribed (CCI), Central Composite Face (CCF). Experimentally data points of the three independent variables for the different Central Composite designs and Box-Behnken design is given in the Figure 1.18 [81,82].

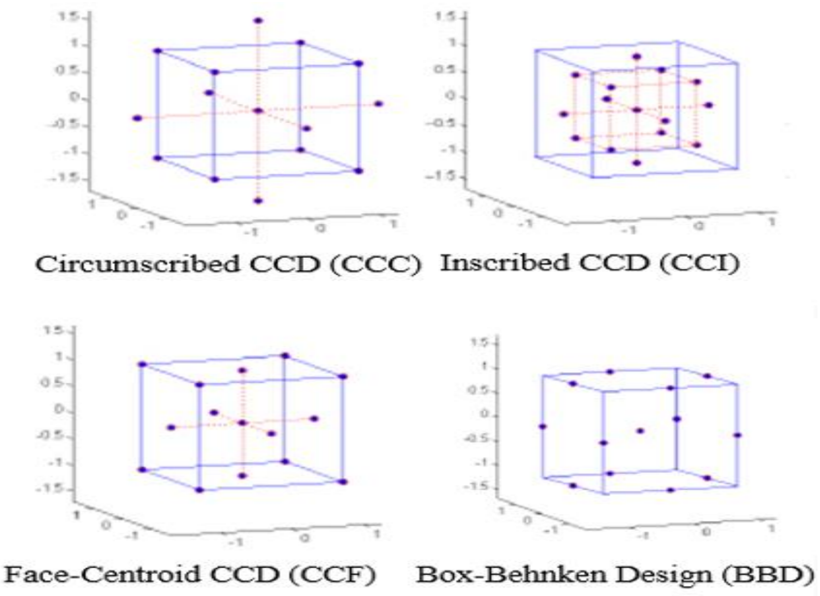

Figure 1.18 : Second Order Model Designs for Response Surface Study [82].

1.2.1.4 Testing of a model and analysis of variance (anova)

The general method to estimate the regression coefficients and test a multiple linear regression model is to control the sum of the squares of errors. Fitting a model can be performed by making regression to find coefficients that are giving minimum sum of squares. Herein *R-Squared* is another parameter to measure of how close the data are to the fitted regression line. R-squared is known as coefficient of determination. R-squared value is always between 0-1 and is calculated by using equation 1.9.

$$R^2 = 1 - \frac{Sum\ of\ squared\ distances\ btw.the\ actual\ and\ predicted\ response\ values}{Sum\ of\ squared\ distances\ btw.the\ actual\ response\ values\ and\ their\ means} \qquad (1.9)$$

The higher R^2 value means that the reduction of amount of variability of response obtained by using determined variables in the model. However a large value of R^2 does not mean the model fits better. Adding a new variable or data can be increase the value of R^2, but this adding value may not significant statistically for the model. To control the significant effect of adding a new variable to the model, *Adjusted-R^2* , or *R^2-adj* is used. The formula given in the equation 1.10 is used to calculate the Adjusted-R^2. "n" is the number of observations and "p" is the number of parameters using in the model.

$$R^2{}_{adj} = 1 - \frac{n-1}{n-p}(1 - R^2) \qquad (1.10)$$

Unnecessary terms for the model lower the Adjusted-R^2 values. Another concept for the R^2 is Predicted-R^2 that is to control how well the model predicts the responses for new observations. equation 1.11 shows the formula to determine the *R^2-Predicted*

$$R^2{}_{predict} = 1 - \frac{Predicted\ residuals\ sum\ of\ squares}{Total\ sum\ of\ Squares} \qquad (1.11)$$

After the determination of R^2, R^2-adj and R^2-Predicted values, testing of significance of individual independent variables and model should be performed by using Analysis of Variance (ANOVA). While analysis of variance some data have to be calculated such as mean, variance, standard deviation, standard error and confidence ıntervals. Table 1.7 consists of the equations required for ANOVA. "Y_i" is the individual response and "n" is the observation [81].

While *Mean* shows the average value of n number of responses, *Variance* represents the difference between the highest and lowest value of responses. The common report for the variability of responses is *Standard Deviation* which is the square root of variance. The standard deviation of a mean is called as *Standard Error*. However the term "*confidence ınterval*" is generally used statistically instead of standard error. The general acceptance for the value of confidence interval is %95 that means the value of mean of a population may have plus or minus %5 standard error.

Before the testing, the alpha level, also called as the significance level, should be determined. The typical value for the alpha level is 0.05.

Hypothesis testing, in most generic form is that;

- Null hypothesis – $H=H_o$
- Alternative hypothesis – $H \neq H_o$

Table 1.7 : Notations and Formulas of Some Statistical Terms [81].

Definition	Notation	Formula
Mean (Average)	$\bar{Y}$	$\bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n}$
Variance (Range)	s^2	$s^2 = \frac{\sum_{i=1}^{n} (Y_i - \bar{Y})^2}{n-1}$
Standard Deviation	s	$s = \sqrt{\frac{\sum_{i=1}^{n} (Y_i - \bar{Y})^2}{n-1}}$
Standard Error	SE	$SE \cong \sqrt{\frac{s^2}{n}}$
Confidence Interval of a Mean	CI	$CI = \bar{Y} \pm t \times SE$

Alpha level is the probability of rejecting the null hypothesis when the null hypothesis is true. After calculation of the probability of $H=H_o$ is true (1-p value), and the comparison of p-value and alpha show the significance of an independent variable and model.

- If p-value > alpha – $H \neq H_o$
- If p-value < alpha – $H=H_o$

F-test is also used to compare two or more treatments. This technique compares the variance among the treatment means versus the variance of individuals within the specific treatments and this procedure is also called as one-way ANOVA which is also test for Type I error (null hypothesis) rate a α=0.05.

Many more tests like mentioned above can be applied for different purposes such as Q-test to decide on outliers in data sheet or T-test for comparison of means of two populations or parameter estimation [83].

2. EXPERIMENTAL STUDY

Bitumen contains a wide range of hydrocarbon molecules and the properties of bitumen are affected by the fraction of these molecules that is the SARA content, mentioned in Section 1. Another important concept is the modification of bitumen and the development of the asphalt properties. The change of properties of bitumen by the addition of some additives such as polymer or viscosity decreasing agent is simultaneously affected by the type of the bitumen. thus the aim of this study was determined as the understanding of the simultaneous effect of variation of bitumen composition, amount of polymer and warm mix additive on the bitumen properties. For this purpose, the experimental procedure and analysis were applied to get the required information.

2.1 Materials

2.1.1 Bitumen

Three neat bitumen samples from different origins, İzmit, İzmir and Batman, were supplied by Turkish Petroleum Refineries Corporation (TUPRAS). The samples have same penetration grade, Penetration 50/70. The bitumen products sales from the TUPRAS have the specifications for paving grade bitumens-TS EN 12591. The physical properties of bitumens used into the experiments were given in the Table 3.1. Since the properties of bitumen can change with time by changing of crude oil processed in the refinery, the samples were stored in excess amount at the beginning of experiments and the same bitumens from one source were used to while performing experiments. Also, SARA (Saturate, Aromatic, Resin and Asphaltene) content of stored bitumen samples were determined by the service procurement.

2.1.2 Polymer

Styrene-Butadien-Styrene (SBS) triblock copolymer were supplied form Kraton Polymers Inc. It is a linear block copolymer based on styrene and butadiene with bound styrene of 30% mass. The powder form of polymer were preferred for mixtures due to the low shear mixer setup. The sales specifications and typical properties of SBS polymer were listed in Table 2.1.

Table 2.1 : Specifications and Typical Properties of SBS Copolymer.

Property	Test Method	Units	Range
Vis, Sol (Toluene) 25.0%w @25	KM 06	Pa.s	1.4 to
Molecular Weight	KM 01	kg/mol	138 to
Polystyrene Content	KM 03	%m	28.5 to
Vinyl Content	KM 03	%	≥35
Triblock Content	KM 01	%	≥90
Total extractable	KM 05	%m	≤1.0
Volatile Matter	KM 04	%m	≤0.3
Antioxidant Content	KM 08	%m	≥0.16
Ash(AS, AT)	ISO 247	%m	0.1 to
Ash(ATM)	BAM 908	%w	4.0 to
Ash(ASM)	ISO 247	%m	2.5 to
Typical Properties			
Property	Test Method	Units	Typical
Hardness, Shore A(15sec)	ASTM D 2240	Hardnes	70
Bulk density	ASTM D 1895 method B	kg/dm^3	0.4
Specific gravity	ISO 2781		0.94
Melt Flow Rate, 200C/5kg	ISO 1133	g/10min	<1

2.1.3 Warm mix additive

Sasobit, synthetic hard paraffinic wax, produced by means of Fischer–Tropsch process were supplied by Sasol Wax. This additive composed of fine crystalline long aliphatic hydrocarbon chains which has generally 22-40 carbon. Low shear mixing were applied to prepare the wax added mixtures and the granular form of Sasobit were used in experiments. Because the mixing of bitumen and wax is an easy process and there are not any homogeneity problems.

2.2 Preparation of Modified Bitumen Samples

A mixing procedure were formed for the tertiary mixtures of bitumen, SBS and Sasobit and all samples in the test matrix were prepared by using procedure given below.

-Before mixing the neat bitumen was kept in the oven at 130 ^oC until the bitumen became soft enough for preparing mixtures (according to EN 12594).

-Low shear mixer (Figure 2.1), namely, IKA RW-20 mechanical stirrer having three-blade propeller was used for the preparation of modified samples.

-The bitumen heated at 130 °C in the oven was placed into the mechanical stirrer, and then heated until the temperature reaches 160 ^oC with agitation speed of 120 rpm. After that, determined amount of SBS was added slowly while the temperature was increasing from 160 ^oC to 180 ^oC.

-The mixing continued for 1 h at 180 ^oC and then the temperature was decreased to 140 ^oC. Desired amount of Sasobit wax was added to the bitumen-SBS sample at 140 ^oC and the mixing is continued to 15 min at 400 rpm/ 140 ^oC. At the end of this procedure the sample was cooled down and stored for the analysis.

Figure 2.1 : Preparation Setup of Modified Bitumen.

2.3 Analysis Methods

2.3.1 Characterization analysis of materials

The properties of neat bitumen and other materials used in the experiments should be determined to fully understand that how affects an additive to the bitumen characteristics.

Characterization of Neat Bitumen

Since the effect of bitumen chemistry on the properties of modified bitumen is one of the main objectives of this study, the bitumen chemical content were analyzed. The chemical composition of a bitumen, SARA content, had been mentioned the Section 1.1.1.2. Thus, the SARA contents of three different bitumen samples were built by Turkish Petroleum (TPAO) Laboratories with using the method of service procurement. Firstly, Asphaltenes in the bitumen samples were separated by method of precipitation in n-hexane, then the amount of Saturates, Aromatics, and Resins were determined by using the Iatroscan Thin Layer Chromatography-Flame Ionization Detector.

Besides the bitumen chemical content of bitumen samples, the sales specification tests which covers the TS EN 12591 Bitumen standard were performed. Additionally, the standard tests for the modified bitumens, TS EN 14023, tests were carried out and the performance grades of this bitumen samples were determined.

To control the bitumen samples have similar properties with the conventional bitumen samples studied in the literature and to investigate the differences between the three samples, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and GC-Simdis analysis were done.

Characterization of Additives

Similar with the bitumen samples, FTIR analysis were carried out to characterize the SBS and Sasobit additives. Also, DSC analysis were done to determine the thermal transition temperatures such as glass transition and melting temperatures. The loss of weight of SBS and Sasobit with increasing of temperature were determined by the TGA and the mixing procedures of additives were designed with this information. DSC and TGA analysis were carried at the conditions were given below.

- DSC; 5-10 mg bitumen were poured into the DSC sample pan and the temperature were set from -60 ^{o}C to 200 ^{o}C with the 5 ^{o}C/min temperature rate under the nitrogen flow.
- TGA; 5-10 mg bitumen were poured into the TGA sample pan and the temperature were set from 35 ^{o}C to 600 ^{o}C with the 5 ^{o}C/min temperature rate under the nitrogen flow.

2.3.2 Analysis of modified bitumen samples

After the modified bitumen samples which consist both polymer and wax in different percentages were prepares, the bitumen tests that are important by the means of performance and workability were conducted. These tests are dynamic shear rheometer (DSR), Viscosity, Elastic recovery and Bending beam rheometer (BBR).

Dynamic Shear Rheometer (DSR-TS EN 14770)

DSR test was used to determine the viscous and elastic behavior of bitumen binder. Thus, it was determined that the bitumen binder has or not adequate elasticity to show a resistance against to rutting and cracking problems. A bitumen sample was placed between a fixed plate and an oscillating plate in DSR test and an oscillatory stress was applied that is given in the Figure 2.2.

During the test, the oscillating plate starts to motion from point A and arrives to point C after passing through the point B for the one pass.

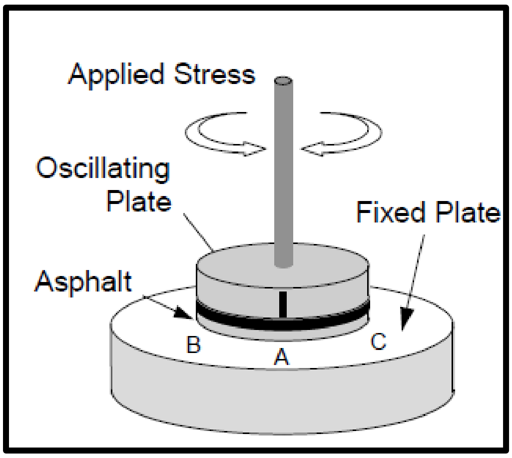

Figure 2.2 : Applied Oscillatory Motion During DSR Test [84].

The temperature during the test should be kept constant since the physical properties of bitumen can changes depends on the temperature. The amount of gap (1 mm or 2 mm) between oscillating and fixed plates depends on the type of the bitumen which is un-aged original binder, RT-FOT-aged (Rolling Thin Film Oven Test) bitumen or PAV-aged (Pressure Aging Vessel) bitumen. Similar with the gap position, the starting test temperature can change with the type of bitumen. Since the modified bitumen samples that were prepared for this experimental study were not aged by RTFOT or PAV, the gap position was kept to 1 mm and the starting temperature is 64 ^{o}C. The bitumen sample which will be tested was poured to silicone molds and was cooled to room temperatures. After the equipment reaches to test temperature, bıtumen sample was placed into the plate and the upper plate started to motion with 10 rad/sec for 10 cycle. The values of Complex modulus (G*) and phase angle were recorded for each cycle and the maximum temperature between the acceptable limits for the complex modulus and phase angle which are given below was recorded as the high-temperature performance of bitumen sample.

Original Binder [G*/sin(delta) > 1.0 kPa]

RTFOT-Aged Binder [G*/sin(delta) > 2.2 kPa]

PAV-Aged Binder [G*/sin(delta) < 5000 kPa]

Viscosity (TS EN 13302)

Test was performed to determine the viscosity of bitumen while it reaches the high temperatures during the road construction and paving studies. Rotational viscometer analysis was carried out to obtain the ınformation that the fluidity of bitumen sample is or not adequate for the pumping, mixing and workability. The required torque value for the rotating of cylindrical mil that was immersed in bitumen sample at 135 ^{o}C at constant speed, 20 rev/min, was measured. Three different dynamic viscosity values were recorded after the temperature and mixing speed stabilizes. The average of three measured values in the unit of cP (centipoise) was calculated as the dynamic viscosity of bitumen at 135 ^{o}C.

Elastic Recovery (TS EN 13398)

The test was used to determine the maximum pulling length of bitumen sample does not break or the elasticity of bitumen in other words. Two different standard experiments which are TS EN 13589 Force Ductility and TS EN 13398 Elastic Recovery tests can be done with the ductilimeter. For the The TS EN 13398 Elastic Recovery test, the melted bitumen sample was poured into the ductility molds given in the Figure 2.3 and waited at 30 minutes at room temperature. After the additional waiting steps for 120 minutes under the water bath at 25 ºC, the mold was placed into the device and the parts of the mold were pulled to opposite directions up to the length of sample reaches the 20 cm. The samples was also waited to 30 minutes after the pulling process. Finally the length of the sample was divided by the original length and the percentage of elastic recovery was obtained.

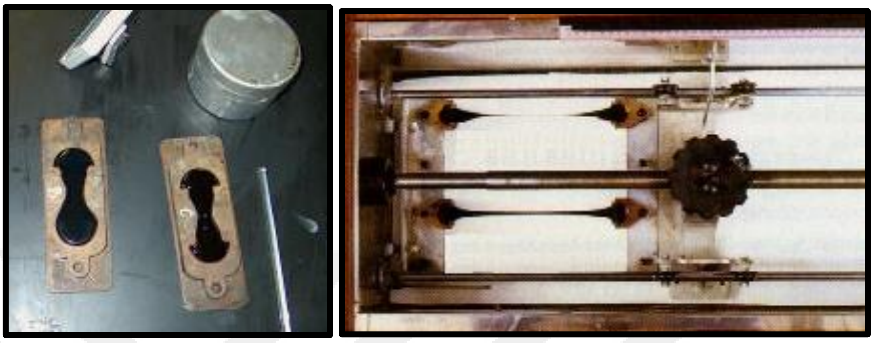

Figure 2.3 : Ductilimeter Molds and Test Field.

Bending Beam Rheometer (BBR-TS EN 14771)

The test provides creep stiffness of bitumen at low temperatures and used to determine the low temperature performance according to SUPERPAVE grading system. Two parameters that are creep stiffness and m-value were determined by using BBR test. While creep stiffness shows the resistance of bitumen under the constant load, m-value is the indicator of the change of creep stiffness with the load. The molds given in the Figure 2.4 were used to prepare the bitumen test sample. Heating and cooling cycles were applied to the samples for 1 hour. Also the sample was conditioned for 60 minutes in BBR bath containing the mixture of ethylene glycol, methanol and water.

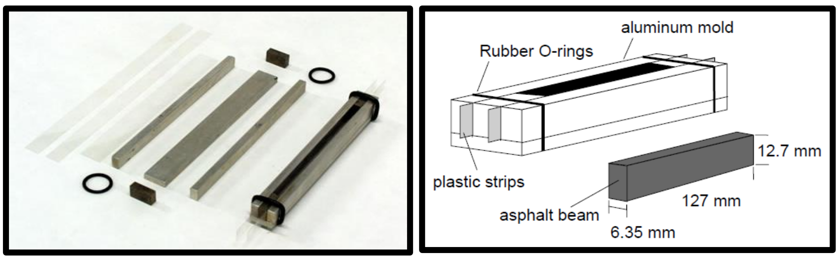

Figure 2.4 : BBR Test Molds and Preparation of Test Samples.

BBR tests were conducted on PAV aged asphalt binder samples. 100 g of load was applied to the center of the beam placed into BBR bath and the deformation versus time on the beam were recorded that is shown in Figure 2.5 the value of creep stiffness was obtained by using the recorded data of deflection. Also the relaxation of bitumen beam is measured while the load on the beam is removed. If the recorded creep stiffness and m-value was in the acceptable limits (m-value≤0.3 and creep stiffness(S)≥300 MPa) for test temperature, 10 °C added value of the test temperature was accepted for the low-temperature performance of bitumen sample.

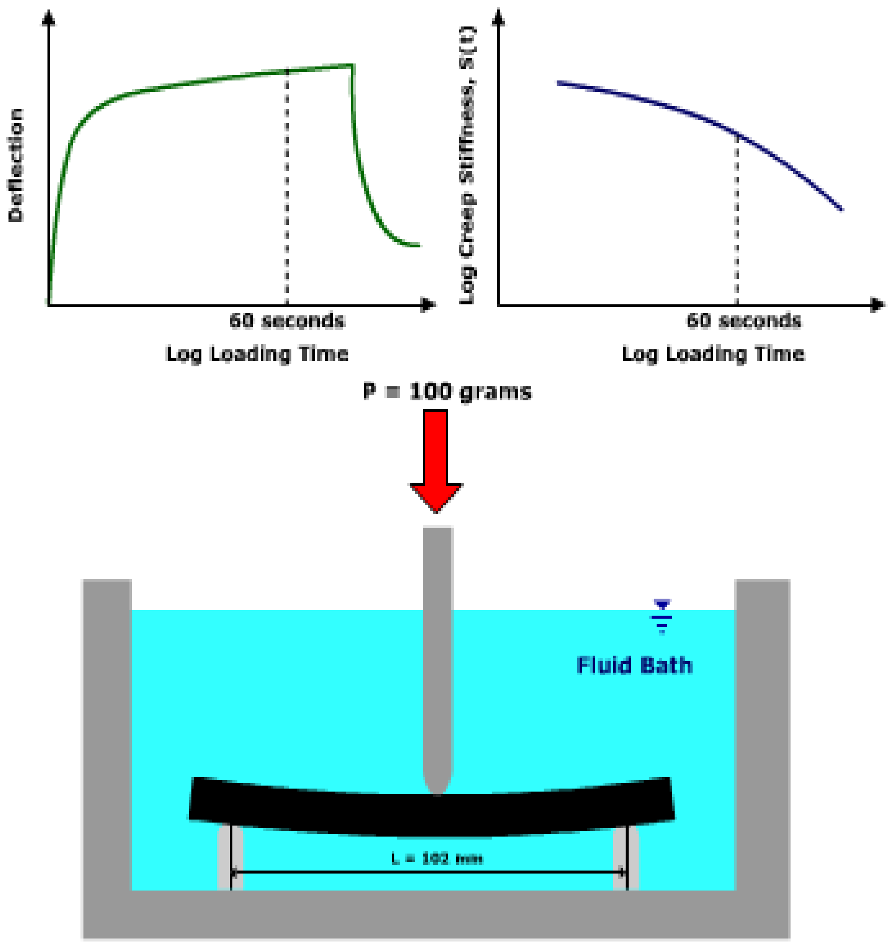

Figure 2.5 : Working Principle of BBR Test [85].

2.4 Design of Experiment

The parameters that affect the properties of bitumen were chosen as independent variables as the suitable for the purpose of this study. These parameters are bitumen SARA content, Amount of polymer and the amount of warm mix additive. Since a bitumen having different percentages of SARA components, there should be a normalized value to represents composition of a bitumen. Gaestel Index (GI) were used to normalize the SARA content to an ındex for one type of bitumen. The formula of Gaestel Index were given in the equation 1.1 and the GI of the selected bıtumen were calculated. Then the ranges of the independent variables and the response factors of bitumen were selected and the Table 2.2 were formed.

Table 2.2 : The Independent Variables and Response Functions of The Design of Experiment.

Source	Independent Variables	Ranges	Response Functions
Bitumen (İzmit/İzmir/ Batman)	GI	0.487-0.622-0.988	DSR, °C Viscosity, cP
SBS	Polymer	2-5, (%)	Elastic Recovery,%
Sasobit	Warm Mix Additive	1-3,(%)	BBR, S-value

Table 2.3 : 2^3 Factorial Screening Design of Experiment.

# of Experiment	Independent Variables			Coded Parameters		
	Gaestel Index	Polymer	Warm Mix Additive	GI	SBS	WAX
1	0.622	2	1	0	-1	-1
2	0.622	3.5	2	0	0	0
3	0.988	5	3	+1	+1	+1
4	0.487	2	3	-1	-1	+1
5	0.487	5	3	-1	+1	+1
6	0.988	3.5	2	+1	0	0
7	0.988	2	1	+1	-1	-1
8	0.988	2	3	+1	-1	+1
9	0.622	5	3	0	+1	+1
10	0.487	3.5	2	-1	0	0
11	0.487	2	1	-1	-1	-1
12	0.622	5	1	0	+1	-1
13	0.487	5	1	-1	+1	-1
14	0.487	3.5	2	-1	0	0
15	0.988	5	1	+1	+1	-1
16	0.622	2	3	0	-1	+1

Full factorial design were used to investigate the whole effect of three independent variables on the bitumen properties were defined as response factors. Table 2.3 shows the matrix of modified bitumen samples for full factorial design.

A statistical tool, JMP® software, were used to design of experiment and RSM analysis in this study. As it was mentioned in Section 1.2.1.2, 2^3 factorial design were formed for three independent variable full factorial design. As the first step of RSM analysis, the screening experiments were done and the most effective variables were determined. Addition to the 2^3 factorial design, there are third level for GI ındex due to the discrete numeric value of this independent variable. Thus the kind of design has 16 experiment that consists of main effects, two level interaction, three level interaction, four replication of center point.

After the screening analysis for four different response functions, the significant parameters for the responses were determined and the RSM analysis were performed to obtain a model for optimum result.

2.5 Bitumen and Asphalt Tests of Optimum Mixture Formulation

Performance tests were carried out to modified bitumen which has the polymer and wax at optımum condition were found with the RSM analysis. Firstly, tests within the scope of TS EN 14023 Polymer Modified Bitumen Standard were performed to determine the performance grade of optimum mixture. Then the asphalt design were studied to find the optimum percentage of modified bitumen which is added to the asphalt mixture. Thereafter, the asphat samples were prepared with the amount of bitumen that found by the design study and performance test were performed. These design and performance test steps were applied to two bitumen samples that were the neat Batman bitumen and modified Batman bitumen at optimum conditions ın this study.

The design of asphalt mixture were performed by using MS-2 method (Marshall) design. The mixture of aggregates and bitumen with different percentages form 4% to 7% (4%, 4.5%, 5%, 5.5%, 6%, 6.5%, 7%) were prepared and compaction were applied to obtain the cylindrical samples were given in Figure 2.6 The samples were weighed before and after the air and water conditioning procedure to calculate the practical specific gravity, air void, void filled with bitumen and voids in mineral aggregates.

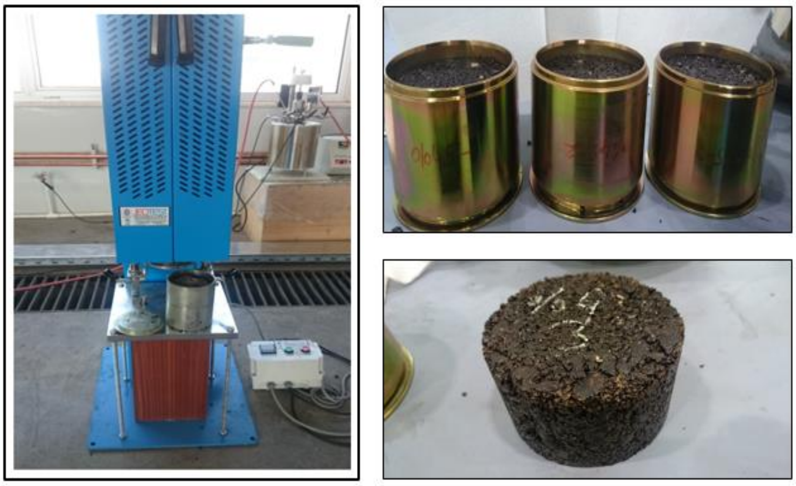

Figure 2.6 : Marshall Compactor and Compacted Asphalt Samples.

The stability and flow values were measured by the equipment were shown in Figure 2.7 at final step of design of asphalt mixture. After the results were collected, the graph of stability, flow, practical specific gravity, void, void filled with bitumen and voids in mineral aggregates versus bitumen content were plotted. The amount of bitumen at which the %4 Void was seen is determined as optimum bitumen percentage for the mixtures with aggregates.

Figure 2.7 : Marshall Stability and Flow Tester.

In order to visualize the performance of the asphalt mixture under the repeated load on the road, the wheel tracking test were conducted and the change on the depth of an asphalt sample which was prepared on the roller compactor was calculated. The equipments required for the wheel tracking test from making asphalt mixture to wheel tracking were shown in Figure 2.8.

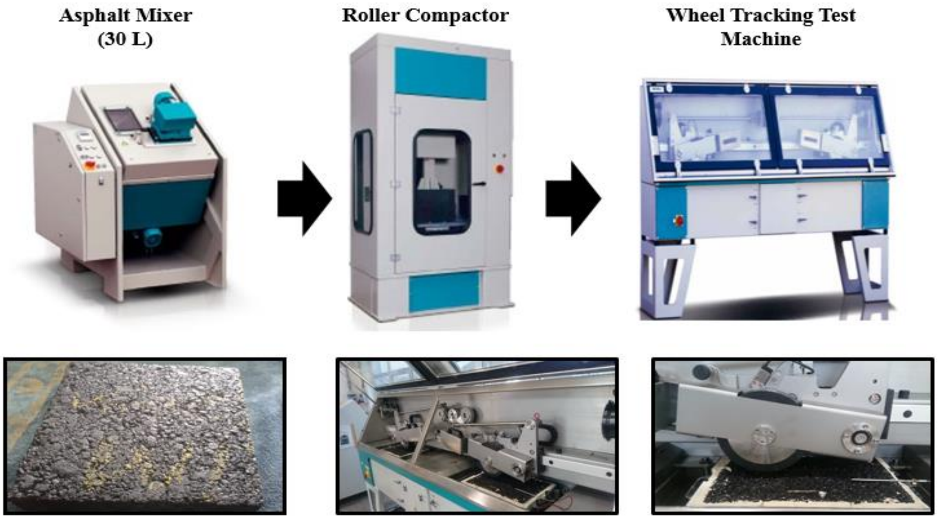

Figure 2.8 : Testing of Asphalt Performance by Wheel Tracker.

3. RESULTS AND DISCUSSION

3.1 Characterization of Materials

Bitumen, polymer and warm mix asphalt additive were used as the materials in this study and the characteristics of these materials were vital for the both experimental procedure and the comment the results. To know the nature of a material also helps to understand of experimental errors and unexpected results.

3.1.1 Tests results of bitumen

Conventional Tests of Bitumen

The bitumen samples obtained from the different regions were tested according to the TS EN 12591 and TS EN 14023 Standards. TS EN 12591 is the sales specification of the bitumen and generally consists of physical properties of bitumen. Penetration is one of the test of TS EN 12591 standard and also represents the grade of bitumen. The test results for the TS EN 12591 were shared in Table 3.1.

Table 3.1 : TS EN 12591 Test Results of Bitumen Samples.

Property	Test Method	Unit	İzmit	İzmir	Batman
Penetration at 25 ^oC	EN 1426	0,1 mm	57	54	57
Softening point	EN 1427	^oC	48.4	49	50.7
Resistance to hardening at 163 ^oC		-	-	-	-
Retained penetration		%	67	65	54
Increase in softening point, Decrease in softening point	EN 12607-1	^oC ^oC	5.8	5	8.4
Change of mass ^{b} (absolute value)		%	0.07	0.03	0.46
Flash point	EN ISO 2592	^oC	304	330	262
Solubility	EN 12592	%	99.85	99.95	99.80
PENERATION GRADE	EN 12591	-	50-70	50/70	50/70

For determination of performance grades of bitumen samples according to the polymer modified bitumen Standardization, TS EN 14023 and AASHTO MP1a, the tests given in the Table 3.2 were carried out. Although the all samples are same penetration grade, the performance grade of Batman bitumen was found as higher than the other region's bitumens.

Table 3.2 : TS EN 14023 Test Results of Bıtumen Samples.

#	TEST NAME	Standard	Unit	İzmit	İzmir	Batman
1	Penetration (25 ºC, 150g, 5sn)	TS EN 1426	0.1 mm	57	54	57
2	Softening Point	TS EN 1427	ºC	48.4	49	50.7
3	Elastic Recovery[b] (25 ºC)	TS EN 13398	%	7	5	10.5
4	Flash Point	TS EN 2592	ºC	304	330	262
5	Specific Gravity	TS EN 15326	g/cm^3	1.03164	1.03633	1.04303
6	Dynamic Shear Rheometer (DSR) ($G^*/\sin\delta > 1$ kPa)	TS EN 14770	ºC	67.9	67.8	71.3
7	Rolling Thin Film Oven Test (RTFOT)[d]	TS EN 12607-1		+	+	+
7.1	Change of Mass		%	0.07	0.03	0.46
7.2	Increasing in Softening Point	TS EN 1427	ºC	5.8	5	8.4
7.3	Retained Penetration	TS EN 1426	%	67	65	54
7.4	Dynamic Shear Rheometer (DSR) ($G^*/\sin\delta > 2.2$ kPa)	TS EN 14770	ºC	66.8	67.9	76.8
8	Tests For RTFOT and Pressure Aging Vessel (PAV) Aged Bitumen	TS EN 14769		+	+	+
8.1	(DSR) ($G^*/\sin\delta < 5000$ kPa)	TS EN 14770	ºC	26.7	30.6	25.8
8.2	Bending Beam Rheometer (BBR) Creep Stiffness ($S \leq 3000$ MPa, $m \geq 0.300$)	TS EN 14771	ºC	-22	-22	-22
	PERFORMANCE GRADE	TS EN 14023/ AASHTO MP1a	-	PG 64-22	PG 64-22	PG 70-22

Determination of SARA Composition

The compositions of bitumen samples were determined since the SARA content is the one of the independent variables of design of experiment. The SARA analysis of bitumen samples by Iatroscan analysis were done by the method of service procurement. The reported values of SARA content of three samples were given in

Table 3.3 and the GI values were determined by using the equation 1.1. Also the report format was attached to the APPENDIX A.

As can be shown in Table 3.3, Three bitumen samples having same penetration grade has different percentages of SARA and depend on these composition the GI values were found as different. While Batman bitumen was found as having highest asphaltene content, İzmir bitumen has lowest.

Table 3.3 : SARA Composition and Calculated GI Values of Bitumen Samples.

Coded Name in The TPAO Report	Bitumen	Saturates, %	Aromatics, %	Resins, %	Asphaltenes, %	GI value
EB101	İzmit	14.91	51.59	10.08	23.42	0.622
EB102	İzmir	11.86	54.46	12.8	20.88	0.487
EB103	Batman	15.3	45.03	5.26	34.41	0.988

Although the production processes of these bitumens were similar, the crude oils to obtain the bitumen may differs. Batman bitumens are obtained by using only domestic crude oils found in domestic reserves. The key point is that the sales specification, penetration grading system, say these bitumen are the same, although it doesn't say that their chemistry. This difference effects the whole performance and modification of bitumen.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR is a analytical method to identify the organic, polymeric materials. This spectroscopic method were performed to investigate the molecular titrations of the three different bitumen. Figure 3.1-a shows the FTIR spectrums of bitumen samples which had been almost same peaks. The peaks at 2923 cm^{-1}, 1464 cm^{-1} and 724 cm^{-1} are the result of different vibrations of carbon-hydrogen (C-H) bonds in the hydrocarbon backbones of bitumen.

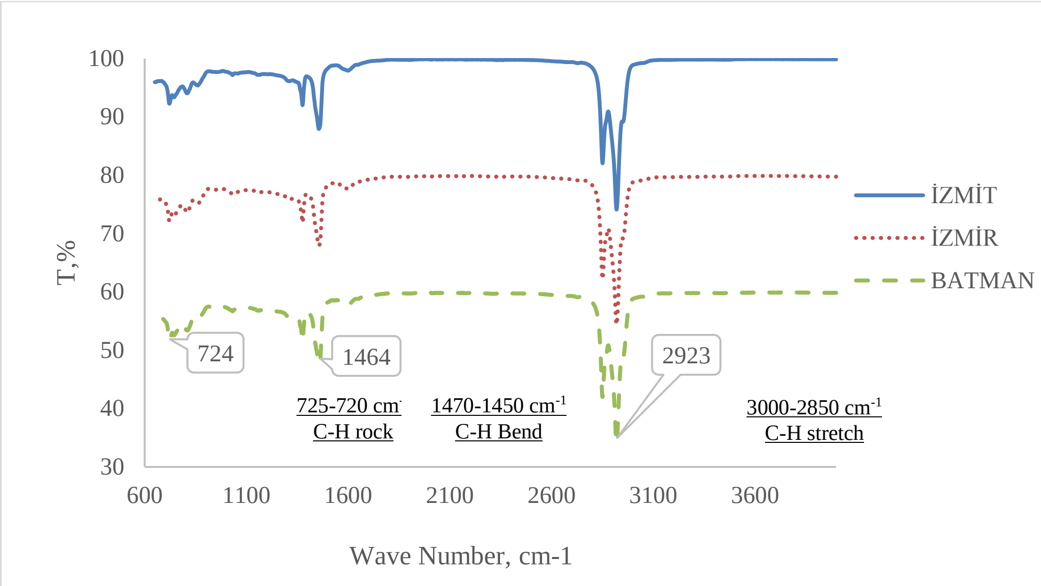

Figure 3.1-a : FTIR Spectra of Bitumen Samples.

The FTIR result showed that the vibrational motions of bıtumen molecules was not sufficient to show the differences of chemical compositions of bitumen samples. Similar with the result of three bitumen samples, the FTIR spectrums of bitumens from different origins can have same molecular vibrational peaks such as the spectra of bitumen given in the Figure 3.1-b. Due to the hydrocarbon content of bitumen, the titration of carbon-hydrogen bond in both literature information and analyzed samples were dominantly seen.

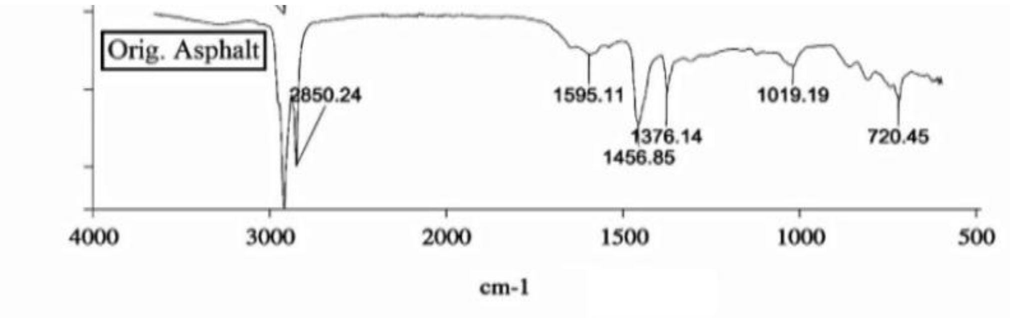

Figure 3.1-b : FTIR Spectra of Bitumen Given in the Literature [86].

GC-Simdis Analysis

Simulated distillation gas chromatography (GC-SimDis) analysis is used to analyze the composition of petrochemical products such as oils or gas etc. by measuring the boiling point range distribution of the sample component. Figure 3.2 represents the distillation curves of bitumen samples that are analyzed by the GC-SimDis. The curves are clearly show that Batman bitumen starts to boil at lower boiling temperatures and almost same final boiling point with other bitumens although it has the highest asphaltene content. If the asphaltene molecules effect the boiling range, the higher boiling temperature was expected to the Batman bitumen. On the other hand, although the amount of saturates in Batman and İzmit bitumens are similar, the distillation profiles are different. The reason of lower initial boiling point of Batman bitumen may results from the difference in the production method. While the Batman bitumen is produced by the atmospheric distillation, İzmit and İzmir bitumens are obtained with both atmospheric and vacuum distillation process. Therefore same penetration bitumens which are produced by different processes, can have varying amount of lighter components in the same type of bitumen fractions. Although the amount of saturates in the Batman bitumen are similar with the İzmit bitumen, the chains of saturates are short and molecular weights are low in the Batman bitumen. This difference results in a lower initial boiling point of Batman bitumen.

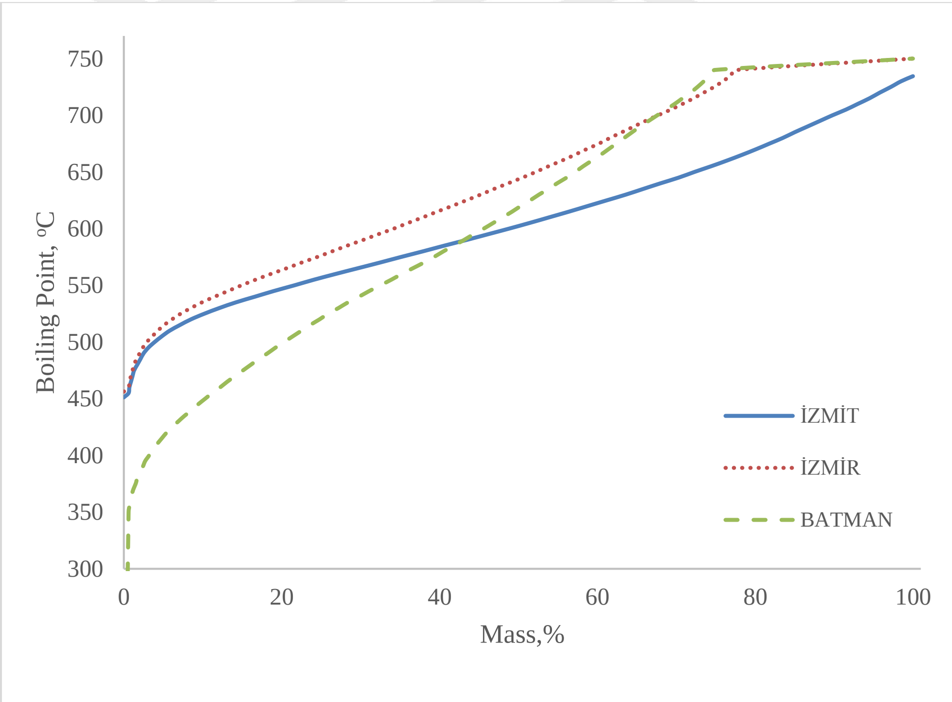

Figure 3.2 : Distillation Curve of Bitumen Samples by GC-Simdis Analysis.

Thermal Behavior Analysis (DSC and TGA)

Differential Scanning Calorimetry (DSC) analysis were used to characterize the thermal behavior of bitumen samples. Meting point, Cyrstalization point and galss transition point can be determined by using DSC analysis. Therefore the type of transition changes with respect to material structure. While crystalline materials shows sharp melting temperature transition, amorphous materials have only glass transition temperature on the DSC spectrum.

The DSC analysis results of three types of bitumen samples were shared at Figure 3.3. Since the bitumen was a amorphous material, there were not shown a melting point peak. However the glass transition of three bitumen samples were detected.

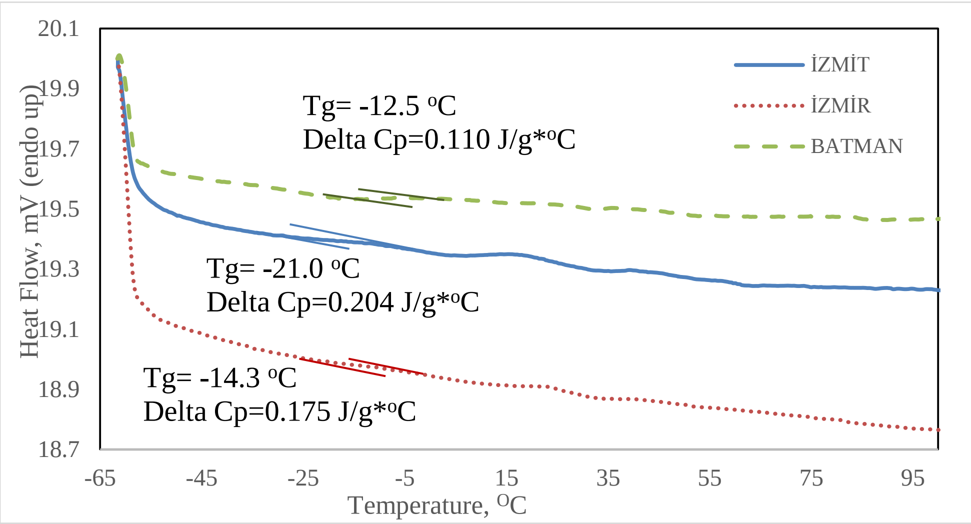

Figure 3.3 : DSC Thermogram of Bitumen Samples.

Table 3.4 : Glass Transition Temperatures of 15 Different Bitumen [87].

ASPHALT	Tg (ᵒC)	Delta Cp ($Jg^{-1} K^{-1}$)
A	-25.0	0.177
B	-27.0	0.180
C	-22.2	0.220
D	-42.4	0.120
E	-29.0	0.160
F	-31.3	0.130
G	-32.2	0.166
H	-35.7	0.149
I	-23.2	0.181
J	-29.0	0.160
K	-17.0	0.240
L	-29.1	0.149
M	-24.9	0.187
N	-25.7	0.296
O	-33.5	0.157

The glass transition temperature (Tg) of samples are crucial as it is a tip for the behavior of asphalt pavement at low temperatures [87]. Claudy et al. determined the glass transition temperature of 15 different bitumen samples were listed in the Table

3.4. and they claimed that the glass transition attributed to the aromatic fraction on bitumen and in part to the saturates and the result of increasing these fractions on the bitumen content reduces the Tg value.

The Tg results of İzmit, İzmir and Batman bitumen samples were found as -21.0 °C, -14.3 °C, -12,5 °C, respectively. The summation of the aromatic and saturate content of the İzmit, İzmir And Batman bitumen were calculated as 66.5, 66.3, and 60.3.according to Table 3.3. Thus the Tg values of bitumen samples decreases with increasing of aromatic and saturate content of bitumen as it was expected from the literature [87]. When the results were compared to the reported study [87], the summation of the saturates and aromatic fractions of bitumen A and D in Figure 3.4. were 73.7 and 70.5 wich were higher than the fractions of our bıtumen samples. Therefore the Tg values which were reported as -25 °C and -42 °C are lower than our bitumen samples.

Another thermal analysis, Thermal Gravimetric Analysis (TGA) were performed to determine the loss of weight and the decomposition temperature of bitumen samples. Figure 3.4 represents the loss of weight graph of bitumen samples as the result of TGA.

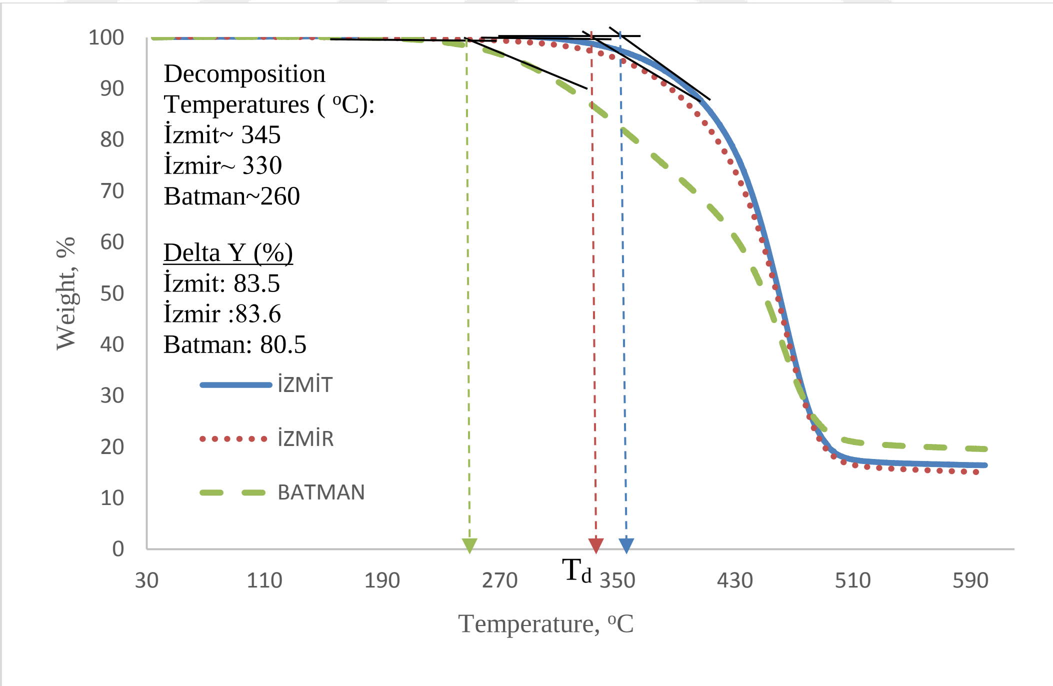

Figure 3.4 : Loss of Weight Curve of Bitumen Samples by TGA Analysis.

Similar with the GC-Simdis analysis, TGA shows the availability of vaporization of the bitumen fractions not the amount of light components. The remaining part the end of TGA, mostly asphaltenes, is the hardest components to vaporize in the bitumen fraction. Therefore the least weight loss was shown in the Batman bitumen since the highest asphaltene content was found on it. İzmit and İzmir have the similar trends due to the near asphaltene contents. The starting point of weight loss for the Batman bitumen, approximately 260 °C, was also consistent with the GC-Simdis results.

3.1.2 Tests results of additives

Characterization of Polymer Additive (SBS)

The FTIR spectrum of SBS copolymer was given in the Figure 3.5 and there were more than one absorbing group. Mainly the $–CH_2$ and C=C units and derivatives comes from the styrene and butadiene blocks absorbs the light and results in a peak in the spectrum. To understand the SBS copolymer used in the experiments have similar properties with the conventionally available polymer, the result were compared with the literature data.

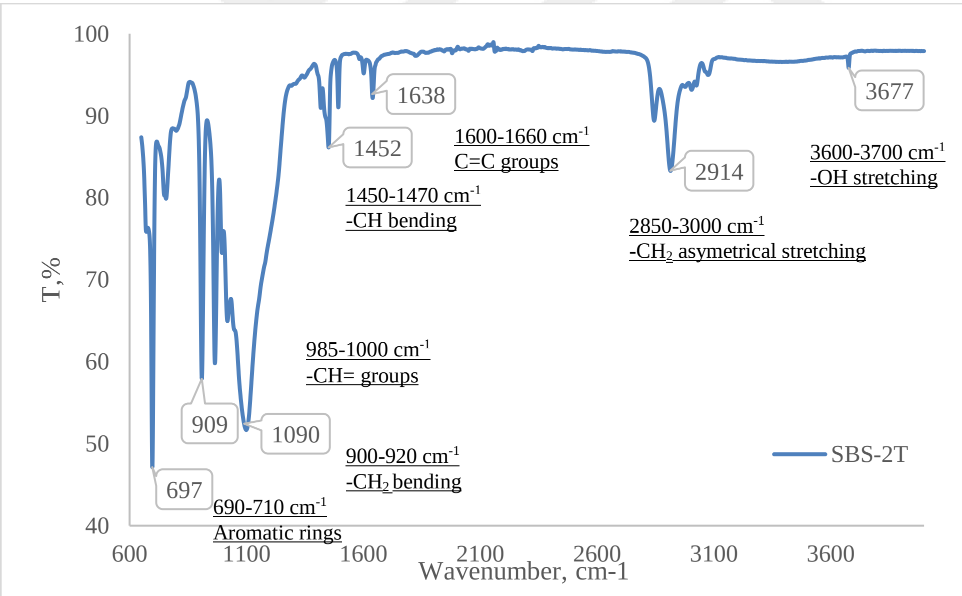

Figure 3.5 : FTIR Spectra of SBS Copolymer.

Munteanu et al.[88] published a study about the characterization of styrene-butadien copolymers with different architectures and the Figure 3.6 shows the IR spectra of three different shape Butadien-Styrene (BS) two-block copolymers. The absorption frequencies of Figure 3.5 and Figure 3.6 were tabulated in Table 3.5 and the bond type and functional groups were determined. For the peak at the 690 cm^{-1} is typical for the monosubstituted bonds on the aromatic rings, due to the polystyrene content the this frequency was shown in the IR spectra. On the other hand $-CH_2$ and –CH= units near the vinyl groups on the polybutadiene backbone results in frequencies at 900-920 cm^{-1} and 985-1000 cm^{-1}, respectively. Addition to these bonds, some alkane and alkenes structures were determined from the peak frequencies such as asymmetrical CH_2 bending between 3000-2850 cm^{-1}, C=C bond between 1660-1600 cm^{-1} and –CH bending between 1470-1450 cm^{-1}. When the results of analyzed FTIR and the literature values compared, only one peak shown in the 3677 cm^{-1}on the analyzed FTIR was shown as different. However, although the author was not repot this values in the journal, a noise was seen form the spectrum given in the Figure 3.6. Also the humidity comes from the air can cause this type of –OH stretching frequency.

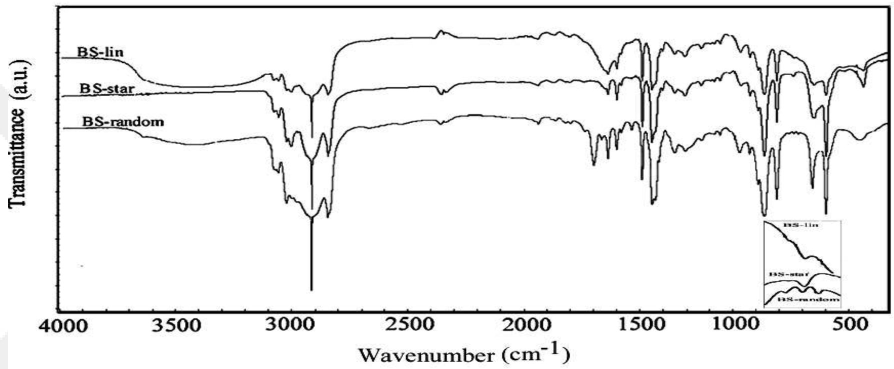

Figure 3.6 : FTIR Analysis of Different Shape SBS Copolymers Published in Literature [88].

Table 3.5 : The Comparison of FTIR Peaks of SBS Copolymer.

Characteristic Wavenumber Range, (cm^{-1})	Literature [88]	SBS-2T (analyzed)	Bond Type	Functional Group
3700-3600	-	3677	-OH stretching	Alcohol, Phenol
3000-2850	2920	2914	Asymetrical CH_2 stretching	Alkane
1660-1600	1639	1638	(C=C)	Alkene
1470-1450	1451	1452	-CH bending	Alkane
1000-985	993	1090	-CH= groups	monosubstituted alkene
920-900	911	909	$–CH_2$ bending groups (near the double bond of PB units)	monosubstituted alkene
710-690	699	697	X-Ph	monosubstituted aromatic ring

Thermal analysis were also carried out to the SBS copolymer to investigate the behavior of the polymer with the change of temperature within the bitumen medıum.

Same conditions given in experimental section with the bitumen samples were applied during DSC and TGA analysis of copolymer. The DSC thermogram of copolymer was given in the Figure 3.7.

Munteanu et al. [84] also reported the DSC analysis of three BS copolymer given in the Figure 3.8. The Tg values of BS copolymers were reported as 80 ^oC for star-BS, and 75 ^oC for linear-BS copolymers. As it was expected, Random-BS copolymer did not show any Tg transition due to the amorphous structure. Tg value of our sample was determined as 76.3 ^oC and this was an expected result cause it was a linear copolymer same with the literature sample. After from approximately 250 ^oC the polymer started to decomposition. The higher glass transition value of SBS copolymer improves the resistance to the deformation at high temperatures within the bitumen. Therefore star or branched SBS copolymer can be preferred since they have higher Tg values. But the homogeneity problems with such copolymers may also increase.

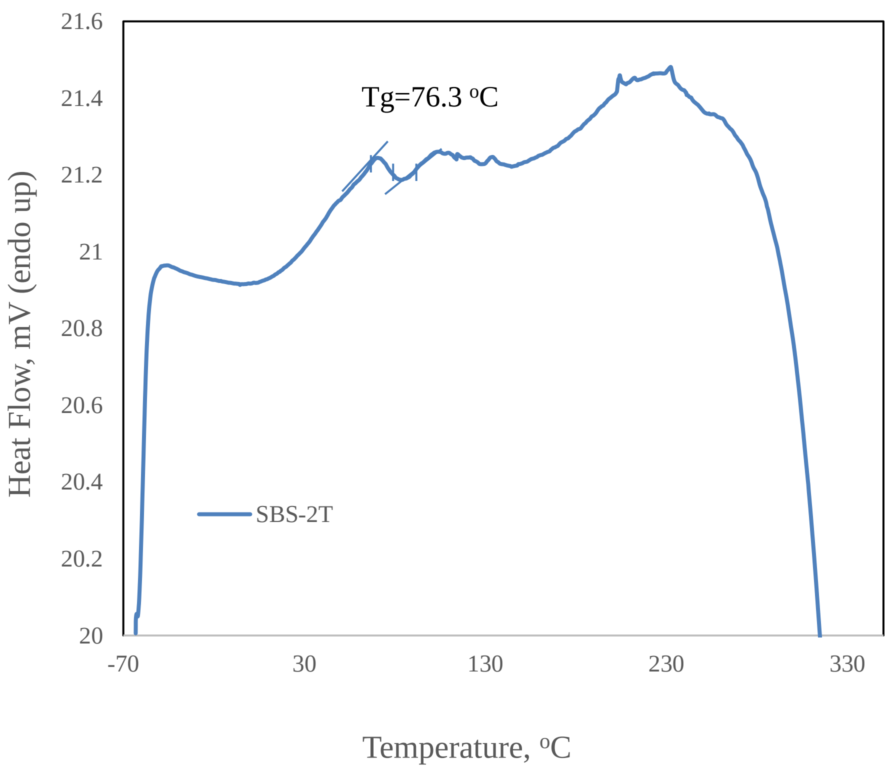

Figure 3.7 : DSC Thermogram of SBS Copolymer.

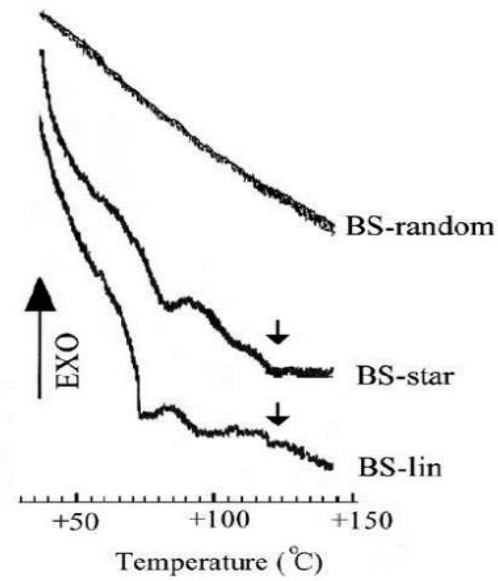

Figure 3.8 : DSC Analysis of Different Shape SBS Copolymers Published in Literature [88].

The result of TGA of SBS copolymer was given in the Figure 3.9 that shows the weight loss of polymer was %95.9 and the starting point for decreasing of weight was around 400 °C as it was also seen from DSC decomposition point. Thermal analysis, both DSC and TGA, means that SBS-bitumen mixture should be prepared higher from the glass transition temperature to soft the polymer and lower than the 400 °C to avoid the decomposition of polymer.

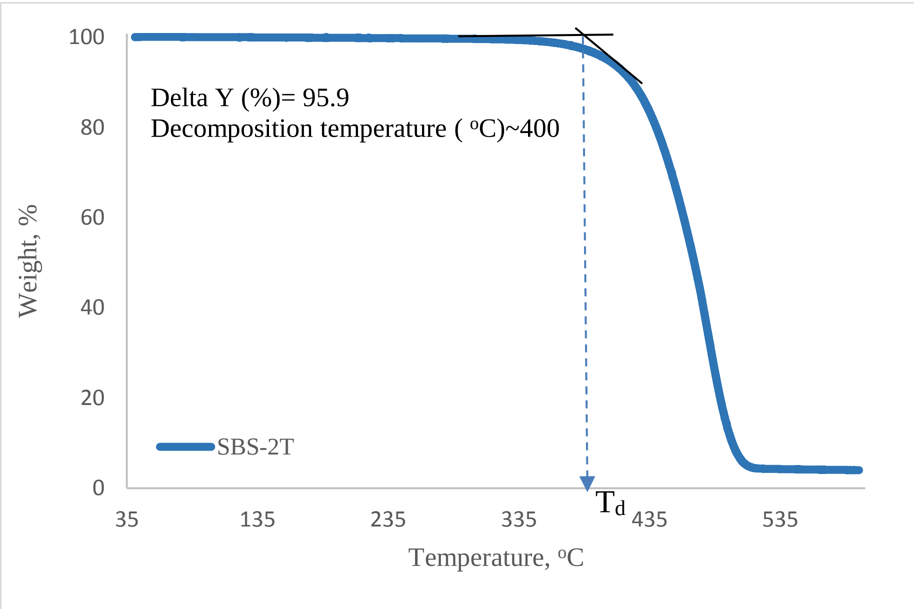

Figure 3.9 : Loss of Weight Curve of SBS Polymer by TGA Analysis.

Characterization of Warm Mix Asphalt Additive (Wax)

Similar characterization tests with the SBS polymer were carried out for wax additive. Figure 3.10 represents the IR spectra of wax and the absorption frequencies were signed on the spectrum. Due to the hydrocarbon content of wax, the IR peaks were very close to bitumen samples. This similarity makes the additive is fully soluble into the bitumen. There were mainly three types of bonds can be seen from the peaks that were attributed to C-H rock at 719 cm^{-1} , C-H bending at 1472 cm^{-1} and C-H stretching vibrations at 2849-2916 cm^{-1}. Since this additive has small number of molecule on the backbone and all chains are linear, the spectra was seen smoother than the bitumen results. For this reason the peaks were also sharp and clear.

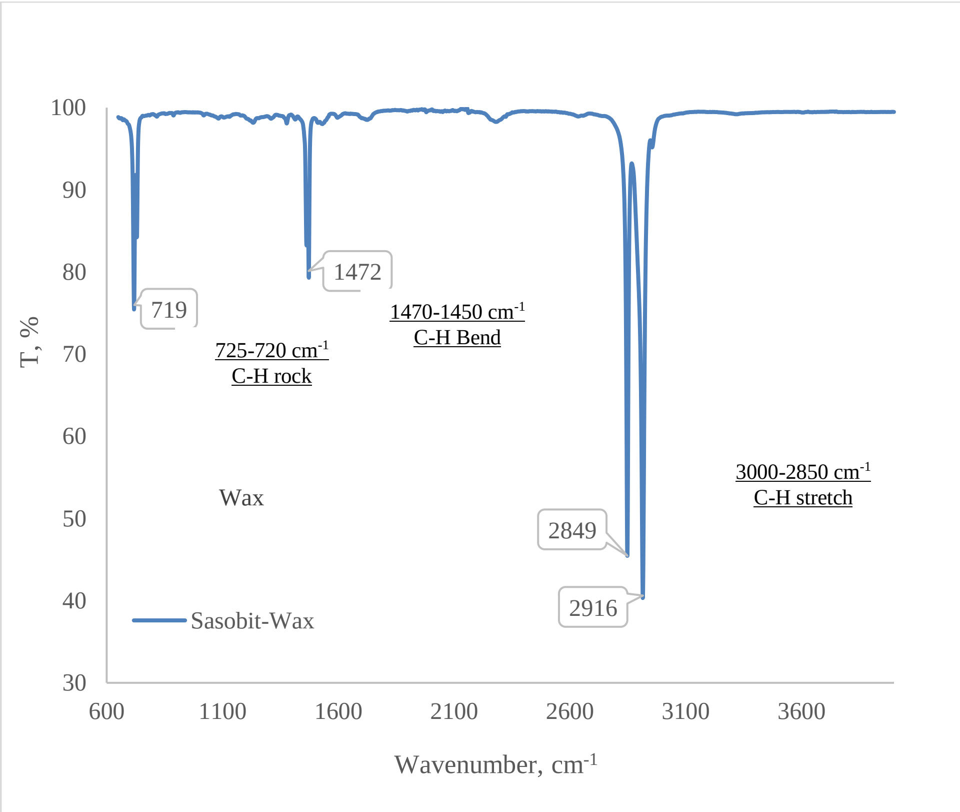

Figure 3.10 : FTIR Spectra of Wax Sample.

The result of DSC and TGA analysis to collect the information about the thermal behavior of wax additive were given in the Figure 3.11 and 3.12.

The melting temperature of the wax were found as 114.4 ^{o}C which is the consistent with the literature information [61]. Low number of carbon on the chain and non-branched structure of the material results in a low energy requirement to melting. That’s why the melting peak was not seen high and sharp in the thermogram.

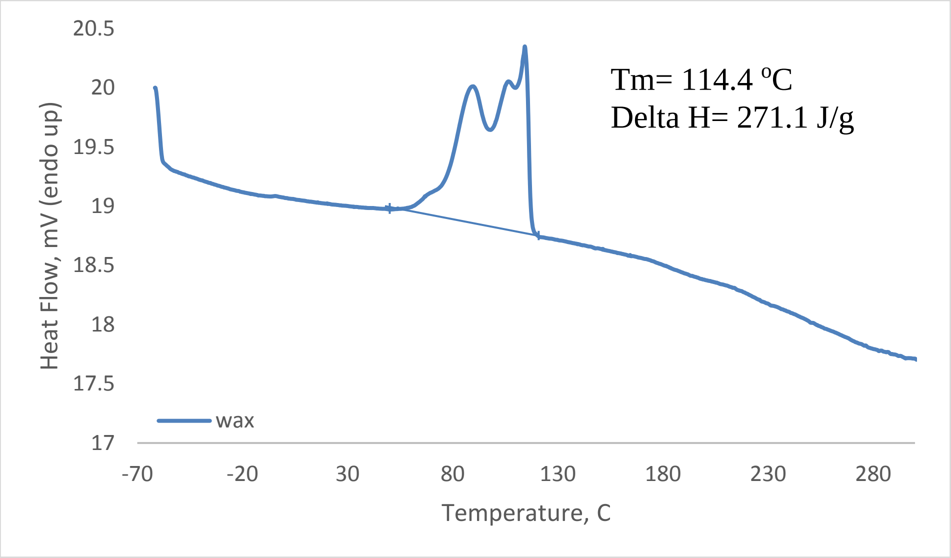

Figure 3.11 : DSC Thermogram of Wax Sample.

The weight loss of the wax was found as %99.9 that can be seen from the Figure 3.12. Almost all sample was vaporized and very small part of the sample was remained as coke at the end of the test. The starting point of weight loss was determined around the 335 ^{o}C which is higher than the mixing temperature of bitumen and additive.

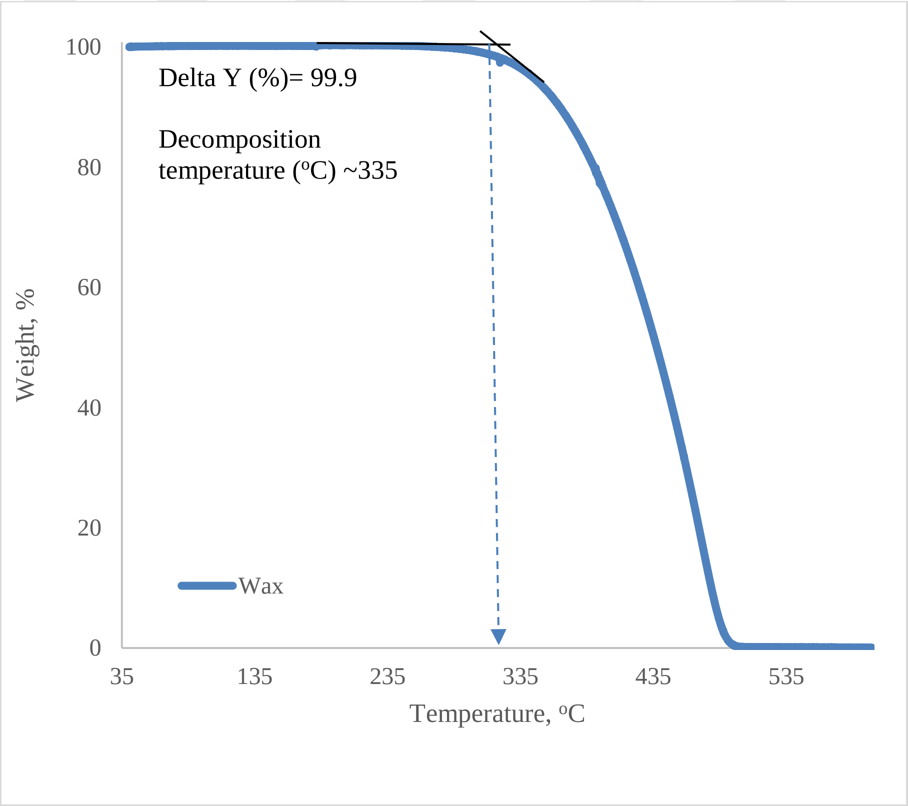

Figure 3.12 : Loss of Weight Curve of Wax Sample by TGA Analysis.

3.2 RSM Analysis of Individual Response Functions

The materials, were used in this study, were examined with the characterization tests in detail. The molecular structures, chemistries and the thermal behavıors of both bitumen and additives were determined. After that the mixtures which were determined with the 2^3 factorial design and given in Table 2.3 were prepared. As it was stated before, the effect of three factors which are bitumen composition, amount of polymer and amount of wax were investigated on the four response functions of resulting mixture. These response functions were chosen as DSR, Viscosity, Elastic recovery and BBR and they are the characteristic tests to show the performance of a bitumen. Therefore the individual responses and the relationship between the independent factors and the response were designated and then the all responses were evaluated to optimize the mixture content. The individual response results were shared in following sections.

3.2.1 Dynamic shear rheometer (dsr)

DSR analysis basically the sign of the high temperature performance of bitumen binding materials. The detailed information about physical meaning of this test were given in the introduction and experimental sections. The results of the response variables that were obtained from the experiments are given in Table 3.6. The highest value was found as 100 ^oC and the lowest was 74.3 ^oC amoung the results. It can be shown that all parameters affects the DSR result but which one has highest effect and what interactions occur between these parameters are the questions which should be answered. Therefore RSM analysis were carried out to understand the phenomena.

The system stability during the experiments were checked before the analysis of response function. For this purpose the graph of response versus pattern of coded parameters were plotted and the trend was investigated.

Figure 3.13 represents the oneway analysis of DSR response by coded parameter pattern. The distribution of the experiments throughout the whole experimental study was shown as random. There were not any overlap means that each result are independent from others and system was stable during the tests.

After the determination of time dependency of experiments, the response functions analysis were carried out and the model fitting were studied. Initially, the terms were chosen as full factorial model specifications for the screening analysis and determination of insignificant parameters.

Table 3.6 : The DSR Results of Experimental Design Matrix.

# of Experiment	Polymer (SBS), %	Warm Mix Additive (Wax),%	Gaestel Index (GI)	DSR (ºC)
1	2	1	0.622	75.3
2	3.5	2	0.622	79.2
3	5	3	0.988	100
4	2	3	0.487	78.8
5	5	3	0.487	91
6	3.5	2	0.988	87.6
7	2	1	0.988	82.2
8	2	3	0.988	83.8
9	5	3	0.622	95
10	3.5	2	0.487	80.4
11	2	1	0.487	74.3
12	5	1	0.622	82.1
13	5	1	0.487	87.4
14	3.5	2	0.487	80.2
15	5	1	0.988	94
16	2	3	0.622	77.6
		Additional Data		
17	3.5	3	0.622	80.2
18	3.5	1	0.487	77.4
19	2	1.5	0.487	75
20	3.5	1	0.988	86.6
21	2	1.5	0.988	81.8

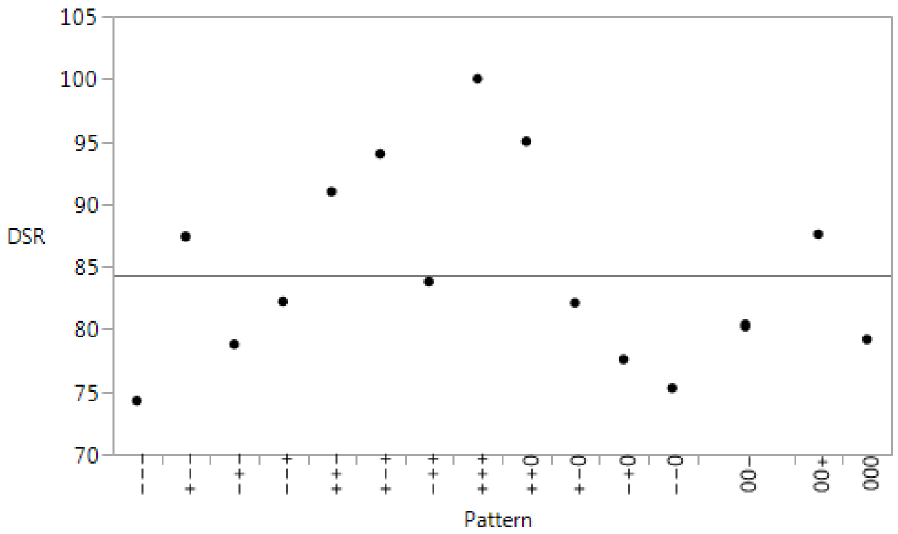

Figure 3.13 : Oneway Analysis of DSR by Pattern.

Table 3.7 shows the result of the full factorial model fitting. The terms have Prob>F (p-value) value is higher than the 0.05 were found as significant and written as bold in Table 3.7. Both model and three individual parameter were found as significant. This results also states that the interaction between the terms both binary and ternary were not significant for the DSR properties of bitumen mixtures. Although the terms for the binary and ternary interaction of parameters were designated, the half normal plot, was given in the Figure 3.14, would be checked.

Table 3.7 : Model Fitting Results for the Screening Analysis of DSR Responses.

Full Factorial Screening Analysis		
Model Specifications	Parameter	Prob>F
	Model	0.0006
SBS	SBS	<0.0001
Wax	GI	0.0013
GI	Wax	0.0152
SBS*Wax	SBS*Wax	0.1750
SBS*GI	SBS*GI	0.6842
Wax*GI	Wax*GI	0.7447
SBS*Wax*GI	SBS*Wax*GI	0.7607
2nd Analysis With Significant Terms		
	Model	<0.0001
SBS	SBS	<0.0001
Wax	GI	0.0002
GI	Wax	0.0038
SBS*Wax	SBS*Wax	0.1238

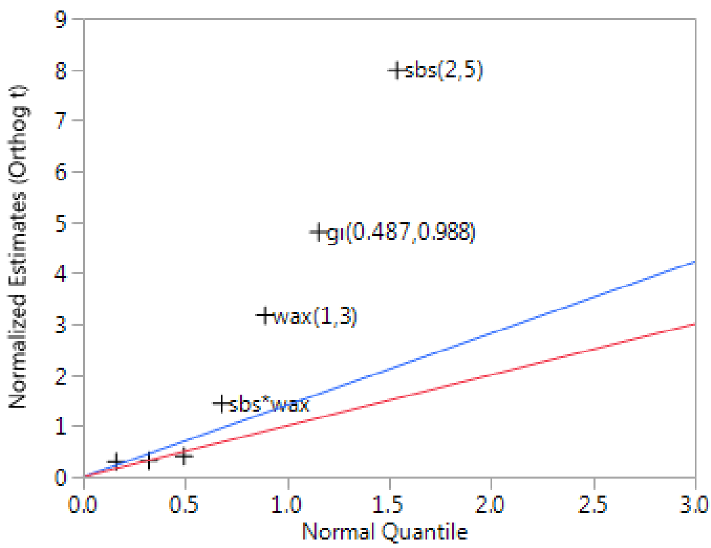

Figure 3.14 : Half Normal Plot of Full Factorial Model Fitting Analysis of DSR.

Although the SBS and Wax interaction terms were seen insignificant from the p-value, there were still a possibility for significance. That is why 2nd analysis were performed and only terms which were located in the half normal plot were selected. Even though the half normal plot showed that SBS and Wax interaction term may significant, the second analysis result in Table 3.7 indicated as insignificant same with 1st analysis.

To continue to RSM analysis and determine the difference of the effect of these significant terms, 5 additional result were added to the results were in the Table 3.6. İncreasing number of point on the surface may help to indicate the small differences on the effect of parameters. After the screening step, RSM analysis were chosen to get both linear and nonlinear effects.

Table 3.8 were obtained by performing RSM analysis with the twenty-one DSR results. As seen from the results, it is determined that there are non-linear terms in the model. There were not found extra significant terms by checking the half normal plot. Therefore the 2nd analysis were performed by using the significant terms found in RSM analysis.

As in all analysis, half normal plot were checked for the second analysis and extra term were not observed. The coefficient of determination, called as R-squared, was found 0.96 and adjusted value for this coefficient was 0.94 at the end of the 2nd analysis. Figure 3.15 (left) was constructed to see the actual by predicted responses and the outlier points were established from this figure.

To narrow the confidence interval of actual by predicted plot and increase the R-squared values, 9th and 12th data were excluded. After two points were eliminated from the data table, 3rd analysis were carried out by choosing the significant terms found in 2nd analysis. Interestingly, SBS*Wax term was obtained as insignificant by elimination of two outlier points. This result has shown that the outlier points may cause some non-important terms to appear as significant.

Figure 3.15 (right) were obtained at the end of point elimination and 3rd analysis. Besides R-squared and adjusted-R-Squared values were increased to 0.99 and 0.98 by elimination of two points. This result pointed out that the excluded points have some error while they were measured and removal of these point was a requirement to obtain successful predictions.

Table 3.8 : Model Fitting Results for the RSM Analysis of DSR Responses.

RSM Analysis (R^2=0.96, R^2_{adj}=0.94)		
Model Specifications	Parameter	Prob>F
	Model	<0.0001
SBS	SBS	<0.0001
Wax	GI	<0.0001
GI	Wax	0.0003
SBS*Wax	GI*GI	0.0090
SBS*GI	SBS*SBS	0.0207
Wax*GI	SBS*Wax	0.0421
SBS*SBS	SBS*GI	0.4360
Wax*Wax	Wax*GI	0.4768
GI*GI	Wax*Wax	0.7954
2nd Analysis with Significant Terms (R^2=0.96, R^2_{adj}=0.94)		
	Model	<0.0001
SBS	SBS	<0.0001
GI	GI	<0.0001
Wax	Wax	<0.0001
GI*GI	SBS*SBS	0.0030
SBS*SBS	GI*GI	0.0047
SBS*Wax	SBS*Wax	0.0287
3rd Analysis with Significant Terms (excluding 9th and 12th points-R^2=0.99, R^2_{adj}=0.98)		
	Model	<0.0001
SBS	SBS	<0.0001
GI	GI	<0.0001
Wax	Wax	<0.0001
GI*GI	GI*GI	<0.0001
SBS*SBS	SBS*SBS	0.0014
SBS*Wax	SBS*Wax	0.1949
Final Analysis with Significant Terms (excluding 9th and 12th points-R^2=0.99, R^2_{adj}=0.98)		
	Model	<0.0001
SBS	SBS	<0.0001
GI	GI	<0.0001
Wax	Wax	<0.0001
GI*GI	GI*GI	<0.0001
SBS*SBS	SBS*SBS	0.0015

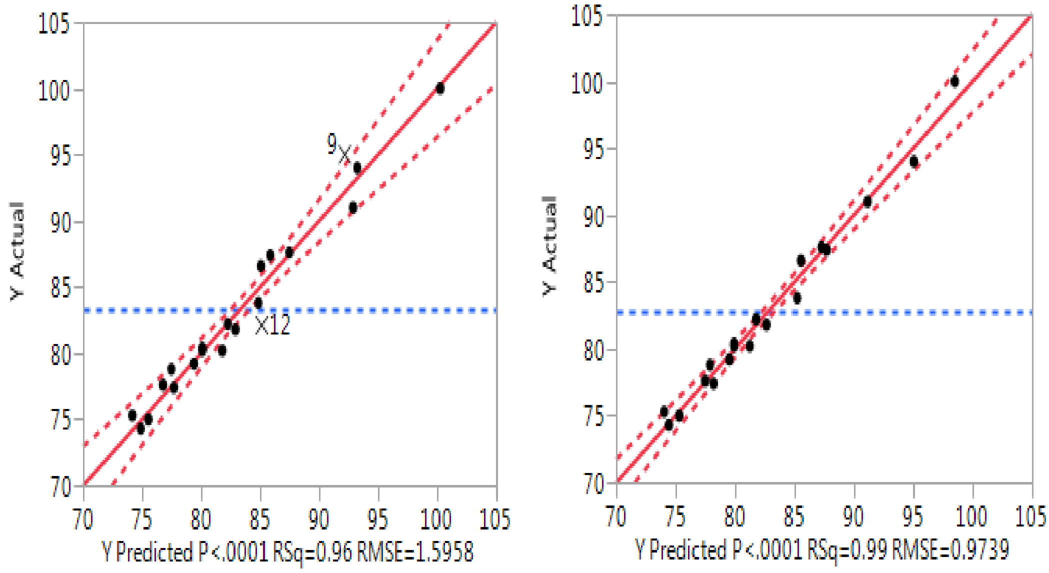

Figure 3.15 : Actual by Predicted Plot for DSR Response. (left-2nd analysis, right-3rd analysis excluding 9th And 12th data)

Model prediction expression was obtained as below after the all model fitting analysis. The expression has both linear and nonlinear terms. It also has the effect of all independent parameters with having different amount of contribution. The bitumen composition, amount of polymer and amount of warm mix additive have effect on the DSR response of modified bitumen. This behavior was also stated in literature [35,42-46, 56-58] However, Bitumen composition (GI value) and amount of polymer(SBS) have higher effect than the wax on the rheological properties of bitumen since the model has 2nd order non-linear terms of these parameters.

$$DSR\ (°C) = 80.57 + 6.63 \times \left(\frac{(\mathrm{SBS} - 3.5)}{1.5}\right) + 1.73 \times (\mathrm{Wax} - 2) +$$

$$3.67 \times \left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right)^2\right) \times 2.88 + \left(\left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right)^2\right) \times 3.016 \qquad (3.1)$$

To validate the prediction expression and observe the deviation from the measured values, three different bitumen was used and the modifications with SBS and Wax were studied. After the mixtures were prepared, The DSR values were measured and Table 3.9 were constructed with the help of measured and predictions obtained by model equation.

The difference between the actual and predicted values were calculated and It has been found that the DSR values of randomly selected modified bitumens can be determined with very small deviations.

Table 3.9 : Validation of Model Equation and Prediction Values of DSR.

Sample Name	SBS, %	Wax,%	GI	Measured, °C	Prediction, °C	Difference
A	1.5	3	0.618	78.5	77.5	1.0
B	1.5	3	0.962	88	84.3	3.7
C	1.5	3	0.650	79.2	77.7	1.5

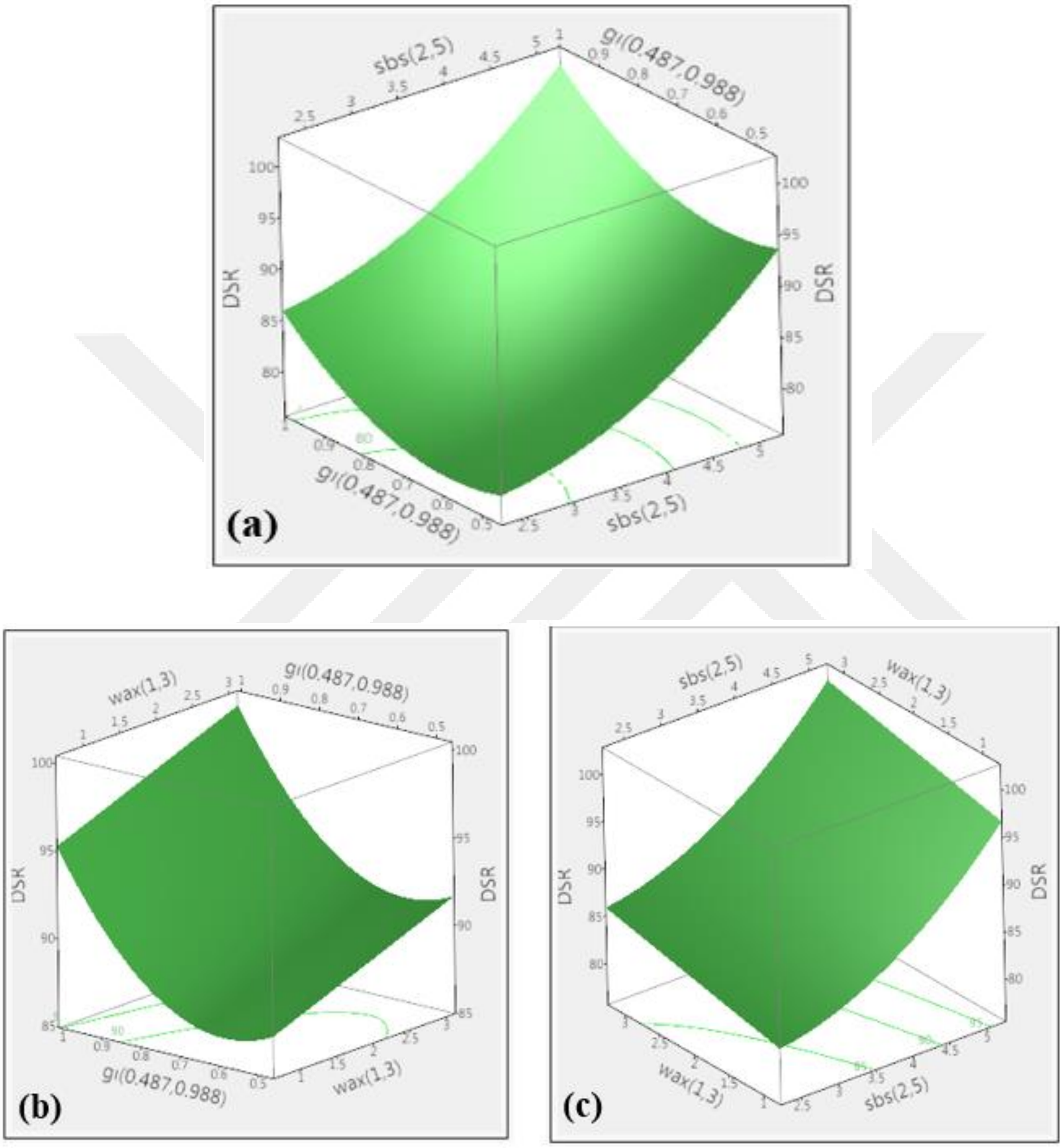

Figure 3.16 : Response Surface Profile of DSR (a) constant wax (b) constant SBS (c) constant GI.

The response surface profile that was obtained from model of DSR results was given in the Figure 3.16. The exponential increasing of the DSR value was obtained with the increasing of SBS content and Gaestel Index of bitumen. This was an expected trend due to the second-order terms on the model. On the other hand at constant SBS and Wax content (Figure 3.16-b), DSR response first decreases and then increases with the increasing of GI value of bitumen. This result exactly means that the different results be obtained for different GI value bitumen samples by using same amount of SBS and Wax and the results have not a trend with steady increasing or decreasing. The contour plot, below the response surfaces, also showed the rising trend of DSR values with increasing of three parameters except the situation mentioned above.

3.2.2 Viscosity

Viscosity is one of the crucial properties of bitumen used in the asphalt pavements. This is because the too viscous bitumen means that requirement more heating energy to make fluid and more energy during the mixing it with aggregates. Especially addition of polymer also increases the bitumen viscosity and makes this property important. The experiments were listed in Table 3.10 were carried out to indicate the effect of bitumen fractions and amount of additives on the viscosity of bitumen. The highest and lowest values of modified bitumens were measured as 3031.5 and 529 cP, respectively.

Table 3.10 : The Viscosity Results of Experimental Design Matrix.

# of Experiment	Polymer (SBS), %	Warm Mix Additive (Wax),%	Gaestel Index (GI)	Viscosity, cP
1	2	1	0.622	659.65
2	3.5	2	0.622	749.6
3	5	3	0.988	3031.5
4	2	3	0.487	486.3
5	5	3	0.487	1093
6	3.5	2	0.988	2310
7	2	1	0.988	1210
8	2	3	0.988	1070
9	5	3	0.622	1490
10	3.5	2	0.487	759
11	2	1	0.487	529
12	5	1	0.622	1437
13	5	1	0.487	1409
14	3.5	2	0.487	771
15	5	1	0.988	3206
16	2	3	0.622	539.4
Additional Data				
17	3.5	3	0.622	825.8
18	3.5	1	0.487	879
19	2	1.5	0.487	623
20	3.5	1	0.988	1925
21	2	1.5	0.988	1167

Before starting statistical analysis, the time stability of system were controlled with the help of Oneway Analysis of Viscosity by Pattern which was given in the Figure 3.17. As it shown from Figure 3.17, The sequent two points were not similar each other and most of the point spread into the plane. There may be only two points out of the plane. So the outlier points should be investigated at the end of the analysis. Apart from these, the system was accepted as stable and there were not any restriction or unexpected condition.

As the first step of RSM analysis, screening analysis were done and whether there were unimportant terms were investigated. Table 3.11 demonstrates the analysis specifications and the results of Prob>F values for the terms. Since the "GI, SBS and SBS*GI" terms were found as significant, 2nd analysis were performed only with these terms.

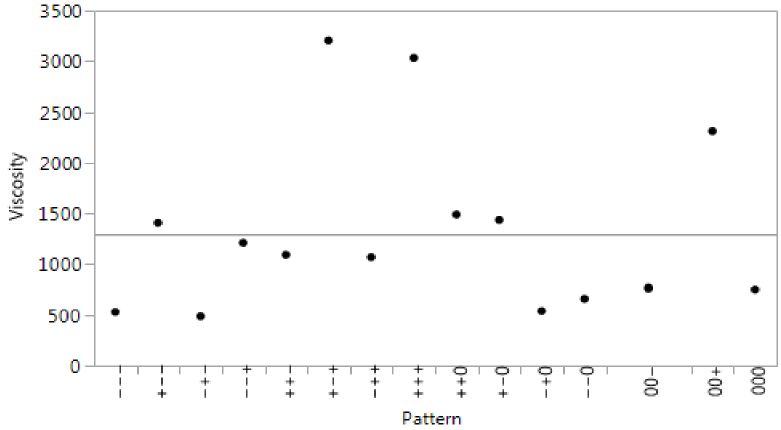

Figure 3.17 : Oneway Analysis of Viscosity by Pattern.

The half normal plot was also controlled after the full factorial analysis. However there were not seen any additional terms. Thus, it was found that the amount of wax added was not an important parameter on the viscosity.

In the continuation of screening analysis, RSM analysis were performed to examine the importance of the nonlinear terms. Table 3.12 represents the p-value results of the RSM analysis. Same result as screening analysis neither linear nor non-linear terms of Wax was found as unimportant by RSM analysis. 2nd analysis were conducted with the significant terms and half normal plot was investigated after each analysis. Since the additional significant term was not located at the half normal plot, the R-squared and confidence interval was examined for 2nd analysis.

Table 3.11 : Model Fitting Results for the Screening Analysis of Viscosity Responses.

Full Factorial Screening Analysis		
Model Specifications	Parameter	Prob>F
	Model	0.0299
	GI	<0.0001
SBS Wax GI SBS*Wax SBS*GI Wax*GI SBS*Wax*GI	SBS	<0.0001
	SBS*GI	0.0017
	Wax	0.3283
	SBS*Wax*GI	0.8230
	SBS*Wax	0.8878
	WAX*GI	0.9501
2nd Analysis With Significant Terms		
	Model	<0.0001
SBS Wax GI SBS*Wax	GI	<0.0001
	SBS	<0.0001
	SBS*GI	0.0002

As it was shown in Figure 3.18-left, the 13th point was detected as outlier point and final analysis were carried out after removal of this point. The significant terms remained same with the previous analysis but the adjusted R-squared and confidence interval were affected to excluding of 13th point that can be seen in Figure 3.18-right. Finally, both the R-squared and adjusted R-squared values were reported as 0.98.

Model expression -equation 3.2- were generated by using the significant terms obtained after the RSM analysis. This equation has the nonlinear terms similar with the DSR results. Since the Wax term was found as insignificant for the response, the model expression has not any term including Wax. In fact this is a debatable result because wax is known as viscosity decreasing agent used as warm mix asphalt additive [56,61-64]. However the results showed that the viscosity decreasing effect of wax has not any significance besides the effect of polymer and bitumen on viscosity.

Additionally, the effect of bitumen composition higher than the addition of polymer. The viscosity values increase exponentially with the increase of GI ındex od bitumen by using the equation 3.2.

Table 3.12 : Model Fitting Results for the RSM Analysis of Viscosity Responses.

RSM Analysis (R^2=0.98, R^2_{adj}=0.97)		
Model Specifications	Parameter	Prob>F
	Model	<0.0001
SBS	GI	<0.0001
Wax	SBS	<0.0001
GI	SBS*GI	<0.0001
SBS*Wax	GI*GI	0.0062
SBS*GI	SBS*SBS	0.0905
Wax*GI	Wax	0.1768
SBS*SBS	Wax*Wax	0.5848
Wax*Wax	Wax*GI	0.6291
GI*GI	SBS*Wax	0.7328
2nd Analysis with Significant Terms (R^2=0.98, R^2_{adj}=0.97)		
	Model	<0.0001
SBS	SBS	<0.0001
GI	GI	<0.0001
SBS*GI	SBS*GI	<0.0001
GI*GI	GI*GI	0.0019
Final Analysis with Significant Terms (excluding 13th points-R^2=0.98, R^2_{adj}=0.98)		
	Model	<0.0001
SBS	SBS	<0.0001
GI	GI	<0.0001
SBS*GI	SBS*GI	<0.0001
GI*GI	GI*GI	0.0032

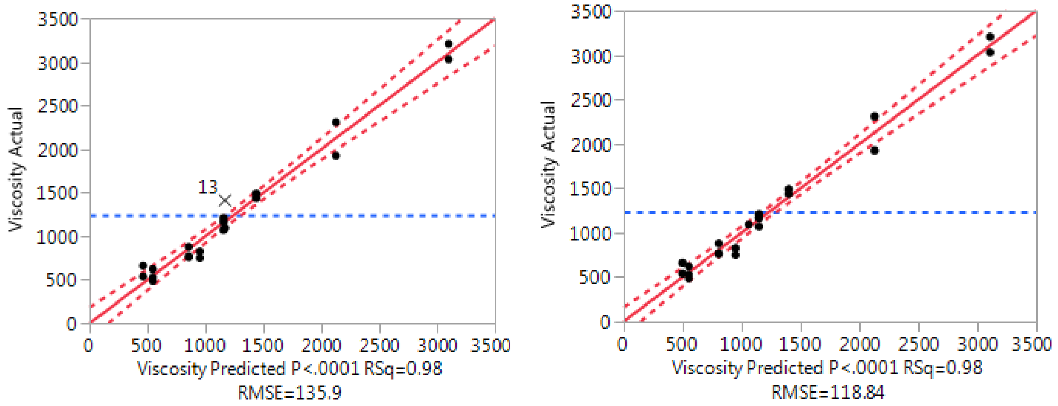

Figure 3. 18 : Actual by Predicted Plot for Viscosity Response (left-2nd analysis, right- 3rd analysis 13th data).

$$\text{Viscosity } (cP) = 1197.45 + 617.07 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) + 660.77 \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + 362.90 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\text{GI}-0.7375)}{0.2505}\right)^2\right) \times 270.27 \qquad (3.2)$$

Verification of the predictions were done with the samples were shown in Table 3.13 at which both measured and predicted result were listed. Differences between the measured and predicted viscosity values of A, B and C bitumens were calculated. The highest difference was found for Bitumen B. The reason may be the GI value of bitumen B that is the highest value. Since the GI highly affects the viscosity value in the proposed model equation, the deviation increases, as well.

Table 3.13 : Validation of Model Equation and Prediction Values of Viscosity.

Sample Name	SBS, %	Wax,%	GI	Measured, cP	Prediction, cP	Difference
A	1.5	3	0.618	389.9	351.8	38.1
B	1.5	3	0.962	1666	750.3	915.7
C	1.5	3	0.650	371.7	345.9	25.8

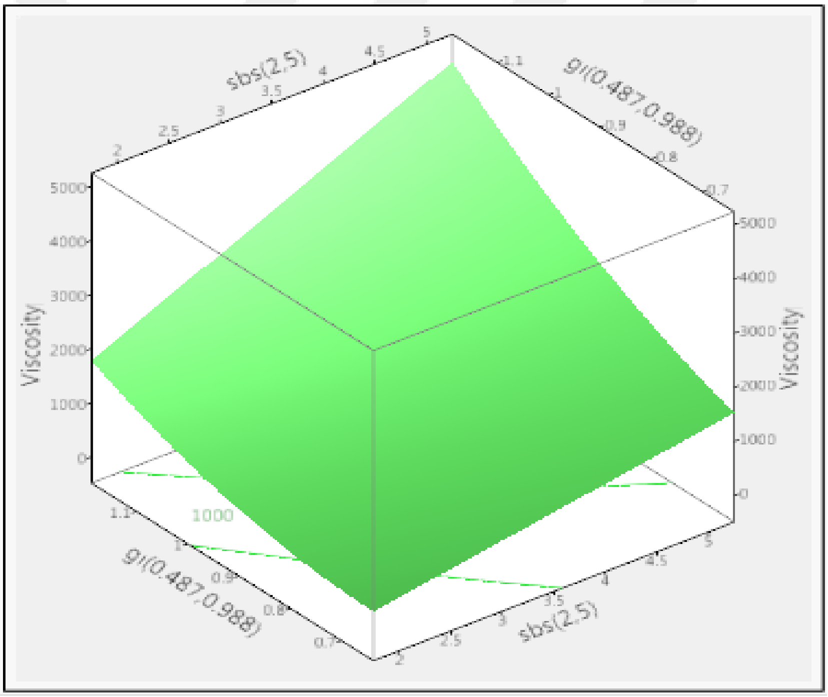

Figure 3.19 : Response Surface Profile of Viscosity.

The graph of response surface for viscosity were shown in Figure 3.19 which has the SBS and GI ındices on its axis because the wax was not stated in the model equation. Rising of both SBS and GI value increases the viscosity. Also, the contour plots below the surface show the increasing trend as independent from the wax addition. In order to get the lower viscosity to make easy the application during the mixing, the bitumen having low GI value that contains low percent of saturate and asphaltene or high percent of resin and aromatic in its composition.

3.2.3 Elastic recovery

Ductile properties of bitumen is indispensable for the polymer modified bitumen since the polymer addition gives to bitumen elasticity and this characteristic makes the polymer modified bitumen recoverable against the deformations. However each bitumen has not the same chemical composition, the polymer does not indicate the same recovery behavıor on the bitumen with same amount of addition. Furthermore, addition different chemicals, like warm mix additive in this case, may cause a negative effect on the elastic behavıor of bitumen.

In this study, experiments, represented in Table 3.14, were performed to investigate this phenomena. The highest value was found as 90% with the addition of only 3.5% polymer addition to İzmit 50/70 penetration bitumen. The lowest value was measured as 33% with the use of high amount of warm mix additive.

Initially, oneway graph of elastic recovery by time, Figure 3.20, were plotted and the stability of experiments were studied. There were four points at the bottom of graph and these measurement may cause extra errors on the model predictions. Thus these points may be eliminated at the end of analysis by checking the results. Out of these points measurements were performed at randomly can be said.

The results of screening analysis were listed in Table 3.15 and the significant terms which has the p-value was determined smaller than 0.005, were displayed by bold. After the first, full factorial, half normal plot were investigated to control the additional term(s) were significant or not. Since the extra term was not found at the half normal plot, “SBS, SBS*GI and GI” terms were selected and 2nd analysis given in the Table 3.15 were carried out and significant terms were not change with this analysis. Same result as viscosity, there were not found any Wax related term is significant.

Screening analysis suggested an idea about the important parameters. However nonlinear terms may have an effect on the elastic recovery properties of bitumen. The analysis were contınued with response surface method to search the effect nonlinear term of independent parameters. Five experimental result were added to previous results to develop the prediction of model and to show real effects of independent parameters.

Table 3.14 : The Elastic Recovery Results of Experimental Design Matrix.

# of Experiment	Polymer (SBS), %	Warm Mix Additive (Wax),%	Gaestel Index (GI)	Elastic Recovery,%
1	2	1	0.622	41.2
2	3.5	2	0.622	61.2
3	5	3	0.988	80.5
4	2	3	0.487	33
5	5	3	0.487	81.2
6	3.5	2	0.988	74.6
7	2	1	0.988	78
8	2	3	0.988	76
9	5	3	0.622	82.3
10	3.5	2	0.487	81
11	2	1	0.487	41
12	5	1	0.622	86.5
13	5	1	0.487	83.8
14	3.5	2	0.487	77.3
15	5	1	0.988	87
16	2	3	0.622	39.8
		Additional Data		
17	3.5	3	0.622	58.5
18	3.5	1	0.487	90
19	2	1.5	0.487	37
20	3.5	1	0.988	77.8
21	2	1.5	0.988	76

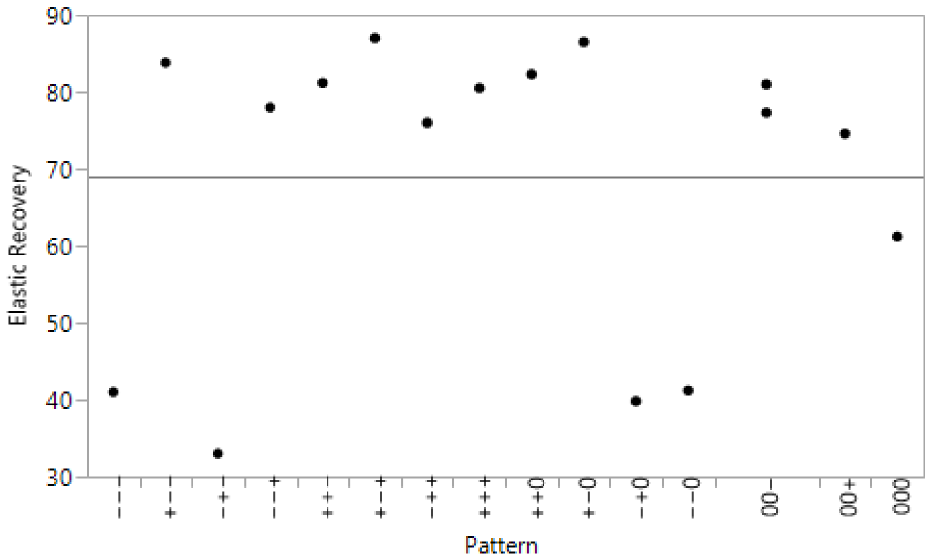

Figure 3.20 : Oneway Analysis of Elastic Recovery by Pattern.

Table 3.15 : Model Fitting Results for the Screening Analysis of Elastic Recovery Responses.

Full Factorial Analysis		
Model Specifications	Parameter	Prob>F
	Model	0.0073
SBS	SBS	0.0010
Wax	SBS*GI	0.01560
GI	GI	0.03640
SBS*Wax	Wax	0.5007
SBS*GI	SBS*Wax*GI	0.7659
Wax*GI	SBS*Wax	0.9153
SBS*Wax*GI	Wax*GI	0.9763
2^{nd} Analysis With Significant Terms		
	Model	0.0015
SBS	SBS	<0.0001
SBS*GI	SBS*GI	0.0036
GI	GI	0.0119

Table 3.16 were obtained to the result of RSM analysis. "SBS, SBS*GI and GI" terms were found as significant with the first RSM analysis that gave the same result as screening analysis. However the half normal plot of RSM analysis that was shown in Figure 3.21 demonstrated that the "Wax , SBS*SBS and GI*GI" Terms were also significant. 2^{nd} analysis were conducted to control the significance of these terms and "GI*GI" term which was not seen in previous analysis were determined as significant. It is very important for the resulting response to find the new second-order term added to the model equation. The overall trend of response has changed with the addition of non-linear terms.

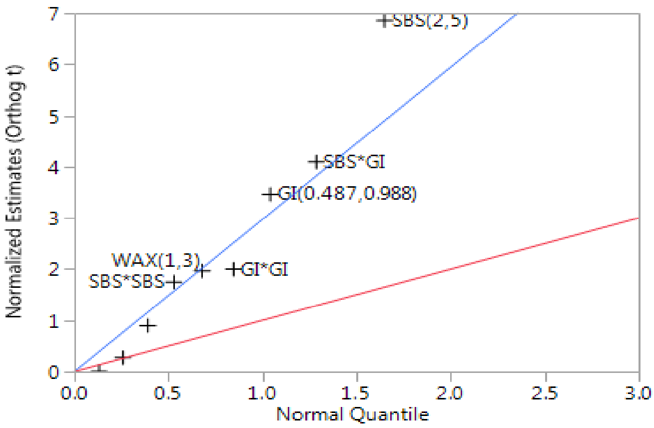

Figure 3.21 : Half Normal Plot of RSM Model Fitting Analysis of Elastic Recovery.

Table 3.16 : Model Fitting Results for the RSM Analysis of Elastic Recovery Responses.

RSM Analysis (R^2=0.89, R^2_{adj}=0.80)		
Model Specifications	Parameter	Prob>F
	Model	0.0004
SBS	SBS	<0.0001
Wax	SBS*GI	0.0015
GI	GI	0.0279
SBS*Wax	GI*GI	0.0693
SBS*GI	SBS*SBS	0.1318
Wax*GI	Wax	0.2828
SBS*SBS	Wax*GI	0.4407
Wax*Wax	Wax*Wax	0.8099
GI*GI	SBS*Wax	0.9352
2nd Analysis with Significant Terms and Wax , SBS*SBS and GI*GI Terms (R^2=0.88, R^2_{adj}=0.83)		
SBS	Model	<0.0001
SBS*GI	SBS	<0.0001
GI	SBS*GI	0.0005
Wax	GI	0.0185
SBS*SBS	GI*GI	0.0416
GI*GI	SBS*SBS	0.0782
	Wax	0.1754
3rd Analysis with Significant Terms (R^2=0.83, R^2_{adj}=0.79)		
	Model	<0.0001
SBS	SBS	<0.0001
SBS*GI	SBS*GI	0.0009
GI	GI	0.0336
GI*GI	GI*GI	0.0369
Final Analysis with Significant Terms (excluding 5th, 10th, 14th and 18th points-R^2=0.98, R^2_{adj}=0.97)		
	Model	<0.0001
SBS	SBS	<0.0001
SBS*GI	SBS*GI	<0.0001
GI	GI	<0.0001
GI*GI	GI*GI	0.0377

3rd analysis were executed following the terms determined to be important at 2nd analysis. Distinctive result were not found but when R-squared values were found to

be insufficient. Actual by predicted plot were constructed at this point to search the terms which could cause the R-squared value to reduce. It was determined that four points (5th , 10th , 14th , 17th) were out of confidence ınterval in Figure 3.22-left. Final analysis were carried out with terms determined to be significant in advance and by discarding these four points. The final results were obtained that the Figure 3.22-right which has more narrow confidence interval and higher R-squared value (0.98). We may have used less data by throwing out four data points. But the result is more reliable and accurate at this time. On the other hand, the same terms as the significant terms determined in the viscosity results were found. This result means that the independent parameters have parallel effects on both viscosity and elastic recovery responses even though these tests measures completely different properties of bitumen.

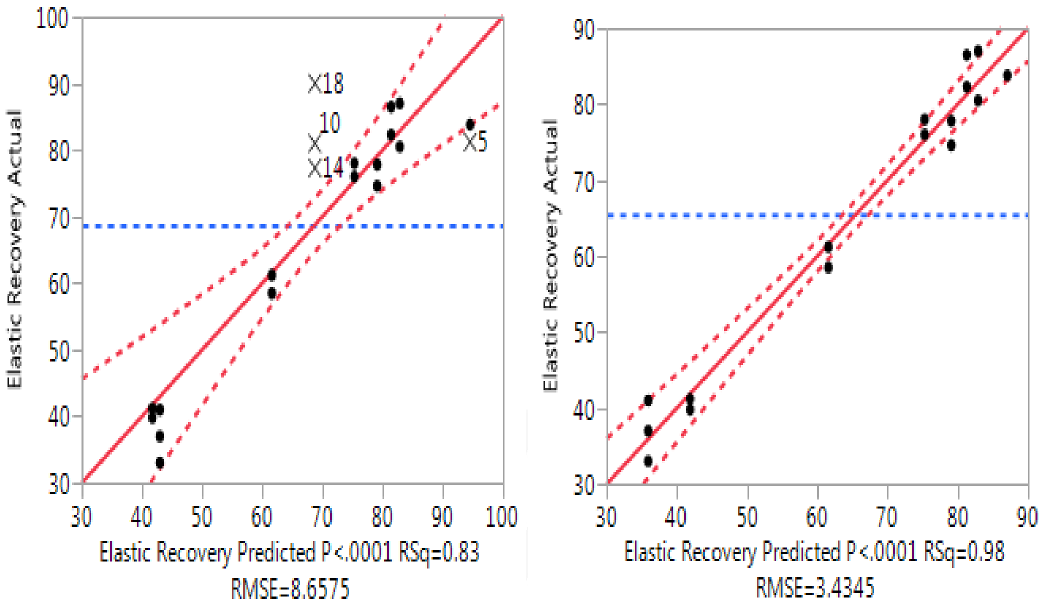

Figure 3.22 : Actual by Predicted Plot for Elastic Recovery Response (left-3rd analysis, right- Final analysis excluding 5th, 10th,14th and 18th data).

$$Elastic\ Recovery\ (\%) = 64.39 + 14.69 \times \left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right) + 8.81 \times \left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right) + \left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right) \times (-10.89) + \left(\left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right)^2\right) \times 5.91 \quad (3.3)$$

The model equation 3.3 were obtained at the end of the analysis. The equation has both linear and non-linear terms. Similar to the viscosity result, the model does not contain Wax term and contains effect of GI as second order non-linear term. Interestingly, the interaction term of SBS and GI has negative sign coefficient that means the interaction has an adverse effect on the elastic recovery of bitumen although the individual terms of SBS and GI has positive effect on this property.

In order to determine the validity of the model, three measurements were made as in other results. A, B and C bitumen have different GI values from the bitumen used in this study. When the same amount of SBS and Wax were added to these bitumen samples, different elastic recovery results were obtained that was given in Table 3.17. As a good result, ıt can be seen that very close values can be obtained when the prediction results determined by using model expression.

Table 3.17 : Validation of Model Equation and Prediction Values of Elastic Recovery.

Sample Name	SBS, %	Wax,%	GI	Measured, %	Prediction, %	Difference
A	1.5	3	0.618	40.1	35.0	5.1
B	1.5	3	0.962	75.2	70.5	4.7
C	1.5	3	0.650	40.2	37.4	2.8

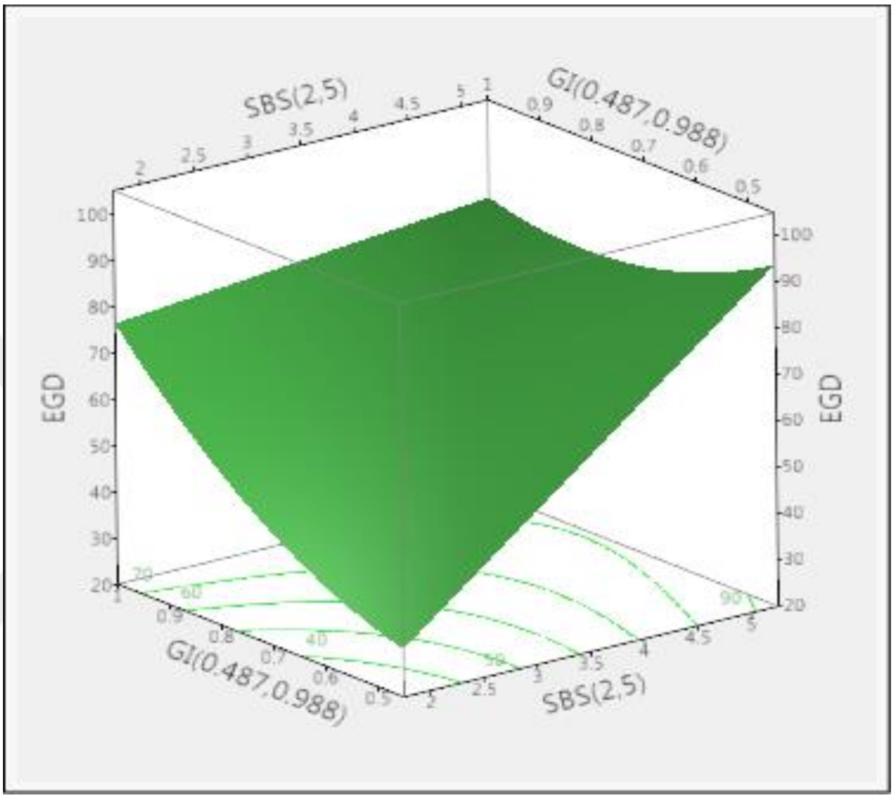

Figure 3. 23 : Response Surface Profile of Elastic Recovery.

Figure 3.23 shows the result of response surface profile of elastic recovery. Wax has not any effect on the elastic recovery, the only response surface for the elastic recovery were constructed for SBS and GI parameters. As can be seen in the contour plots on the bottom of the surface profile, the percent value of recovery increases with the rising amount of SBS and increasing GI value of bitumen. According to equation(1.1), the GI value increases with the higher amount of saturates and asphaltenes in the bitumen composition or lower amount of resin and aromatic.

3.2.4 Bending beam rheometer (bbr)-creep stiffness

The rheological properties is an indicator of performance for a bitumen sample. The Bending beam rheometer displays the low temperature performance of a bitumen. Two values, S value (creep stiffness) and m-value (change of creep stiffness with the load), were obtained to this test. There are two conditions, m-value≥0.3 and creep stiffness(S)≤300 MPa, to accept the test result as “PASS” at measured temperature.

Table 3.18 : The BBR Results of Experimental Design Matrix.

# of Experiment	Polymer (SBS), %	Warm Mix Additive (Wax),%	Gaestel Index (GI)	m-value	BBR-Creep Stiffness (MPa)
1	2	1	0.622	0.301294	252.9
2	3.5	2	0.622	0.253375	214.6
3	5	3	0.988	0.286426	128.5
4	2	3	0.487	0.268423	316.9
5	5	3	0.487	0.217525	326.5
6	3.5	2	0.988	0.268644	127.3
7	2	1	0.988	0.277807	114.6
8	2	3	0.988	0.255957	139.8
9	5	3	0.622	0.249607	303.6
10	3.5	2	0.487	0.213863	302.9
11	2	1	0.487	0.289446	300.5
12	5	1	0.622	0.280285	247.9
13	5	1	0.487	0.206349	311.6
14	3.5	2	0.487	0.208694	298.5
15	5	1	0.988	0.271675	112.9
16	2	3	0.622	0.238696	273.9
Additional Data					
17	3.5	3	0.622	0.262295	238.6
18	3.5	1	0.487	0.206449	282.9
19	2	1.5	0.487	0.281113	307.9
20	3.5	1	0.988	0.271106	97.1
21	2	1.5	0.988	0.284627	102.5

The test temperature during the experiments were given in the Table 3.18 was -12 ^{o}C. Since the all m-values (except one) were found below the test criteria, the acceptable test temperature should be -6 ^{o}C instead of -12 ^{o}C. However the creep stiffness values were found variable. For this reason, the factors affecting the S-value were investigated. Figure 3.24 represents the oneway analysis of creep stiffness vs. measurements. It can be said that random measurements have been made as a system despite the fact that most of the measurements are accumulated above the grans mean line.

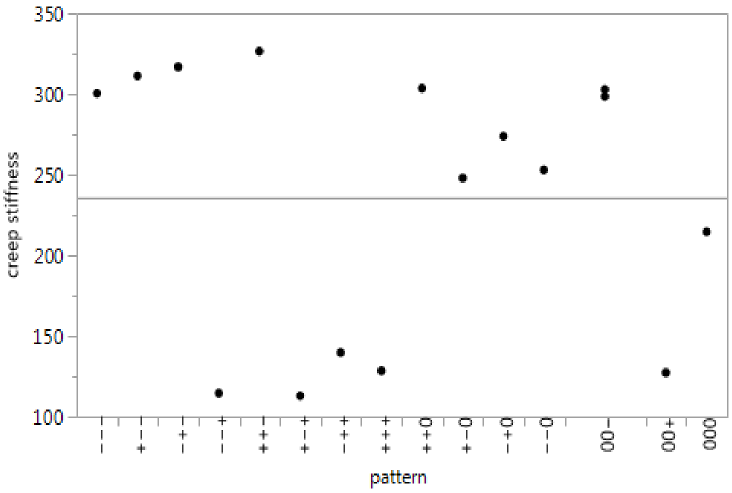

Figure 3.24 : Oneway Analysis of BBR-Creep Stiffness by Pattern.

Table 3.19 : Model Fitting Results for the Screening Analysis of BBR- Creep Stiffness Responses.

Full Factorial Analysis		
Model Specifications	Parameter	Prob>F
SBS Wax GI SBS*Wax SBS*GI Wax*GI SBS*Wax*GI	Model	<0.0001
	GI	<0.0001
	Wax	0.0658
	SBS*GI	0.5151
	SBS*Wax*GI	0.7317
	SBS	0.7462
	SBS*Wax	0.7888
	Wax*GI	0.9547
2nd Analysis With Significant Term and Wax		
GI Wax	Model	<0.0001
	GI	<0.0001
	Wax	0.0223

The results of screening analysis were listed in Table 3.19. The only significant term was found as GI by the full factorial analysis. Additionally Wax term was observed by plotting the half normal graph for full factorial analysis that was given in Figure 3.25. When 2nd analysis were carried out with the significant terms found in full factorial analysis and half normal plot, it made sure that the terms GI and Wax were significant.

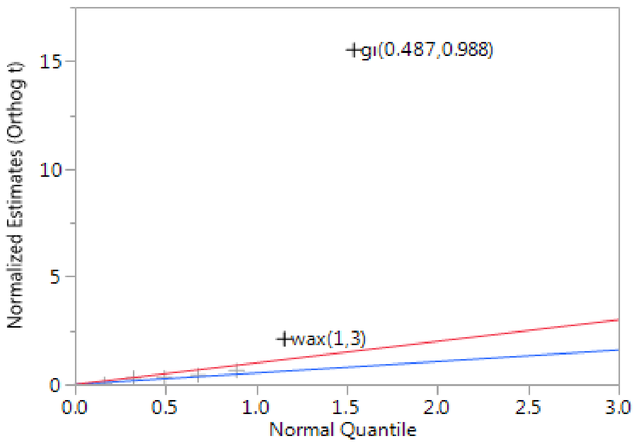

Figure 3. 25 : Half Normal Plot of Full Factorial Model Fitting Analysis of BBR-Creep Stiffness

RSM analysis was conducted to investigate the effect of non-linear terms following the screening analysis. Table 3.20 contains the all results about the RSM analysis. Initially SBS*SBS term was added to the significant terms by RSM analysis. When the 2nd analysis were performed with the significant terms found in RSM analysis, there was not determined different significant terms and Figure 3.26-left were obtained. As it was seen in the graph of actual by predicted value, four points (2nd , 6th , 9th , 17th) were located out of the confidence interval. In order to improve the model predictions and make narrow the confidence interval, these data were excluded and analysis were repeated. Extra important terms were not found with the final analysis but R-squared and adjusted R-squared values were increased.

Model output as a result of all analyzes were given in equation 3.4 which the terms having all independent parameters with different levels. The effect of Wax and GI parameters were linear and there were not any interaction between other parameters. However the polymer term has both linear and non-linear effects on the creep stiffness. Furthermore GI value has negative sign coefficient means that the increasing amount of saturates and asphaltenes in the bitumen decreases the value of creep stiffness. In the situation of increasing amount of SBS, value of creep stiffness increases exponentially. It results in a poor low temperature performance result since the S-value criteria is exceeded.

$$Creep\ Stiffness\ (MPa) = 202.62 + 10.72 \times (\mathrm{Wax} - 2) \pm 96.22 \times \left(\frac{(\mathrm{GI} - 0.7375)}{0.2505}\right) + 1.16 \times \left(\frac{(\mathrm{SBS} - 3.5)}{1.5}\right) + \left(\left(\frac{(\mathrm{SBS} - 3.5)}{1.5}\right)^2\right) \times 14.93 \qquad (3.4)$$

Table 3.20 : Model Fitting Results for the RSM Analysis of BBR-Creep Stiffness Responses.

RSM Analysis (R^2=0.98, R^2_{adj}=0.97)		
Model Specifications	Parameter	Prob>F
	Model	<0.0001
	GI	<0.0001
	Wax	0.0156
SBS Wax GI SBS*Wax SBS*GI Wax*GI SBS*SBS Wax*Wax GI*GI	SBS*SBS	0.0357
	SBS	0.4416
	GI*GI	0.5370
	SBS*GI	0.6602
	SBS*Wax	0.7562
	Wax*GI	0.9075
	Wax*Wax	0.9168
2^{nd} Analysis with Significant Terms (R^2=0.98, R^2_{adj}=0.98)		
	Model	<0.0001
GI Wax SBS*SBS	GI	<0.0001
	Wax	0.0036
	SBS*SBS	0.0039
Final Analysis with Significant Terms (excluding 2^{nd}, 6^{th}, 9^{th} and 17^{th} points-R^2=0.996, R^2_{adj}=0.996)		
	Model	<0.0001
GI Wax SBS*SBS	GI	<0.0001
	Wax	<0.0001
	SBS*SBS	0.0012

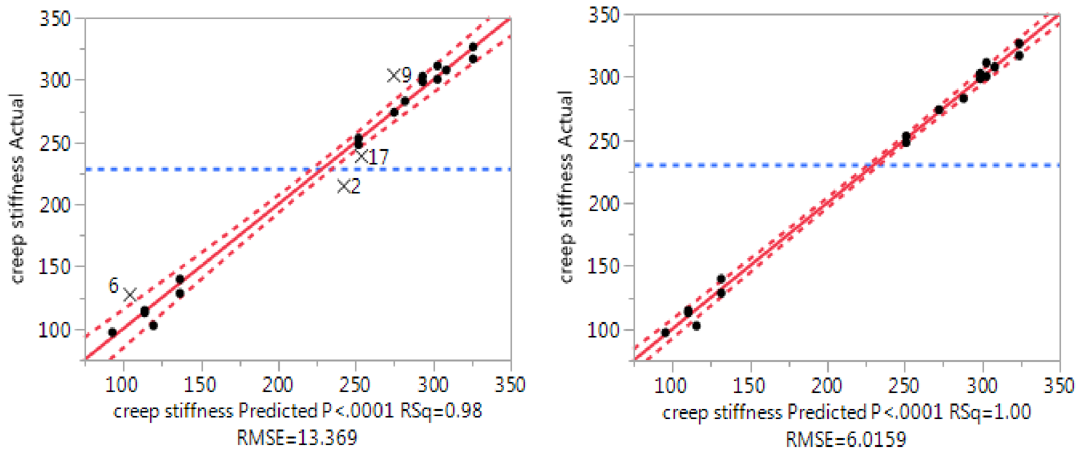

Figure 3.26 : Actual by Predicted Plot for BBR-Creep Stiffness Response (left-2nd analysis, right- Final analysis excluding 2nd, 6th, 9th and 17th points).

Same as the other responses, BBR test were carried out to three bitumen samples to determine the creep stiffness values and Table 3.21 were got with the results which were both measured and calculated with the help of model obtained by RSM analysis. Although the modified bitumens have same amount of additives, different creep stiffness values were obtained as it expected by the result of RSM analysis. The decreasing effect of GI term was also shown on the results.

Table 3.21 : Validation of Model Equation and Prediction Values of BBR-Creep Stiffness.

Sample Name	SBS, %	Wax,%	GI	Measured, MPa	Prediction, MPa	Difference
A	1.5	3	0.618	272.4	284.2	11.8
B	1.5	3	0.962	147.9	152.1	4.2
C	1.5	3	0.650	251.2	271.9	20.7

The response surfaces for the creep stiffness with respect to independent parameters were given in Figure 3.27. There were a plane surface for the constant SBS (Figure 3.27-a). The reason is that the model has not any polynomial term with Wax or GI. On the other hand the surfaces related to the SBS (Figure 3.27 b-c) has curvature due to the 2nd order polynomial term of SBS in the model expression. When the Figure 3.27 b-1 and Figure 3.27 b-2 were compared, the SBS axis having range for low percentages appears surface to be plane since it causes a small increases in creep stiffness. Surface having SBS axis range for higher SBS percentages shows curvature since the effect of SBS increases exponentially. Same phenomena occurred to the constant wax surface that were Figure 3.27 c-1 and Figure 3.27 c-2.

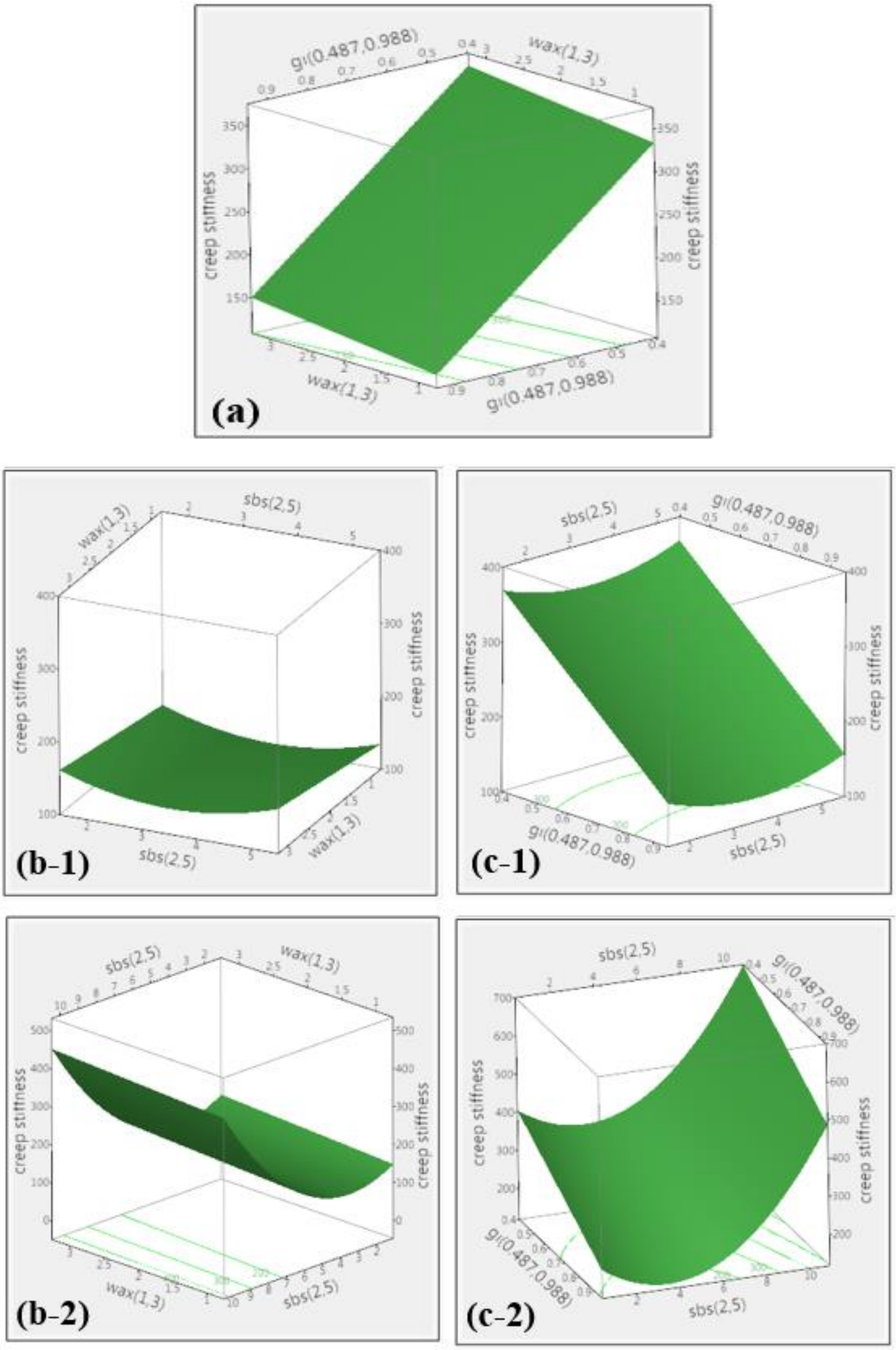

Figure 3.27 : Response Surface Profile of Creep Stiffness (a) constant SBS (b-1), (b-2) constant GI with different SBS ranges (c-1), (c-2) constant Wax with different SBS ranges

3.3 Simultaneous RSM Analysis of All Response Functions and Optimization of System

The effect of independent variable on each response function were investigated previous sections. In this section all independent variable were considered together and simultaneous RSM analysis were carried out to get the effect of parameter with the interaction of each other. While performing multiple RSM analysis, the response limits were defined in program as different from the individual analysis. Maximization, or Minimization were defined as criteria for the desired values of responses. Maximization for DSR and Elastic recovery responses and minimization for viscosity and creep stiffness were chosen as response limits in this study. Furthermore the points which were excluded during the individual analysis were thrown out in multiple RSM analysis, as well. The results were obtained by multiple RSM analysis were given in Table 3.22. When the significant terms for the responses were examined, some changes were attracted. Some significant terms were found as insignificant at multiple analysis.

One of the nonlinear terms of DSR Response, GI*GI, were not found with the multiple RSM analysis. When the other responses were investigated in Table 3.22, ıt can be noticed that all response functions have the GI term as significant and the same situation about the GI*GI term was valid for the viscosity and elastic recovery. Since the response limits were given in the analysis, ıt may be normal to conclude that the result give the most significant terms for each parameter at the same time. Therefore the GI*GI term were disappeared to three responses cause the creep stiffness has any effect by the GI*GI term.

Moreover the coefficient of determination were found for the each response functions were shared in Table 3.23. Although the general trend was in the side of increasing of R-squared values, the change in negative was seen in elastic recovery function. The values of R-squared of elastic recovery may be improved but the values for the other functions may change. Therefore, the decrease in the values of R-Squared of elastic behavıor may be seen in terms of achieving optimum result with the other functions.

The desirability functions were plotted to perform the optimization of four response functions. Figure 3.27 indicates the all the trends of response functions with the change of independent parameters.

Table 3.22 : Model Fitting Results for the Simultaneous RSM Analysis of All Responses.

RSM Analysis with Significant Terms for All Responses
(excluding 2nd ,6th, 9th, 12th, 13th , 17th points)

Model Specifications
SBS
Wax
GI
SBS*GI
SBS*SBS
GI*GI

DSR		Viscosity		Elastic Recovery		Creep Stiffness	
Individual	Multiple	Individual	Multiple	Individual	Multiple	Individual	Multiple
SBS	SBS	GI	GI	SBS	SBS	GI	GI
GI	GI	SBS	SBS	SBS*GI	SBS*GI	Wax	Wax
Wax	Wax	SBS*GI	SBS*GI	GI	GI	SBS*SBS	SBS*SBS
GI*GI	-	GI*GI	-	GI*GI	-		
SBS*SBS	SBS*SBS	-	Wax	-	SBS*SBS		
		-	SBS*SBS				

Table 3.23 : R-squared and Adjusted R-squared values of Simultaneous RSM Analysis.

	DSR		Viscosity		Elastic Recovery		Creep Stiffness	
	Individual	Multiple	Individual	Multiple	Individual	Multiple	Individual	Multiple
R^2	0.99	0.99	0.98	0.996	0.98	0.93	0.996	0.997
R^2_{adj}	0.98	0.98	0.98	0.99	0.97	0.87	0.995	0.995

As it was defined in the response limits, the desirability functions, were given in Figure 3.28., were maximized and the GI value of bitumen, amount of SBS and amount of Wax were determined at these conditions. The optimum formulation for desired properties were found that the Batman bitumen having GI value is 0.988 and containing 3.2% of SBS and %3 Wax as additives.

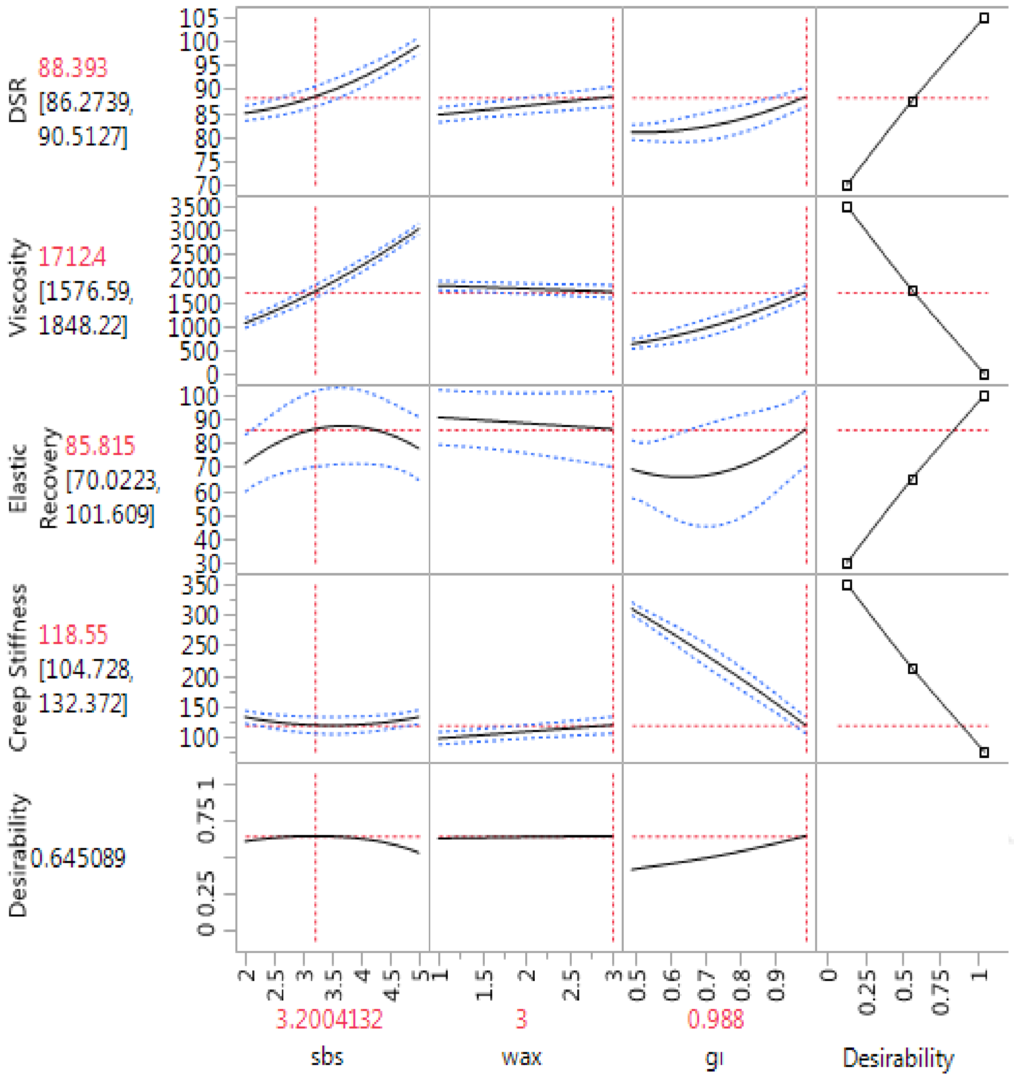

Figure 3.28 : Prediction Profile of Simultaneous RSM Analysis.

The model outputs of the simultaneous RSM analysis for each functions were given in the Equations 3.5-3.8 When the equations 3.1-3.4 were examined, it was seen that the coefficients found with individual analysis of responses were very close to coefficients of significant terms of responses below. It can be said that small differences are due to new terms added to the equations as a result of multiple analyzes.

$$\boldsymbol{DSR}\ (°\boldsymbol{C}) = 81.95 + 6.66 \times \left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right) + 1.90 \times (\mathrm{Wax}-2) + 3.81 \times \left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right)^2\right) \times 2.29 + \left(\left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right)^2\right) \times 2.05 + 0.41 \times \left(\frac{(\mathrm{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\mathrm{GI}-0.7375)}{0.2505}\right) \quad (3.5)$$

$$\textbf{Viscosity}\ (\boldsymbol{cP}) = 1121.60 + 657.52 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) + -64.76 \times (\text{Wax}-2) + 611.63 \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\text{SBS}-3.5)}{1.5}\right)^2\right) \times 137.34 + 328.240 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\text{GI}-0.7375)}{0.2505}\right)^2\right) \times 135.34 \qquad (3.6)$$

$$\boldsymbol{Elastic\ Recovery}\ (\%) = 73.35 + 14.54 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) \pm 2.49 \times (\text{Wax}-2) + 6.10 \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + \left(\left(\frac{(\text{SBS}-3.5)}{1.5}\right)^2\right) \times (-12.38) + \left(\frac{(\text{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) \times -11.37 + \left(\left(\frac{(\text{GI}-0.7375)}{0.2505}\right)^2\right) \times 9.98 \qquad (3.7)$$

$$\boldsymbol{BBR - Creep\ Stiffness}\ (\boldsymbol{MPa}) = 208.36 + 1.26 \times \left(\frac{(\text{SBS}-3.5)}{1.5}\right) + 10.91 \times (\text{Wax}-2) \pm 95.82 \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) + \left(\frac{(\text{SBS}-3.5)}{1.5}\right) \times \left(\frac{(\text{GI}-0.7375)}{0.2505}\right) \times (-1.27) + \left(\left(\frac{(\text{SBS}-3.5)}{1.5}\right)^2\right) \times 13.88 + \left(\left(\frac{(\text{GI}-0.7375)}{0.2505}\right)^2\right) \times (-5.45) \qquad (3.8)$$

At the end of the multiple analysis, the sample was prepared in the optimum formulation determined by desirability functions to determine the accuracy of the obtained model data. The results in Table 3.24 were obtained by the measurement of modified bitumen prepared at optimum conditions and predictions with the help of equations 3.5-3.8. The accuracy of DSR, viscosity and Creep Stiffness responses were found as high due to the high value of R-Squared. Some differences seen on the response of DSR, Viscosity and Creep stiffness despite the high r-squared values results from random errors.

Table 3.24 : Validation of Model Equation and Prediction Values of All Responses.

Sample Name	SBS, %	Wax,%	GI	Property		
				DSR		
				Measured, ^{o}C	Prediction, ^{o}C	Difference
				88.6	88.4	0.2
				Viscosity		
				Measured, cP	Prediction, cP	Difference
				1636	1712.4	76.4
Optimum Mixture	3.2	3	0.998	Elastic Recovery		
				Measured, %	Prediction, %	Difference
				77.3	85.8	8.5
				Creep Stiffness		
				Measured, MPa	Prediction, MPa	Difference
				161.0	118.5	42.5

3.4 Investigation of Performance and Asphalt Properties of Modified Bitumen at Optimum Conditions

The output of this study for the end user is the ability to provide the required amount of additive for different bitumens to get the desired performance grade and asphalt properties. The chosen response parameters are enough to predict the performance grade of bitumen binder. Table 3.25 shows the performance grade of neat Batman bitumen and modified form of Batman bitumen at the optimum condition to reach the higher performance grade.

Table 3.25 : Comparison of EN 14023 Bitumen Specifications of Neat and Modified Bitumen at Optimum Conditions.

#	TEST NAME	Standard	Unit	Neat Batman Bitumen	Modified Batman Bitumen (Optimum- %3.2SBS and %3 Wax)
1	Penetration (25 ºC, 150g, 5sn)	TS EN 1426	0.1 mm	57	35
2	Softening Point	TS EN 1427	ºC	50.7	79
3	Elastic Recovery[b] (25 ºC)	TS EN 13398	%	10.5	77.3
4	Flash Point	TS EN 2592	ºC	262	272
5	Specific Gravity	TS EN 15326	g/cm^3	1.04303	1.03802
6	Dynamic Shear Rheometer (DSR) ($G^*/\sin\delta > 1$ kPa)	TS EN 14770	ºC	71.3	88.6
7	Rolling Thin Film Oven Test (RTFOT)[d]	TS EN 12607-1		+	+
7.1	Change of Mass		%	0.46	0.35
7.2	Increasing in Softening Point	TS EN 1427	ºC	8.4	9.5
7.3	Retained Penetration	TS EN 1426	%	95	71
7.4	Dynamic Shear Rheometer (DSR) ($G^*/\sin\delta > 2.2$ kPa)	TS EN 14770	ºC	76.8	100
8	Pressure Aging Vessel Aged Bitumen	TS EN 14769		+	+
8.1	(DSR) ($G^*/\sin\delta < 5000$ kPa)	TS EN 14770	ºC	25.8	-
8.2	Bending Beam Rheometer (BBR) ($S \leq 300$ MPa, $m \geq 0.300$)	TS EN 14771	ºC	-22	m-value: 0.23 S-Value:161.01
	PERFORMANCE GRADE	TS EN 14023/ AASHTO MP1a	-	PG 70-22	PG 82-16

When the results were investigated, the high temperature performance grade of bitumen were increased from value of 70 to 82 that is the upper limit of high temperature performance according to the TS EN 14023 standardization. However the decreasing were shown in the low temperature performance due to the addition of SBS. As it was shown in the section of BBR response, the addition of SBS increases the value of creep stiffness and also reduces the m-value lower than the critical limit of 0.3. Therefore the modification of bitumen with minimum %3 SBS results in the low temperature performance value at -16 ^{o}C and the amount of SBS is the limiting reagent for the low temperature performance of modified bitumen.

Although the bitumen is a binder material and the only 4-7 %of asphalt is bitumen, the most effective parameter on the asphalt properties is the bitumen performance. After the determination of improvement of the performance of Batman bitumen by the SBS and Sasobit modifications, Asphalt properties were investigated. For this purpose, the first step is the design of the asphalt composition were carried out and the optimum percentage of bitumen that should be used in the asphalt mixture were determined.

Table 3. 26 : Grain size Distribution of Aggregates (Sieve Analysis) (TS EN 933-1).

Mesh Size	Sieve Size	Design of Neat Bitumen			Design of Modified Bitumen		
inch	mm	12-19 mm	5-12 mm	0-5 mm	12-19 mm	5-12 mm	0-5 mm (No:4-0)
3/4"	19	100	100	100	100	100	100
1/2"	12.5	47	99.4	100	47	99.4	100
3/8"	9.5	21.9	83.6	100	21.9	83.6	100
no 4	4.75	1.3	17.4	99.6	1.3	17.4	99.6
no 10	2	0.6	7.1	58.7	0.6	7.1	58.7
no 40	0.42	0.6	3.7	26	0.6	3.7	19.1
no 80	0.18	0.6	2.8	18	0.6	2.8	11.5
no 200	0.075	0.4	2.3	12	0.4	2.3	7.7

While doing the asphalt design the aggregates having the sieve analysis result that was given in Table 3.26 were used with a gradation were shown in Table 3.37 and the asphalt mixtures (aggregates and bitumen) were prepared by using the increasing amount of bitumen from 4% to 7% (4%, 4.5%, 5%, 5.5%, 6%, 6.5%, 7%). Because the amount of aggregates between the size of 0-5 mm used in modified bitumen was lower than the aggregates used in neat bitumen, the higher amount of filler was preferred in the mixture preparation. After the mixing and compaction steps that were shared in experimental section, the graphs of asphalt composition which were given in APPENDIX B were constructed and the results in Table 3.28 were obtained.

The optimum amount of bitumen were found as higher for the modified bitumen than for the neat bitumen. The reason may be that the modified bitumen has lower neat bitumen binder within the formulation containing SBS and Sasobit. The second reason may be the binding and stripping properties of the modified bitumen cause that the higher percentages of voids for lower amount of modified bitumen. The difference between the other parameters of design were results from the using modified bitumen as it was expected.

Table 3.27 : Ratios of Aggregates and Gradation of Mixture.

Sieve Size, mm		12-	5-12	0-5
Amount in Mixture,%		12	48	40
	Technical Specifications of highways			
Gradation Of Mixture	Specification		Mixture Formulation	
100	100		100	
93.4	88	100	88	96
82.8	72	90	76	84
48.3	42	52	45	52
27	25	35	28	34
12.2	10	20	10	16
8.6	7	14	7	11
6	3	8	4	8

The wheel tracking test were performed with the asphalt molds having the optimum amount of bitumen for neat and modified bitumen. The test results showed that the modified bitumen reduced the amount of rutting property by half. Thanks to this test, the 50 % improvement of the rutting resistance by using modified bitumen with the addition of SBS and Sasobit has been shown in the road behavior of the asphalt.

Table 3.28 : The Results of Design and Wheel Tracking Test.

TEST	Test Standard	Neat Batman Bitumen	Modified Batman Bitumen (Optimum-%3.2 SBS +%3Wax)
Percent of Bitumen,%	TS EN 12697-1	4.8	6.2
Marshall Stability, kg @4.8% bitumen	TS EN 12697-6	1060	1255
Practical Specific Gravity, g/cm^3@4.8% bitumen	TS EN 12697-34	2.422	2.357
Voids, % @4.8% bitumen	TS EN 12697-8	4	4
Void filled bitumen, % @4.8% bitumen	TS EN 12697-8	71	72
Voids in the mineral aggregate, % @4.8% bitumen	TS EN 12697-8	14.20	17.30
Flow, mm @4.8% bitumen	TS EN 12697-34	2.90	3.60
Wheel Tracking, % (20000 cycle @ 60 ^oC)	TS EN 12697-22	13	6.7

4. CONCLUSIONS AND FUTURE WORKS

In this thesis study, the effective parameters on the major properties of bitumen were investigated in the presence of different chemistries of bitumen and varying amount of additives. As a result of studies the following statements can be deduced;

- The same penetration grade of bitumen samples obtained from different origins can have different chemistries which was determined by the SARA analysis. Besides, the performance grades of these bitumens can be different due to the same manner of chemistries of bitumen as can be seen in three bitumen samples, İzmit, izmir and Batman Bitumen, which were selected in this study.
- The SARA content of bıtumens can change the almost all characteristics of bitumen such as boiling behavıor, thermal transitions and physical hardness etc. This difference was also observed in GC-Simdis, DSC and TGA analysis for the three selected bitumen samples except FTIR analysis.
- Each fraction of SARA effect the different properties of bitumen. While the presence of higher amount of saturates and aromatics reduces the glass transition temperatures, the amount of asphaltenes in the bitumen varied the rheological and ductility properties. Moreover, the length of saturates varies the initial boiling point of bitumen. Two bitumen with a similar amount of saturate fractions, the one having lighter saturates chains were found as having lower initial boiling point. TGA analysis also supported this expression.
- The characteristics of SBS and Sasobit additives were compared to the same additives whereof the literature studies. These additives were investigated that whether they were commercially available. It was proved that additives using in the experimental study have not any special properties.
- The thermal transitions and change of weights of SBS and Sasobit were checked to ensure the preparation temperature of bitumen-additives procedure. It was determined that there would be no undesirable volatilization during preparation of the mixtures.
- Successful results have been obtained by using “Response Surface Methodology” to model the DSR, Viscosity, Elastic recovery and Creep stiffness properties of

bitumen based on the bitumen content (GI), amount of SBS and Sasobit additives and determine the optimum mixing ratios.

- It was found that all ındependent parameters effect the DSR results when it analyze the individual response. But the change of bitumen composition and amount of SBS was found as the most effective parameters on the DSR response due to the second order terms on the model expression.
- The response of viscosity properties was found as affected by the bitumen content and SBS addition. Despite the Wax additives were used to decreasing the viscosity of binder during the asphalt mixing and layout, the term was insignificant among the other independent parameters. This may be the result of the fact that the viscosity decreasing effect of Wax is very small, besides the increasing effect of the SBS and GI. This result can also said the type of bitumen is the key parameter for the viscosity response. The SARA fractions of the bitumen can change the all trend of the viscosity behavıor.
- When the effect of independent parameters on the response of elastic recovery properties were evaluated, ıt was seen that the amount of Wax was still ineffective. Viscosity and Elastic recovery were affected by the same parameters although they represents the different properties of bitumen. As the GI index has asphaltene and saturates on the numerator of ratio, the rising amounts of these fractions increases the GI value. The modelling result showed that the higher GI value enhances the higher viscosities.
- Unlike the other results, BBR response was interpreted differently. Because there were two values, m value and S value, for the results of this test. All m-values were found as below the criteria means that the test result FAİL at -12 ºC. All modified bitumens, having the low temperature performance was found as (-22) originally, decreases the performance grade to (-16) in the modification of higher than the %2 SBS and %1 Sasobit. In order to ensure the value of creep stiffness of modified bitumen when the low temperature performance grade was -16, the effect of independent parameters were examined on the response of creep stiffness. The result showed that all parameters affects the creep stiffness properties but the SBS addition was most effective. Only the ınfluence of linear terms was examined, the effect of the addition of SBS would be ignored. Whereas the SBS addition is the most significant parameter on the creep stiffness of bitumen with the second order nonlinear term. The addition of SBS increases the creep stiffness exponentially but

the amount of SBS is restrained since there are a limit for the value of creep stiffness as 300 MPa.

- By the optimization study of four distinct responses, in a simultaneous analysis, the most effective independent parameters were determined with the limitation of responses. Addition of Wax was found as important for the DSR and BBR responses and not for the Viscosity and Elastic recovery same as the individual responses. Despite the bitumen composition influences the all responses linearly, the nonlinear term on the individual models of DSR, viscosity and Elastic Recovery responses were got lost. The reason may be explained as that the limitation for the maximization of DSR and Elastic recovery were defined while the minimization for the viscosity response were given in the analysis. Furthermore, it seems that SBS modification of bitumen influences all the properties of bitumen in all conditions.
- Finally, it has been found that the bitumen in the desired properties can provide improvement up to 50% in the rutting properties of asphalt. The bitumen modifications and the affecting parameters need to be precisely determined in order to have high quality roads, as in the case of this research.

This study is the first step for more detailed researches on this topic in the future. Only four properties of bitumen were investigated in this study since the major effects of this responses being on the asphalt performance. However there are lots of features of bitumen that should be examined further. Also the area of this study may be improved by the studying of different additives and the ranges. Moreover the SARA fractions of bitumen changes with the type of crude oil processed. The modelling of the SARA content of bitumen based on the type of crude oils and results of this study can be interpreted together again.

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APPENDICES

APPENDIX A : Service Procurement Reports
APPENDIX B : Asphalt Graphs

APPENDIX A

TÜRKİYE PETROLLERİ

TÜRKİYE PETROLLERİ ANONİM ORTAKLIĞI GENEL MÜDÜRLÜĞÜ (TP)

TÜRKİYE PETROLLERİ AR-GE MERKEZİ

Sayı :43146480-151.2/E.17389 01.03.2016

Konu :Rapor

İSTANBUL TEKNİK ÜNİVERSİTESİNE

(Bilimsel Araştırma Projeleri Birimi)

(Ayazağa Yerleşkesi Rektörlük Yeni Bina Maslak/İSTANBUL)

(Prof. Dr. Mustafa Hulusi ÖZKUL)

İlgi : 04/02/2016 tarihli yazınız.

İlgide kayıtlı yazınız ile talep edilen, 4 adet (latroscan) (kantitatif) numunesinin analizi, Ortaklığımız Ar-Ge Merkezi Daire Başkanlığı Laboratuvarlarında tamamlanmış olup, numune analizine ilişkin Rapor ekte gönderilmektedir.

Bilgilerinizi arz ederiz.

e-imzalıdır
Abdullah ÖNER
Daire Başkan Yardımcısı

e-imzalıdır
Süleyman ÇALIK
Daire Başkanı

Ek : Rapor (2 sayfa).

GÜVENLİ ELEKTRONİK İMZALI
ASLI İLE AYNIDIR

Not: 5070 Sayılı Elektronik İmza Kanunu uyarınca bu belge elektronik imza ile imzalanmıştır.

Evrak Doğrulama Kodu : FOHFHGPLGWFHTDRJTQXE Evrak Takip Adresi: http://belgedogrulama.tpao.gov.tr

TEKNİK HİZMETLER MÜDÜRLÜĞÜ

Bilgi için:Nezihe Gülsün TÜRÜN
Servis Görevlisi (Tek.Hiz)-A
Telefon No:(312) 207 24 63

Figure A.1 : The Result of SARA Analysis Reported by TPAO.

TÜRKİYE PETROLLERİ
AR-GE MERKEZİ

JEOKİMYA
MÜDÜRLÜĞÜ LABORATUVARLARI
Söğütözü Mah. 2180. Cadde No:10
06530 Çankaya/ANKARA
DENEY RAPORU
RAPOR NO: 5062

5062
02-16

Müşteri Adı/Adresi	:	İSTANBUL TEK. ÜNİVERSİTESİ İnşaat Fakültesi Maslak 34469/İSTANBUL
İstek Numarası	:	04.02.2016 tarihli yazı
Numunenin Adı ve Tarifi	:	Ağzı kapaklı cam şişeler içerisinde 4 adet numune
Numune Kabul Tarihi ve Numarası	:	05.02.2016/2965
Açıklamalar	:	4 adet numunede Asfalten Giderme ve Iatroscan analizi yapılmıştır.
Deneyin Yapıldığı Tarih	:	26.02.2016
Raporun Sayfa Sayısı	:	2

☑ Numune Müşteri tarafından alınıp TP ARGEM'e teslim edilmiştir.
☐ Numune TP ARGEM personeli tarafından alınmıştır. Açıklamalar bölümünde "Numune Alma Miktarları ve Dağıtımı İş Kuralı" veya ilgili numune alma standartlarına atıfta bulunulmuştur.
☐ Deney ve/veya ölçüm sonuçları, genişletilmiş ölçüm belirsizlikleri (olması halinde) ve deney metodları raporun tamamlayıcı kısmı olan takip eden sayfalarında verilmiştir.

Tarih
01.03.2016

Sema SAYILI	Recep Hayrettin SANCAY	Abdullah ÖNER
ÜNİTE MÜDÜRÜ	**DAİRE BAŞKAN YRD.**	**DAİRE BAŞKAN YRD.**
Deney(ler) Sorumlusu	Laboratuvar Yöneticisi	Teknik Hizmetler

Bu raporda yer alan deney sonuçları sadece deneyi yapılan numuneye aittir.
Bu rapor, laboratuvarların yazılı izni olmadan kısmen veya tamamen kopyalanıp çoğaltılamaz.
İmzasız ve mühürsüz raporlar geçersizdir.
Deney sonuçlarına rapor tarihinden itibaren 1 ay boyunca itiraz edilebilir.

1 /2

Figure A.1 (continued) : The Result of SARA Analysis Reported by TPAO.

	TP AR-GE MERKEZİ JEOKİMYA MÜDÜRLÜĞÜ ANALİZ RAPORU	
		5062
		02-16

Numune Kodu:	5062
Numunenin Üniteye Geliş Tarihi:	09.02.2016
Yapılan Analiz(ler):	Iatroscan analizi yapılmıştır.
Analiz Tarihi:	26.2.2016

IATROSCAN ANALİZ SONUCU

REFERANS BİLGİLER

Aşağıdaki analizler Iatron MK6 (TLC/FID) İnce Tabaka Kromatografi cihazında "North Sea Oil" standardı kullanılarak yapılmıştır.
% Doymuş Hidrokarbon (Saturate)
% Aromatik (Aromatic)
% Polar (Resin)
% Asfalten (Asphaltane)

ANALİZ SONUÇLARI

No	Numune Adı	Asfalten(%)	Doymuş Hidrokarbon(%)	Aromatik Hidrokarbon(%)	Polar(%)
1	EB101	23,42	14,91	51,59	10,08
2	EB102	20,88	11,86	54,46	12,8
3	EB103	34,41	15,3	45,03	5,26
4	EB104	24,59	13,93	51,54	9,94

ANALİZİN YAPILDIĞI ÜNİTE	YAZAN	ONAYLAYAN
JEOKİMYA MÜDÜRLÜĞÜ	PINAR YILMAZER Kıdemli Uzman Mühendis	SEMA SAYILI Müdür

Bu raporda yer alan deney sonuçları sadece deneyi yapılan numuneye aittir.
Bu rapor, laboratuvarın yazılı izni olmadan kısmen veya tamamen kopyalanıp çoğaltılamaz.
İmzasız raporlar geçersizdir.
Deney sonuçlarına 1 ay boyunca itiraz edilebilir.

2/2

Figure A.1 (continued) : The Result of SARA Analysis Reported by TPAO.

APPENDIX B

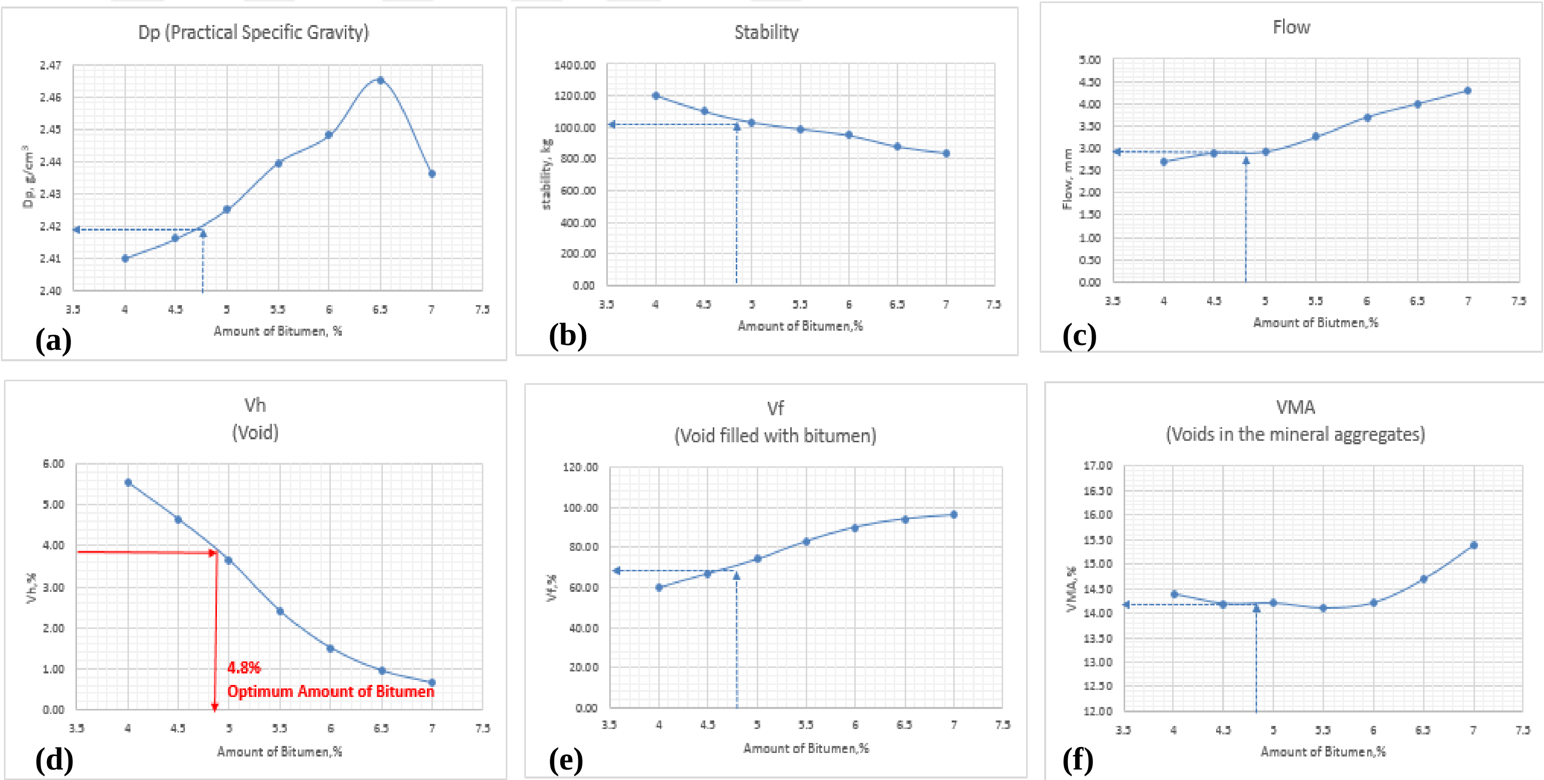

Figure B.1 : The Marshall Graphs of Asphalt Design of Unmodified Bitumen (a) Practical specific gravity (b) Stability (c) Flow (d) Void (e) Void filled with bitumen (f) Voids in the mineral aggregates.

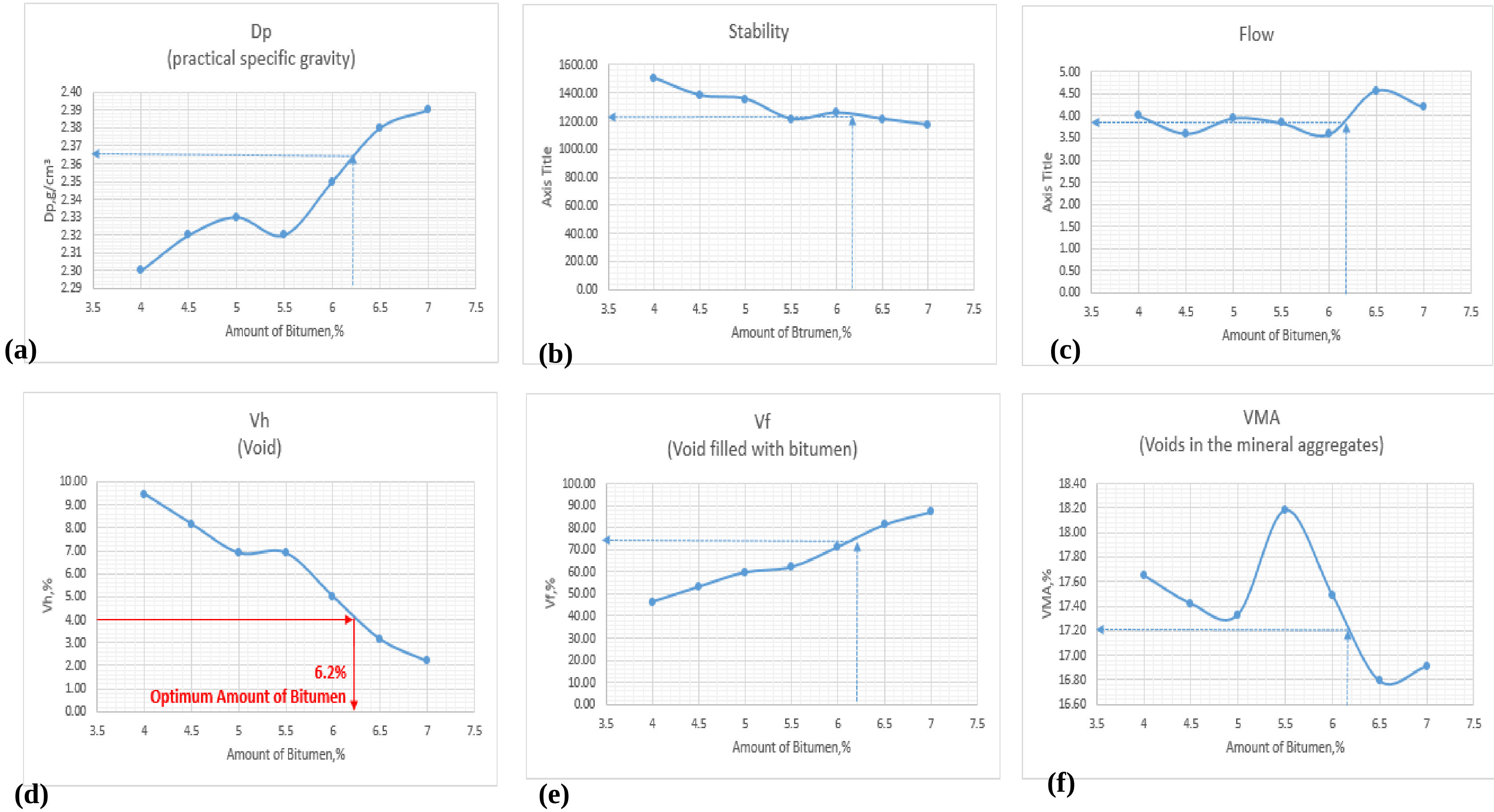

Figure B.2 : The Marshall Graphs of Asphalt Design of Modified Bitumen (a) Practical specific gravity (b) Stability (c) Flow (d) Void (e)Void filled with bitumen (f) Voids in the mineral aggregates.

CURRICULUM VITAE

Name Surname : Emel Baskent

Place and Date of Birth : Kars 19.04.1990

E-Mail : emel_baskent@hotmail.com

EDUCATION:

- **B.Sc.** : 2013, Middle East Technical University, Faculty of Engineering, Department of Chemical Engineering

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2015 - continue R&D Chief - TUPRAS
- 2013 - 2015 R&D Engineer - TUPRAS

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- Baskent, E. Ozkul M.H. 2016: Investigation of Parameters Affecting the Bitumen Modifications by Using Response Surface Method- World Polymer Congress, MACRO 2016, July, istanbul Turkey
- Baskent, E. Ozkul M.H. 2016: Tepki Yüzeyi Yöntemi Kullanılarak Bitüm Modifikasyonlarını Etkileyen Parametrelerin İncelenmesi-Ulusal Kimya Mühendisliği Kongresi, UKMK 2016, İzmir Turkey