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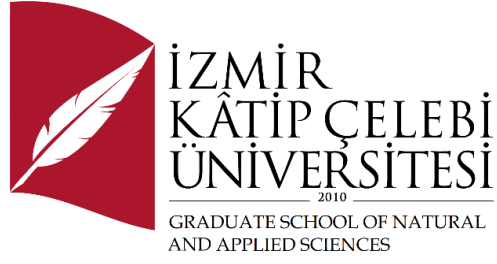
Hybrid Surface Modification For Fiber Reinforced EPDM Composites

Department of Material Science and Engineering
Doctoral Thesis

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Hybrid Surface Modification For Fiber Reinforced EPDM Composites

Abstract

EPDM is a conventional rubber type, very well known with its good ozone and weather resistance, fair temperature resistance, successful resistance to polar liquids like water and coolant and poor resistance to hydrocarbons. Fibers that are used in the study are carbon, basalt, PA2 glass, PP4 glass and aramid. Carbon fiber is very well known with high tenacity, high modulus of elasticity, high brittleness, low creeping tendency, chemically inert behaviour, low heat expansion and good electrical conductivity. Basalt fiber is capable to withstand very high temperature and can act as fire blocking element. It has good thermal resistance, strength, high friction coefficient and low wear rate. It has superior electrical insulating properties. It has high sea water and UV radiation resistance. Glass fibers have a high tenacity at a low elongation combined with low density. Aramid fibers are a class of heat-resistant and strong synthetic fibers. Fibers are blended with EPDM rubber to have improved characteristics of the components separately in a composite structure like higher mechanical properties, thermal resistance, fluid resistance and insulating properties. Hence fiber filled EPDM composites are held.

Firstly 2, 5, 10 PHR fiber ratios are used to be blended inside EPDM rubber mixture. Curing characteristics, mechanical properties, resistance to hot air and coolant ageing

effects are investigated. 5 PHR fiber ratio is found the most successful value by considering all test results.

Study is proceeded by surface treatment of fibers to have better bonding properties to the tubber matrix and to have a more compatible structure. As 5 PHR fiber ratio is selected the mixtures are filled with 5 PHR surface treated fibers. Surface treatment methods are alkali, EPDM solution and alkali + EPDM solution (hybrid). Rheological, mechanical, hot air and coolant ageing, SEM analysis, Raman analysis and contact angle measurements are run. It is decided to continue the study by focusing on basalt and PA2 glass fiber trials with further surface modification methods by examining the whole test results.

Further surface treatment methods are applied to basalt and PA2 glass fiber. Silane treatment, alkali (%2) treatment, silane + alkali (%2) treatment (hybrid) are conducted on basalt fiber whereas baring operation is applied to PA2 glass fiber. For PA2 glass fiber alkali, EPDM solution, alkali + EPDM solution (hybrid) treatmetns are applied processed in both oven and hot water. All these treated fiber types are blended in 5 PHR ratio into EPDM rubber mixture. After rheological, mechanical, hot air and coolant ageing, SEM analysis, Raman analysis and FTIR analysis are finished it is seen that hybrid surface treated basalt fiber is the optimum formulation with superior results.

Lastly RPA tests are run to see the processability of some trials to have idea about process characteristics. In RPA test machine before, during and after cure properties are gained from cure test, frequency sweep test and strain sweep test. Hybrid surface treated basalt fiber gives the optimum process characteristics in terms of easy extrusion flow, surface structure and low die swell.

When all these findings are combined it can be said that surface treatment brings lots of advantages to the fibers in case they need to be mixed with rubber blends. 5 PHR fiber ratio is suitable to be used. Hybrid surface treatment gives good results among the other surface treatments.

Keywords: EPDM, rubber, fiber, basalt, composite, surface treatment

Elyaf Takviyeli EPDM Kompozitler İçin Hibrit Yüzey Modifikasyonu

Öz

EPDM, iyi ozon ve hava dayanımı, idare eder sıcaklık dayanımı, su ve antifriz gibi polar sıvılara olan dayanımı ve hidrokarbonlara olan zayıf dayanımı ile iyi bilinen geleneksel bir kauçuk tipidir. Bu çalışmada kullanılan elyaf tipleri karbon, basalt, PA2 cam, PP4 cam ve aramiddir. Karbon elyaf yüksek çekme mukavemeti, yüksek elastik modülüs, yüksek kırılma, düşük sürünme eğilimi, kimyasal inert davranış, düşük ısı genleşmesi ve iyi elektriksel iletkenlik özellikleri ile iyi bilinmektedir. Bazalt elyaf çok yüksek sıcaklığa dayanabilir ve yangın engelleme elementi olarak davranabilir. İyi termal dayanıma, kuvvete, yüksek sürtünme katsayısına ve düşük yırtılma hızına sahiptir. Yüksek deniz suyu ve UV radyasyon dayanımına sahiptir. Cam elyaflar düşük uzamada yüksek çekme mukavemetine ve düşük yoğunluğa sahiptirler. Aramid elyaflar sıcaklık dayanımlı ve güçlü sentetik elyaf grubundalardır. Elyaflar, komponentlerin kompozit bir yapıda ayrı ayrı üstün özelliklerinden yararlanıp, daha yüksek mekanik, termal dayanım, sıvı dayanımı ve yalıtıcılık özellikleri elde etmek için EPDM kauçuk ile karıştırılırlar. Böylece elyaf takviyeli EPDM kompozitler oluşur.

Öncelikle, 2, 5, 10 PHR elyaf oranları, elyafları EPDM kauçuk karışımında karıştırmak için kullanılır. Pişim özellikleri, mekanik özellikler, sıcak hava ve

antifiriz yaşlanma özellikleri incelenir. Tüm test sonuçlarını göz önünde bulundurarak 5 PHR elyaf oranı en başarılı değer olarak bulunmuştur.

Çalışma, elyafların kauçuk matris içinde daha iyi yapışma özelliklerine ve daha uyumlu bir yapıya sahip olmaları için elyafların yüzey iyileştirmesi ile devam eder. Daha önceden 5 PHR elyaf oranı seçildiği için, karışımlar 5 PHR yüzey iyileştirilmesi yapılmış elyaflar ile devam eder. Yüzey iyileştirme metotları, alkali, EPDM solüsyon, alkali + EPDM solüsyondur (hibrit). Reolojik, mekanik, sıcak hava ve antifiriz yaşlandırması, SEM analizi, Raman analizi ve kontak açı ölçümleri yapılmıştır. Tüm test sonuçlarını göz önünde bulundurarak, basalt ve PA2 cam elyafa odaklanılması ve daha fazla yüzey iyileştirmesi yapılması kararlaştırılmıştır.

Daha fazla yüzey iyileştirme metotları basalt ve PA2 cam elyafa uygulanmıştır. Bazalt elyafa silan, alkali (%2) ve silan + alkali (%2) (hibrit) yüzey iyileştirmesi uygulanırken, PA2 cam elyafa hem etüvde hem de sıcak suda işlem gören alkali, EPDM solüsyon, alkali + EPDM solüsyon (hibrit) yüzey iyileştirmeleri uygulanmıştır. Tüm bu iyileştirilen elyaflar 5 PHR oranında EPDM kauçuk karışımında karıştırılmıştır. Reolojik, mekanik, sıcak hava ve antifiriz yaşlanması, SEM analizi, Raman analizi ve FTIR analizi yürütüldükten sonra hibrit yüzey iyileştirmesine giren bazalt elyafın en iyi sonuçlar ile en optimum formülasyonu

Son olarak, RPA testleri proses karakteristikleri hakkında bilgi sahibi olmak için, bazı denemelerin proses edilebilirliğini görmek için yapılmıştır. RPA test makinasında pişim öncesi, pişim esnası ve pişim sonrası özellikler, pişim testi, frekans süpürme testi ve gerilim süpürme testinden elde edilir. Hibrit yüzey iyileştirilmesi uygulanmış bazalt elyaf kolay ekstrüzyon akışı, yüzey yapısı ve düşük kalıp şişme özellikleri bakımından en optimum proses özelliklerini vermiştir.

Tüm bulgular birleştirilince, yüzey iyileştirmesi elyaflara kauçuklar ile karıştırılması durumunda Büyük avantajlar sağlarlar. 5 PHR elyaf oranı kullanıma uygundur. Ayrıca hibrit yüzey iyileştirmesi diğer denemelerin arasında daha iyi sonuçlar vermiştir.

Anahtar kelimeler: EPDM, kauçuk, elyaf, basalt, kompozit, yüzey iyileştirme



To my family...

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List of Abbreviations

SBR	Stiren butadien rubber
NBR	Acrylonitrile butadiene rubber
IPPD	N-isopropyl-N'-phenyl-p-phenylene diamine
ODPA	Octylated-diphenylamine
MBI	Mercaptobenzimidazole
MBTS	2-2'-Dithiobis(benzothiazole)
TMTD	Tetramethylthiuram Disulfide
ZDBC	Zinc dibutyldithiocarbamate
PVI	N-(Cyclohexylthio) phthalimide
EPDM	Ethylene propylene diene monomer
EPM	Ethylene propylene monomer
DCDP	Dicyclopentadiene
ENB	Ethylidene norbornene
HD	Hexadiene
E-P	Ethylene- propylene
PHR	Parts hundred rubber
SRF	Semi-reinforcing furnace
FEF	Fast extrusion furnace
HAF	High Abrasion Furnace
ISAF	Intermediate Super Abrasion Furnace
MBT	2- Mercaptobenzothiazole
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide

ZMBT	Zinc-2-mercaptobenzothiazole
DTDM	4,4'-Dithiodimorpholin
TMTD	Tetramethylthiuram Disulfide
DPTT	Dipentamethylenethiuram tetrasulfide
TMTM	Tetramethylthiuram Monosulfide
UV	Ultraviolet
IIR	Butyl rubber
NR	Natural rubber
Pphm	Parts per hundred million
SiO ₂	Silicone dioxide
A-glass	Alkali-lime glass with little or no boron oxide
C-glass	Alkali-lime glass with high boron oxide content, used for glass
D-glass	Borosilicate glass, named for its low dielectric constant
E-glass	Alumino-borosilicate glass
ECR-glass	Electrical/Chemical Resistance; alumino-lime silicate with less
R-glass	Lumino silicate glass without MgO and CaO with high
S-glass	alumino silicate glass without CaO but with high MgO content
E-modulus	Elastic modulus
PET	Polyethylene terephthalate
(Mg,Fe) ₂ SiO ₄	magnesium iron silicate, olivin
BF	Basalt fiber
SB	Short basalt
S 80	Suphur
MDR	Moving die rheometer
RPA	rubber process analyser
SEM	Scanning electron microscopy
FTIR	Fouirer Transform Infrared Spectrophotometer

PLC	Programmable logic controller
SAE	Society of Automotive Engineers
NaOH	Sodium hydroxide
APTES	Triethoxysilylpropylamine
PBO	poly (p-phenylene-2,6-benzobisoxazole)
PSA	Polysulfonamide
PLA	polylactide
POE-g-MAH	polyoxyethylene grafted with maleic anhydride
EPDM-g-	ethylene-propylene-diene rubber grafted with maleic anhydride
EAGMA	ethylene-acrylate-glycidyl methacrylate copolymer
SGF	short glass fiber
PP	polypropylene
WAXD	wide-angle X-ray diffraction
DSC	differential scanning calorimetry
TGA	thermogravimetric analyzer
SiO ₂	silicon dioxide
Al ₂ O ₃	Aluminium oxide
CF	carbon fiber
EPO-PHE	epoxy/phenoxy
PI	polyimide
PHE	phenoxy

List of Symbols

T _g	Glass transition temperature
° C	Celsius
MV	Mooney viscosity
MWD	Molecular weight distribution
M _w	Weight- average molecular weight
M _n	Number-average molecular weight
kV	Kilovolt
MU	Mooney unit
wt	Weight
g	Gram
kg	Kilogram
VI	Viscosity index
ml	Milileter
mm	Milimeter
cm ³	Centimetercube
cpm	Cycle per minute
rpm	Revolution per minute
ML	Minimum torque
MH	Maximum torque
T _{s2}	Scorch time
T ₁₀	The time required for the state of cure to reach 10 % of the full
T ₅₀	The time required for the state of cure to reach 50 % of the full

T90	The time required to reach 90 % of full cure
S'	Elastic torque
S''	Viscous torque
G'	Storage shear modulus
G''	Loss shear modulus
η^*	Complex dynamic viscosity
η'	Real dynamic viscosity
Hz	Hertz
TS	Tensile strength
TSb	The value recorded at breaking point
EAB	Elongation at break

Chapter 1

Introduction

1.1 Basic Terms

Polymers are macro molecules that are composed of the covalent connection of small molecules called monomers to each other. Polymers are the most important building structures of the indispensable basic materials of human life. The chemical reactions in which monomers are joined together to form a polymer are called polymerization reactions.

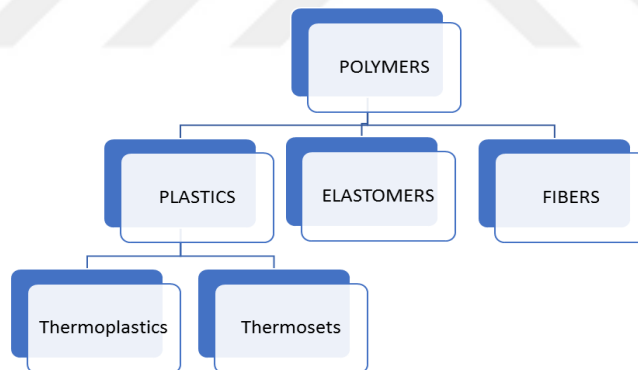


Figure 1.1: Classification of polymers

Elastomers are the network structures that are formed by the seldom cross linking of rubber (polymer). They are polymeric materials which can elongate at least to the twice of its original length at room temperature and turn to their original length when the deforming force on them is removed. They are as hard as glass at very low temperatures and do not show fluid-like properties even at very high temperatures. They can show elastic properties in a broad range starting from room temperature till cracking temperature.

In real it is the name of a tree (weeping tree). The materials gained from this tree and its latex found area of usage in industry [10]. Rubbers are not cross linked but have the ability of cross linking. They are polymers that can be vulcanized. They can be shaped under high temperatures and under deforming forces.

1.2 History of Rubber

1751- It is the first time that rubber is used technically. 1803- First rubber factory in Paris was established.

1839- Charles Goodyear discovered vulcanization.

1888- John Boyd Dunlop produced first pneumatic bicycle tyre.

1909- F. Holman produced first synthetic rubber in Bayer laboratories in Germany and got first patent in the world.

1912- First automobile tyre from %100 synthetic rubber was produced in Germany.

1916- First synthetic rubber producing factory started working with a capacity of 150 ton/ month.

1929- Hermann Staudinger gained SBR and NBR from butadiene rubber.

1937- The production of this rubber type started.

1937- American chemists Sparks ve Thomas produced Butyl rubber.

1.3 Classification of Rubber Types

Whole around the world over 15 million rubber is produced, 1/3 of it is natural rubber and the rest is synthetic rubber [16]. Natural Rubber: It is gained from the latex that pours out of the rubber tree (*Hevea brasiliensis*). Synthetic Rubber: It is produced from the chemicals that is gained from petroleum. There are over 100 types of synthetic rubber.

1.4 Rubber Blends

It is a blend that is composed of rubber, fillers, plasticizers, processing aids, various additives, activators, curing agents and can be vulcanized. The group of the chemicals all of which are selected according to the proper application and creates proportional integrity is called recipe or formulation. In rubber technology, in a recipe, rubber ratio is estimated to be 100 parts (phr) and the ratio of the rest of the chemicals are arranged by considering this fact [34].

- A recipe consists of;
 - Rubber
 - Fillers
 - Plasticizers
 - Processing aids
 - Anti-ageing agents
 - Activators
 - Accelerators (Vulcanization system)
 - Curing agents
 - Retarders
 - Other ingredients (Paint, odorizer, blowing agents)

Fillers: Their grain sizes are small, they provide reinforcing the matrix, improve processing properties, form economical blends and give colour to the blend. Carbon black, calcium carbonate, clay and silica etc.

Plasticizer: Make the process easier, forms the backbone of the blend with filler. Parafinic oil, naphtenic oil, aromatic oil etc.

Processing Aids: They help processing. Their characteristics resemble plasticizers but they are added to the blend in small amounts and they affect physical properties not so much, so that in this point they are separated from plasticizers. Fatty acid derivatives, synthetic resins etc.

Anti-ageing Agents: Uncured or unvulcanized rubber is in ageing tendency. They are the ingredients that prevent the deformation of rubber partially or exactly by time without the existence of a chemical effect. IPPD, ODPA, MBI, etc...

Activators: For vulcanization organic materials called accelerators are needed. The materials that enable the activation of accelerator are called activators. Zinc oxide, active zinc oxide etc..

Accelerators: They are the materials that make a favourable effect on the goods by speeding up the vulcanization. MBTS, TMTD, ZDBC, etc....

Curing Agents: Sulphur: Three dimensional structure formed by the connection of long polymer chains by bridges is provided by vulcanization. The bridge role is taken by sulphur molecules which are connected to each other with long chains and provides the structure to be steady, durable and elastic.

Retarders: They are the chemicals which are added to the recipe to prevent the risk of pre-vulcanization. PVI, etc..

1.5 Rubber Technology

It is the sum of knowledge, technique, skill and methodology applied to produce elastomeric material. Rubber technology should be examined in 3 groups: Preparation of the blend, pre-forming, vulcanization.

Preparation of the Blend: Blend is prepared in an intermeshing rotor type closed mixer which is computer controlled. Rubber, filler, plasticizer and other ingredients that constitute the blend is mixed in this closed chamber. Pressure is provided by hydraulic piston. In intermeshing rotor type, the rotors turn countercurrently and are embedded in each other. They turn with the same speed and squeezes the blend between the rotors and chamber so that high quality mixing is achieved.

Pre-forming: Rubber blend that is prepared in closed mixer is pre-formed before it is vulcanized to be a final product. Pre-forming is made in either open mill or extruder to have required dimensions for the final product. Open mill includes two rollers located horizontally in parallel that turns countercurrently with different speeds. They are in various diameters and lengths. There is friction between rollers, back roll rotates with higher speed. Inner layer; produced in tube extrusion, Textile reinforcement; processed in knitting machine, Outer layer; produced in cross head extrusion. Knitting process have to be ensured with choosing suitable knitting head (as well as needle number) type and adjusting stitch size.

Vulcanization: There are several methods in vulcanization. The most common ones are press and autoclave curing. Compression moulding includes placing the rubber blend between two moulds and curing it under pressure and heat. The rubber blend takes the shape of the mould that it is placed inside. In autoclave curing heat is provided by saturated steam pressure. Rubber parts are cured under definite time and heat. Vulcanization is the process of changing the chemical structure (cross-linking) of rubber and enabling it to have elastic properties irreversibly. High plastic properties before vulcanization yields high elastic properties after vulcanization. The factors that are related with vulcanization are: temperature, pressure, time.

1.6 EPDM Polymer Structure

The commercial rubbers with the lowest density are ethylene-propylene copolymers. To introduce cure sites, a nonconjugated diene monomer may be employed. EPDM has a small number of double-bond cure sites external to the backbone. The ratio of ethylene to propylene varies from 50:50 to 75:25 [35], and a typical T_g is -60°C . EPDMs have excellent resistance to weathering and good heat stability. They can be partially crystalline to give high green strength, but they possess poor building tack. The structure of the regular, alternating amorphous copolymer of ethylene is shown in Figure 1.2.

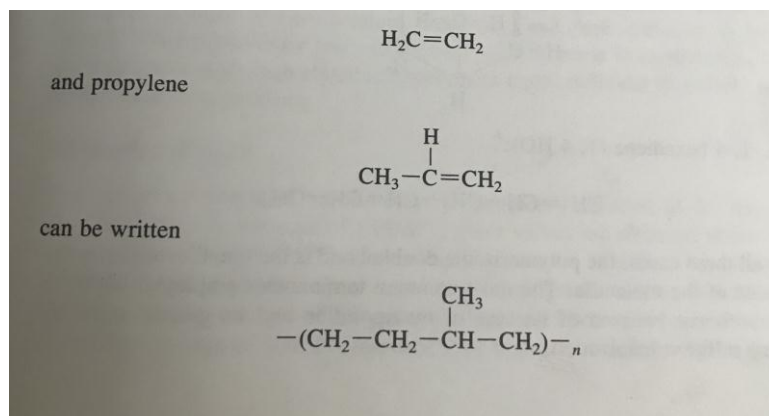


Figure 1.2: The structure of the regular, alternating amorphous copolymer of ethylene [28]

Saturated nature of EPM prevents normal type of sulphur curatives to be employed for vulcanization. In the presence or absence of a coagent peroxide cures are used. Since these cures are difficult and expensive to handle on standard rubber equipment EPDM polymers were developed and are widely used.

EPDM's are EPM's that possess unsaturation. The unsaturation is introduced by copolymerizing the ethylene and propylene with a third comonomer, which is nonconjugated diene. The dienes are structured in a way that only one of the double bonds will polymerize and the unreacted double bond acts as a site for sulphur cross linking. This latter unsaturation is not a part of polymer backbone but a side group. As a consequence, the terpolymer retains the excellent ozone resistance that the copolymer possesses. There are three comonomers exists in industry to introduce unsaturation, they are; Dicyclopentadiene (DCDP), Ethylidene norbornene (ENB) and 1,4 hexadiene (1, 4 HD)

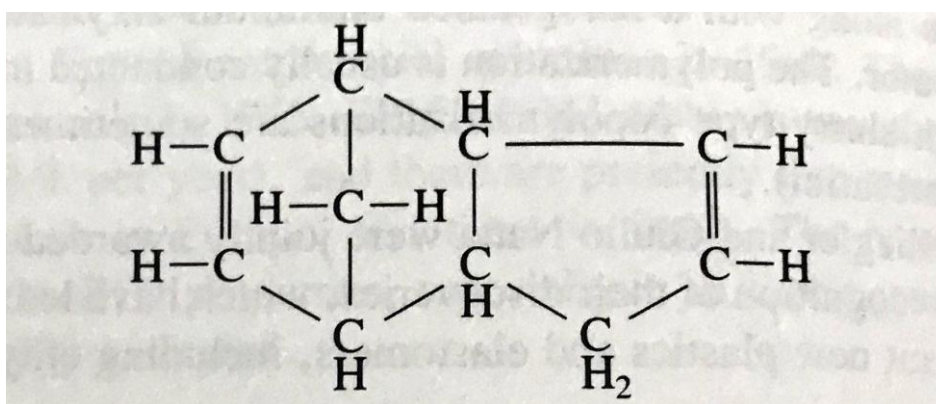


Figure 1.3: Dicyclopentadiene (DCDP) [28]

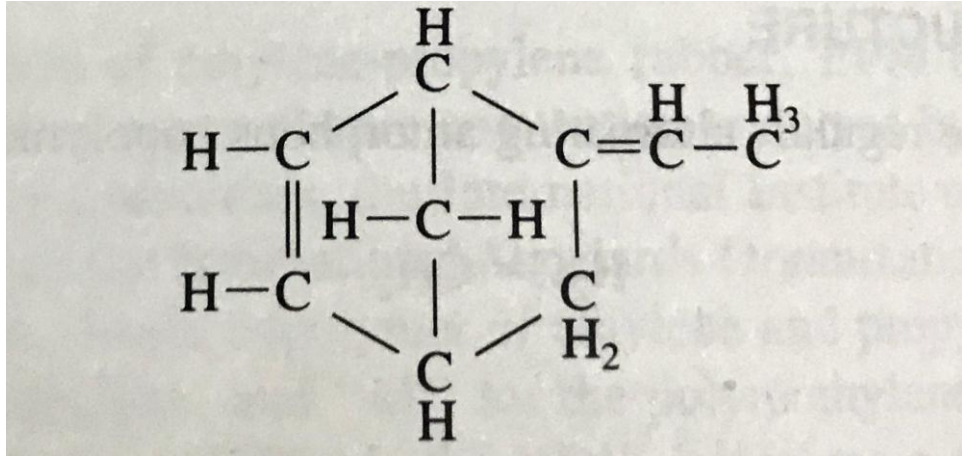


Figure 1.4: Ethylidene norbornene (ENB) [28]

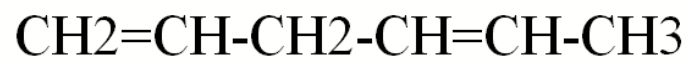


Figure 1.5: 1,4 hexadiene (1, 4 HD) [28]

The polymerizable double bond is the one illustrated on the left side of the molecule in all three cases. The most common monomer is ENB because of its ease of incorporation and its greater reactivity toward sulphur vulcanization.

The structure of EPDM can be illustrated as follows:

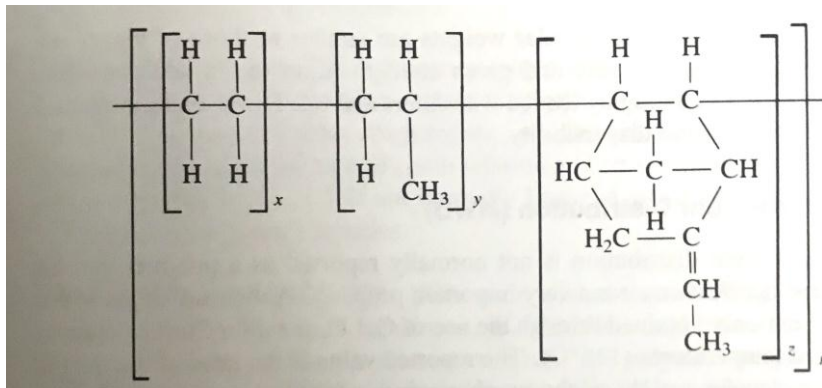


Figure 1.6: The structure of EPDM [28]

1.7 EPDM Polymer Variables and Properties

Several other variations are possible in EPDM's rather than variations resulting from introduction of different termonomers. They affect the resultant properties of EPDM [28].

(E-P) Ethylene- propylene Composition

The contents of E-P elastomers are reported as weight-percent ethylene and vary from 75 to 45 %. Monomers are randomly distributed, resulting in amorphous type copolymers. The higher ethylene content means higher green strength (shape retention), leads to load with high amount of fillers/ oil, results in higher compounded tensile strength, possess better extrusion properties. The disadvantages of higher ethylene content are their poorer mill processing behaviour at lower temperatures, inferior low temperature properties, and their difficulty in being mixed. It is appropriate to store high ethylene terpolymers under sufficient warmth to minimize dispersion problems since crystallinity tends to increase with decrease in temperature.

Molecular Weight

The molecular weight of an elastomer is reported as Mooney Viscosity (MV). In EPDM's these values are obtained at elevated temperatures usually 125 °C. Primary reason for this is to melt out any effect that high ethylene content can produce like crystallization, thus hiding the true molecular weight of the polymer. Polymers with higher molecular weights are extended with oil (25 to 100 phr). Such polymers should be stored in the absence of light since the oils will tend to accelerate oxidative degradation.

Advantages of higher molecular weights are similar to those of higher ethylene contents such as high tensile strength and green strength. In addition these polymers can be highly loaded with fillers and oils. Disadvantages are their poor processing and dispersibility.

Molecular Weight Distribution (MWD)

Molecular weight distribution is very important but is not normally reported as polymer variable. MWD is obtained by Gel Permeation Chromatography at elevated temperatures (135 °C). The reported value is the ratio of the weight- average molecular weight to the number-average molecular weight (M_w/M_n). This value varies between 2 to 5. The polymers with broad molecular weight has excellent mill processing and calendaring capabilities and high green strength. These polymers are extensively used for applications that don't allow large loadings of filler and oil. Their disadvantages are slower cure rate and poorer state of cure. Narrow molecular weight distributions are more common in EPDM's since they result in faster cure rates, better state of cure and smoother extrusions.

Diene Type

There are 3 termonomers that are employed in the manufacture of EPDM's; ENB, 1,4 HD and DCPD. All of them create unsaturation into the EPDM backbone as vulcanization sites, they bring different characteristics to the elastomer because of their different structures.

ENB is the most widely used termonomer and the double bond it introduces has the greatest activity for sulphur vulcanization. Unique characteristic of this termonomer is that it makes it possible to prepare linear as well as branched polymers by varying the conditions under which the polymers are synthesized.

1,4 HD containing polymers exhibit a slower cure rate than ENB but possess certain properties that are superior. One of this property is excellent heat characteristics, which is close to EPM. Polymers that has 1,4 HD are normally linear in structure and possess excellent processing characteristics.

DCPD's main advantage is its low cost and ease of incorporation like ENB. It has the slowest cure rate among three termonomers. As a result of the slight polymerizability of its second double bond, all polymers prepared with it are branched. This branching is useful to bring ozone resistance to diene rubber blends.

Miscellaneous Properties

Even termonomer type will bring slight differences to polymer, a table can be prepared to show general various characteristics of EPDM. Also this table reveals the low density property that a practical compounder can consider for reducing costs in the fabrication of finished EPDM rubber products. Elastomers are bought by weight but consumed by volume. As a result, for a given weight of polymer, more finished products can be produced with EPDM.

Constant	Units	Value
Density	g/cc	0.854
Expansivity $(1/V)(dV/dT)_p$	$(^{\circ}\text{C})^{-1}$	$7.5 \text{ and } 8.8 \times 10^{-4}$
$(1/L)(dL/dT)_p$	$(^{\circ}\text{C})^{-1}$	2.5×10^{-4}
Specific heat, Cp	cal/g/ $^{\circ}\text{C}$	0.53
Thermal conductivity	cal/s/cm/ $^{\circ}\text{C}$	4.2×10^{-4}
Refractive index		1.4740 ^{23°C}
		1.4524 ^{90°C}
		1.4423 ^{120°C}
Dielectric constant	10 ³ Hz	2.5
Dissipation factor	10 ³ Hz	0.2
Diffusion constant, D ₍₀₎	cm ² /s	
benzene 23°C		6.1×10^{-8}
n-hexane 23°C		4.1×10^{-8}
CH ₂ Cl ₂ 23°C		1.3×10^{-7}
CHCl ₃ 30°C		1.2×10^{-7}
Permeability coefficient	cm ² /s/atm°C	
CH ₂ Cl ₂ 30°C		2.8×10^{-7}
H ₂ O 37.5°C		4.5×10^{-8}
Glass-transition temperature	°C	-60

Figure 1.7: Physical constants of Ethylene Propylene Rubbers [28]

1.8 EPDM Processing

1.8.1 Mixing

Usually an internal mixer, such as Banbury is used to accomplish mixing. When mill mixing is necessary to be used, low viscosity, higher propylene EPDM types are preferred. EPDM polymers with higher viscosity and higher ethylene content are considered to be difficult for mill mixing. Compounds with these properties tend to be loaded with more filler and oil that mill mixing is usually impractical from this point alone [25].

Although all types of EPDM's are suitable for internal mixer, according to the property of the polymer, the range of compound quality, and the condition of mixer, mixing techniques are affected [28].

The most popular technique is to load the chemicals in single step and the batch is loaded upside-down (fillers, oils and the others at first and rubber at last). This technique is suitable for low-medium ethylene polymers loaded with mineral fillers or semi-reinforcing carbon blacks like SRF and FEF.

For compounds having high ethylene or high molecular weight EPDM polymers and containing reinforcing carbon blacks like HAF and ISAF, poor dispersion is gained with single step or upside-down mixing method. Better dispersion is handled when polymer is added at first with a defined portion of carbon black. In case oil is added at first good dispersion is not achieved.

Other variations in mixing procedures are successful. If better dispersion and batch to batch consistency is needed two step mixing is also applied.

1.8.2 Extrusion

High ethylene content EPDM's provide good green strength for shape retention therefore they are most useful for extrusion. Good green strength supports the compound to be fed easier to the extruder. Lack of green strength leads to poor feeding characteristics. If compounds are not fed properly and easily, they do not fill the extruder barrel in an equal volumetric flow. This results the dimensional variations in semi-finished extrusion product. Hence high ethylene content is needed in a well designed extrusion compound to obtain good processability.

Cold feed extruders are preferred to provide better control of processing conditions to have more uniform extrusion products. Mostly, the temperature of extrusion screw is higher than the extrusion barrel. To have smooth surface and reasonable extrusion speed, working parameters should be optimized.

1.8.3 Molding

Injection, transfer and compression molding types are used to produce rubber parts. Independent from the molding technology, polymers having medium to high propylene are usually preferred. It may be desirable to use high ethylene content polymers to take the advantage of its greater extendability in applications involving highly extended compounds.

EPDM compounds are suitable for injection molding because they provide fast cure, good flow and do not tend to reverse at high curing temperatures.

1.9 Elements of Compounding EPDM

1.9.1 Vulcanizing Agents

While EPM can only be cross linked with peroxides, EPDM can use peroxides or sulphur and accelerators.

In a formulation if EPDM is substituted without changing cure system, the cure rate and properties will not be the same. Properties can be different because of the differences in third monomer, molecular weight and other variations in polymer characteristics. Polymers with DCPD and 1,4 HD will need more active accelerators or higher amounts to have the same cure level.

EPDM has unsaturation that allows sulphur vulcanization. Combination of accelerators depend on many conditions like processing methods, properties required and cost. Usually cure system will contain a thiazole accelerator (MBT, MBTS or like), a thiuram and/or a dithiocarbamate. Elemental sulphur may be replaced by sulphur donor type accelerators, if heat or compression set requirements are severe. Accelerator bloom may be a problem in some cases. To prevent blooming it is important to have the accelerators below their solubility limits.

The limits for most commonly used elastomers are as follows [28]:

MBT, MBTS, CBS, ZMBT

3 phr

DTDM	2 phr
TMTD	0,8 phr
DPTT, TMTM	0,8 phr

1.9.2 Fillers

Mechanical properties of unfilled rubber are poor therefore EPDM require fillers. Carbon black is the most useful material for filler whereas silica, clay, talc and some other mineral fillers may also be used. To have advantage from their reinforcing effect, fillers have to be well dispersed in the compound. High tensile strength, good tear resistance and improved abrasion resistance are related with good dispersion of fillers. Well mixed and dispersed batches provide better processing for extrusion, molding and so forth.

1.9.3 Plasticizers and Processing Aids

Naphthenic oils provide best compatibility with EPDM compounds at reasonable cost. They are mostly used plasticizers with EPDM. Paraffinic oils with lower volatility and improved UV stability are used at higher temperatures or coloured compounds.

Aromatic oils must not be used with peroxide systems because they have adverse effect on some compound properties.

Stearic acid, zinc stearate and other internal lubricants are included in compound to have easy processing.

1.10 Properties of EPDM Vulcanizates

1.10.1 Mechanical Properties

Type and amount of fillers in the compound determine the mechanical properties. Mechanical properties like tear resistance at initial and hot conditions, tensile strength are well for EPDM compounds. EPDM vulcanizates have a wide range of

hardness. When compared to SBR and IIR, mechanical properties of EPDM vulcanizates are superior. But the level obtained by NR can not be reached. Compression set values are good for EPDM vulcanizates. Third monomer in the system is ENB with a high concentration, which is cured either by peroxide or sulphur with a highly active accelerator system. Peroxide cured EPDM compounds give better compression set values when compared to sulphur curing. Compression set of sulphur cured EPDM increases rapidly at high temperatures whereas peroxide cured EPDM vulcanizes do not [21].

1.10.2 Dynamic Properties

EPDM vulcanizates show good dynamic behaviour and dynamic fatigue resistance.

1.10.3 Heat and Ageing Resistance

EPDM vulcanizates are good in terms of heat and ageing resistance. For example, for 1000 hours at 150C, peroxide cured compounds show good heat resistance without hardening. The heat resistance of sulphur cured compounds are worse than EPDM cured compounds. Because of high heat resistance and improved compression set values of peroxide cured EPDM vulcanizates, this system is mostly chosen and used.

Ageing resistance of EPDM compounds is excellent. An oxidative degradation of vulcanizates will not take place under normal working conditions [21]. Ozone resistance is also excellent. Under exposure to ozone rich air around 100 pphm for many months, compounds will not be deformed.

Weathering conditions are also excellent, on exposure to open air EPDM vulcanizates are not harmed by atmospheric conditions.

1.10.4 Low Temperature Flexibility

Low temperature properties of EPDM compounds are good. EPDM vulcanizates can be used upto -40°C temperature and even with special formulations this can be improved to -50°C [19].

1.10.5 Resistance to Swelling and Chemicals

EPDM vulcanizates have excellent resistance to diluted acids, alkalis, by acetone, alcohol and hydraulic fluids [21]. If inorganic acids are concentrated, they destroy the EPDM vulcanizates.

Swelling occurs highly in aliphatic, aromatic or chlorinated hydrocarbons for EPDM vulcanizates. Since they are non-polar, EPDM compounds swell in these mediums.

1.10.6 Electrical Properties

Electrical insulating properties of EPDM compounds are excellent. EPDM peroxide cured vulcanizates can be preferred for voltages upto 25 kV. Because it can be more easily processed, and it accepts higher filler loadings. Electrical properties are also good at high temperatures and after heat ageing. Because EPDM vulcanizates absorb little moisture, so their electrical properties are not affected so much when they are exposed to water [21].

1.11 Fiber Types Commonly Used in Rubber Industry

Textile fiber materials can be divided into two, natural and chemical fibers. Industrial revolution and growth of world population increased the consumption of fibers. Since 1950 a huge increase in the share of chemical fibers is seen. In 1994, for the first time in history the share of chemical fibers exceeded natural fibers.

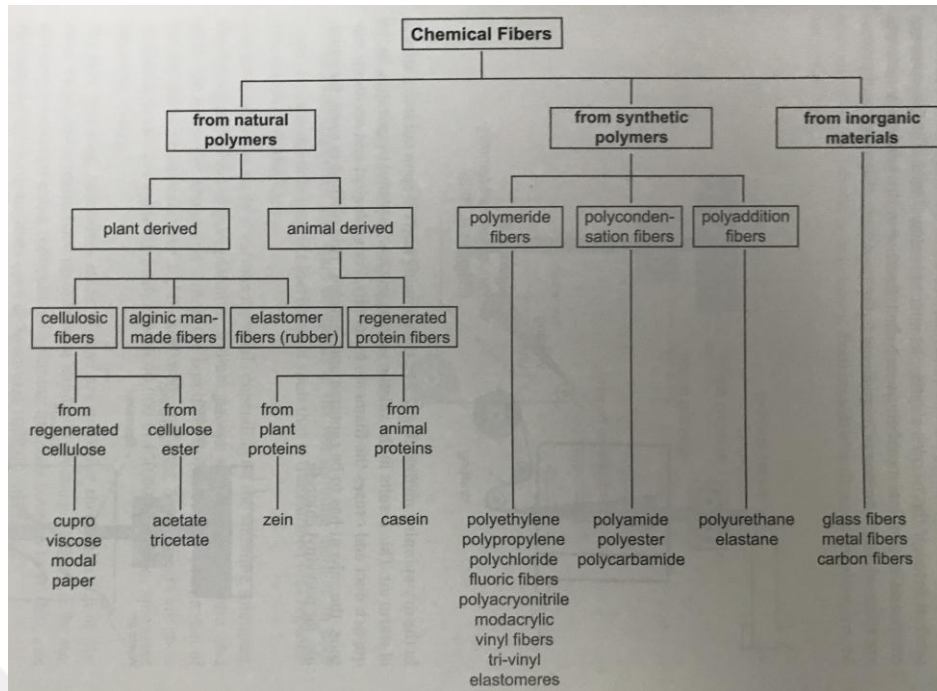


Figure 1.8: Categorization of chemical fibers [20]

1.11.1 Glass Fibers

Glass is an inorganic non metallic material. Glass state is the frozen state of a supercooled material. Suppression of the crystallization of a melt results this.

Silicate glass is composed of two components SiO_2 and silicate.

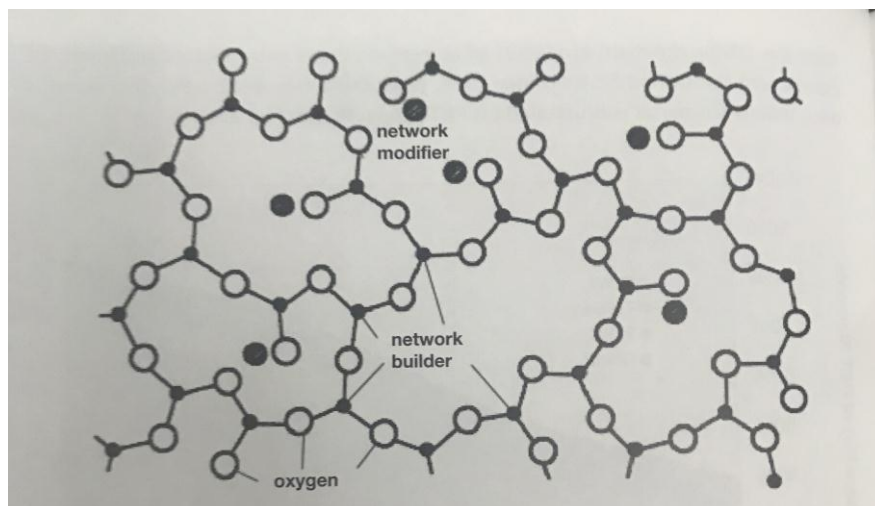


Figure 1.9: Inner structure of glass [20]

Composition, diameter of glass and implementation of additional components determine the type of glass like A-glass, C-glass, D-glass, E-glass, ECR-glass, R-

glass, S-glass and some other types. Important properties of glass fibers are summarized as follows.

	D-glass	E-glass	R-glass	AR-glass
Density (g/cm ³)	2.14	2.6	2.53	2.68
Filament tenacity (MPa)	2500	3400	4400	3000
Filament tenacity in composite (MPa)	1650	2400	3600	1800
Elongation at break (%)	4.5	4.5	5.2	4.3
E-modulus (MPa)	55,000	73,000	86,000	73,000
Softening temperature (°C)	775	846	985	773

Figure 1.10: Typical properties of glass fibers [20]

Textile glass fibers have a high tenacity at a low elongation combined with low density. This results in favorable tenacity or modulus values relative to their weight. Textile glass as a mineral material is naturally inflammable, and when subjected to heat it does not release steam or poisonous gases. Glass is resistant to oils, fats and solvents and is highly resistance to acidic and alkaline solutions. Major producers of glass fiber are China, United States and European Union.

1.11.2 Carbon Fiber

Carbon fibers are well known for their high tenacity, high modulus of elasticity, high brittleness, low creeping tendency, chemically inert behaviour, low heat expansion and good electrical conductivity. Figure 1.11 shows the inner structure of carbon fibers. Carbon layers causing high values of tenacity and E-modulus are clearly seen. Excellent electric conductivity of carbon fibers are caused by free electrons between the layers.

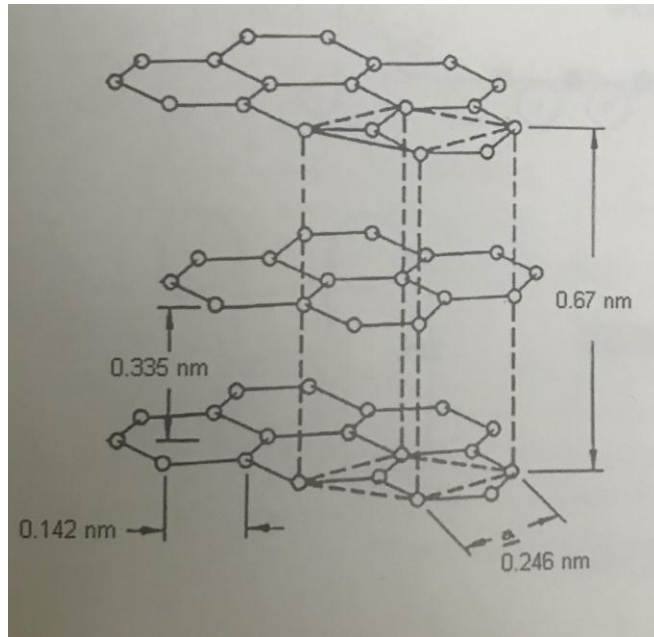


Figure 1.11: Inner structure of carbon fibers [20]

There are two methods used for the production of carbon fibers. One of them is based on polyacrylonitrile with processing steps polymerization, (wet-) spinning, drawing, oxidation, carbonization, and graphite annealing. The other method is based on mesophase pitch with the processing steps thermal treatment, melt spinning and oxidation, carbonization, and graphitization annealing [11]. Graphitization treatment in the last step is done at temperatures upto 3000 ° C. Purpose of both production methods is to arrange graphite layers in fiber direction. For carbon fibers, carbon content needs to be at least 90 %. Carbon fibers can be produced also from viscose fibers. This process is not widely used in market and is for producing textiles for medical applications.

1.11.3 Polyester Fiber

Polyester is a category of polymers which contain the ester functional group in their main chain. Although there are many polyesters, the term "polyester" as a specific material most commonly refers to polyethylene terephthalate (PET). Industrial polyester fibers, yarns and ropes are used in tyre reinforcements, fabrics for conveyor belts, reinforced hoses, safety belts, coated fabrics and plastic reinforcements with high-energy absorption.

1.11.4 Aramid Fiber

Aramid fibers are a class of heat-resistant and strong synthetic fibers. It means aromatic polyamide. They are fibers in which the chain molecules are highly oriented along the fiber axis, so the strength of the chemical bond can be exploited. Aramid (kevlar) chemical and geometrical structures are given below.

1.11.5 Basalt Fiber

Basalt originates from volcanic magma and flood volcanoes, a very hot fluid or semifluid material under the earth's crust, solidified in the open air. Basalt is a common term used for a variety of volcanic rocks, which are gray, dark in colour, formed from the molten lava after solidification. Basalt rock-beds with a thickness of as high as 200 m have been found in the East Asian countries. Russia has unlimited basalt reserves. There are large deposits of these rocks in the Ural, Kam, chatka, Far East, Sakhalin, Kola Peninsula, Northwest Siberia, and the Transcaucasian.

Basalt fiber is a material made from extremely fine fibers of basalt, which is composed of the minerals plagioclase, pyroxene, and olivine. Plagioclase is an important series of minerals within the feldspar family. The pyroxenes are a group of important rock-forming inosilicate minerals found in many igneous and metamorphic rocks. The mineral olivine is a magnesium iron silicate with the formula $(\text{Mg,Fe})_2\text{SiO}_4$. It is similar to carbon fiber and fiberglass, having better physicomechanical properties than fiberglass, but being significantly cheaper than carbon fiber. Basalt fiber (BF) is capable to withstand very high temperature and can act as fire blocking element. They were a replacement for asbestos fibers in recent years because of its thermal resistance, strength, high friction coefficient and low wear rate. It has good electrical insulating properties. They have high sea water and UV radiation resistance. They are divided into 2; short and continuous basalt fibers. When compared to continuous fiber reinforced composites, short fiber reinforced composites can be easily processed with affordable cost. The most important factors in the short fiber reinforcement are fiber dispersion and fiber aspect ratio. The homogeneous fiber dispersion is the most important factor to enhance the mechanical properties. Continuous basalt fibers and short basalt fibers has two main differences;

First; SB has greater deviances in diameter and elastic modulus. Secondly; continuous fibers shows higher modulus and strength values. Both phenomena arise mainly from technological reasons.

Amuthakkannan P. et al studied the effect of fibre length and fibre content on mechanical properties of short basalt fibre reinforced polymer matrix composites. Specimen prepared with short basalt fibre as reinforcing materials and polyester resin as a matrix in polymer composite. Based on the availability, different fibre length was taken and fabrication was done with compression moulding machine, keeping the mould closing as constant and increasing the content of fibre in the composites. Specimens were subjected to tensile strength, flexural strength and impact strength test and the failure of the composite was examined with the help of scanning electron microscopy (SEM). Short basalt fibre reinforced polymer composites have been investigated with different fibre length and fibre content and the following conclusion were drawn. The characterization of the composites reveals that the fiber length is having a significant effect on the mechanical properties of composites and also fibre content. The optimum fibre weight percentage of 68 % of fibre and optimum length of the fibre of 10 mm were investigated. The tensile strength of the Basalt fibre composites revealed that 68 % of fibre and 10 mm length of fibre exhibits better properties than other lengths of fibre. Flexural strength of composites also shows better properties in 68 % of fibre and 10 mm length of fibre. The length of reinforced basalt fibre play a significant impact on some mechanical properties, Impact strength of basalt fibre reinforced composite of 50 mm length shows the maximum impact energy absorption in all the percentage of fibre [2]

Gao G.et al studied an excellent ablative composite based on PBO reinforced EPDM. Short poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers were first used to reinforce ethylene-propylene-diene terpolymer (EPDM) as thermal insulation materials. The effects of PBO fiber length and content on the mechanical and ablative properties of the composites were investigated in detail. As a result, the PBO fibers/composites show significantly higher tensile strength and ablation resistant abilities than the aramid fibers/composites. Moreover, with the length and content of PBO fibers increasing, both the tensile strength and the ablation resistance of the composites increase gradually though the break elongation reduces sharply.

Considering the properties requirement of thermal insulator, PBO fibers with 3.42–5.56 wt% in content and 3–4 mm in length are preferred. The mass loss rate of 0.05 g s⁻¹ and erosion rate of 0.10 mm s⁻¹ under the oxyacetylene flame test are observed in the optimal samples, which is evidently lower than the best aramid fibers/EPDM-based composites reported so far [18].

Jia X. et al studied ablation and thermal properties of Ethylene–Propylene– Diene elastomer composites reinforced with polysulfonamide short fibers. Polysulfonamide (PSA) short fiber/ethylene– propylene–diene elastomer (EPDM) composites were prepared as high-performance thermal insulators. The pyrolysis products and thermal stabilities of the PSA fiber and aramid fiber were analyzed. The ablation and thermal properties of the PSA/EPDM composites were compared with those of the aramid/EPDM composites. The degradation peak temperature of the PSA fiber was 100C higher than that of the aramid fiber. With the fiber content increasing, the ablation rates of both composites decreased up to 10 phr and subsequently increased, whereas the thermal conductivities of both composites increased linearly. In comparison with the aramid/EPDM composites, the ablation rate and thermal conductivity of the PSA/EPDM composites were lower, whereas the thermal degradation temperature and limiting oxygen index of the PSA/EPDM composites were higher. Dynamic mechanical thermal testing and morphology observations revealed that strong interfacial bonding between the fiber and the matrix was developed in the PSA/EPDM composites, and it was beneficial for improving the ablation properties of the composites [23].

Liu T. et al studied basalt fiber reinforced and elastomer toughened polylactide composites: mechanical properties, rheology, crystallization, and morphology. A series of the reinforced and toughened polylactide (PLA) composites with different content of basalt fibers (BF) were prepared by twin screw extruder. The toughness of BF/PLA composites was improved further by the addition of polyoxyethylene grafted with maleic anhydride (POE-g-MAH), ethylene–propylene–diene rubber grafted with maleic anhydride (EPDM-g-MAH), and ethylene-acrylate-glycidyl methacrylate copolymer (EAGMA), relatively. The mechanical properties, rheology, crystallization, and morphology of BF/PLA composites were studied. The results showed that basalt fiber had significant reinforcing and toughening effect in

comparison with glass fiber. The basalt fiber shows reinforcing and toughening effects in the BF/PLA composites [27].

Wang W. et al studied mechanical properties and morphological structures of short glass fiber reinforced PP/EPDM composite. The mechanical properties and crystal morphological structures of short glass fiber (SGF) reinforced dynamically photo-irradiated polypropylene (PP)/ethylene–propylene–diene terpolymer (EPDM) composites were studied by mechanical tests, wide-angle X-ray diffraction (WAXD), optical microscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA). The mechanical properties of PP/EPDM composites, especially the tensile strength were greatly strengthened by dynamically photo-irradiation and the incorporation of SGF. The thermal analysis results show that the incorporation of SGF into PP/EPDM plays an important role for increasing its thermal stability [37].

Arroyo M. et al studied composites based on PP/EPDM blends and aramid short fibres. morphology/behaviour relationship. The effect of both a thermoplastic elastomer (EPDM) and short aramid fibres on polypropylene (PP) crystallization kinetics and tensile behaviour has been investigated. The results have shown that PP/EPDM blends are non-miscible in the melt, and, at low EPDM percentages in the blend (25%), the particles of EPDM act as nucleating agents and co-crystallize with PP. However, at higher percentages, the EPDM obstructs the mobility of PP chains and hence decreases the PP crystallization rate. Aramid fibres are effective nucleating agents for PP crystallization, giving rise to the phenomenon of PP transcrystallinity on their surface. The tensile behaviour of the blends and composites are in intimate relation with the morphological characteristics of these materials. Aramid fibres are effective nucleating agents for PP crystallization giving rise to both an increase of the global rate of the crystallization process and the phenomenon of transcrystallinity with PP, which permits increasing the interaction at fibre/matrix interface and hence the mechanical behaviour of the composites. Transcrystallization of PP decreases as EPDM content in the matrix increases. EPDM and fibres exert a synergistic effect on nucleating action. However, and according to the values of ΔG (free energy for chain folding of PP chains), the nucleating effect of aramid fibres is higher than the effect of EPDM particles. The stiffness of the PP and EPDM

increases as fibre percentage in the composite increases, and decreases as EPDM content in the matrix increases. Blends of PP/EPDM with low percentages of fibre show similar stiffness to the PP with an improved toughness. Tensile strength at break shows a similar behaviour to the stiffness, and the elongation at break generally increases as EPDM percentage in the matrix increases, and decreases as fibre content in the composite increases [3].

Deak T. et al studied chemical composition and mechanical properties of basalt and glass fibers: a comparison. The geometrical and mechanical properties and chemical composition of different basalt and glass fibers have been investigated. Tensile tests were performed on short basalt fiber made by melt blowing, glass fiber and three different types of continuous basalt fibers made by spinneret method. The chemical composition was evaluated by plasma atomic emission spectroscopy. The geometrical and mechanical properties of continuous basalt and glass fibers were similar to each other in terms of diameter, tensile strength and modulus. Short basalt fibers had considerably lower average diameter and mechanical performance with relatively high standard deviation. The SiO₂ and Al₂O₃ content of basalt fibers showed correlation with tensile properties of fibers. Results revealed that continuous basalt fibers were competitive with glass fibers and short basalt fibers were weaker in terms of quality and mechanical properties. It was observed that the joint SiO₂ and Al₂O₃ content of basalt and glass fibers showed correlation with tensile properties of fibers [13].

Colombo C. et al studied static and fatigue characterisation of new basalt fibre reinforced composites. Basalt reinforced composites are recently developed materials. These mineral amorphous fibres are a valid alternative to carbon fibres for their lower cost, and to glass fibres for their strength. In order to use basalt reinforced composites for structural applications, it is necessary to perform a mechanical characterisation. With this aim in the present work experimental results of several static and fatigue tests are described. Two polymeric matrices are taken into account, vinylester and epoxy, to assess their influence on the evaluated parameters. In parallel to these mechanical tests, also the thermal answer of the specimens to mechanical loads is evaluated by means of thermography. From the obtained results it is possible to propose the following conclusions; basalt reinforced epoxy composites evidenced higher mechanical properties with respect to vinylester, both

in the tensile and compressive behaviour, and the failure mode is more compact, since fibres do not tend to explode [12].

Karslı NG. et al studied effects of initial fiber length and fiber length distribution on the properties of carbon-fiber-reinforced-polypropylene composites. In this study, short carbon fiber-reinforced polypropylene composites with three different initial carbon fiber lengths were prepared by using extrusion compounding and injection molding techniques. The physical and morphological properties of the prepared short carbon fiber-reinforced composites were investigated by means of tensile test, differential scanning calorimetry and scanning electron microscopy. Final fiber length distributions of composites were also determined by using an image analyzing program. It was found that the maximum number of fibers was observed in the range from 51 to 100 μ m. Number average final fiber lengths were calculated between 230 and 280 μ m. Regardless of the used initial carbon fiber length, tensile strength and modulus values of the composites increased with the increasing carbon fiber content. It has been concluded that the initial fiber length at the studied range did not have any significant effect on the properties of composites. Rockwell hardness test results showed that the hardness of composites increased tremendously with the increasing CF content while the increasing CF length increased it slightly [24].

Ozkan C. et al studied short carbon fiber reinforced polycarbonate composites: Effects of different sizing materials. In this paper, effects of the sizing material type and level on the mechanical, electrical and morphological properties of the short carbon fiber (CF) reinforced polycarbonate (PC) composites were investigated. Unsized CF and the CFs which were sized with epoxy/phenoxy(EPO_PHE), polyimide(PI) and phenoxy(PHE) were used as reinforcement materials. Fiber length distribution analysis indicated that sizing protected the CFs breakage into the smaller lengths during the processing. Effects of the sizing material type and level on the mechanical properties of CF reinforced PC composites were investigated by means of tensile and izod impact strength tests. Tensile test results revealed that tensile strength and modulus values of sized CF reinforced PC composites were higher than that of unsized CF reinforced PC composites. Besides, effect of the sizing material level on the tensile properties of composites changed with respect to the sizing material type. It was also found that the measured effects of the sizing agent type and level on the notched izod impact strength of composites were not so significant. In

addition to this, it was found that sized CF reinforced PC composites had higher electrical conductivity values than unsized CF reinforced PC composites. Also, PHE sized CF reinforced composites had the highest electrical conductivity value among the other composites. Better interactions between EPO_PHE and PHE sized CF and PC matrix were observed from the scanning electron microscope analysis. As a result of this study, PHE and EPO_PHE sized CFs can be suggested as proper reinforcements for PC matrix.

All of the studies above investigate the properties of the composites which include different fibers and polymers. The effect of fiber length and content on the composites are examined. Due to the requirement of high strength materials with low cost, short fiber composites are widely used to reinforce polymers. The most important factor in short fiber reinforced composites is the dispersion and compatibility of fibers in the polymer matrix. Homogenous fiber dispersion is necessary to enhance mechanical and ageing properties. Among none of the studies a research which is based on EPDM with surface modification of fibers is seen.

The main aim of this study is to investigate the effect of surface and hybrid surface modification of various fibers to the EPDM fiber reinforced composites by changing the fiber content and surface modification methods. In this study EPDM rubber recipe is filled with carbon, basalt, glass and aramide fibers. Various surface modifications are applied to the fibers to have a more homogenous rubber compound and better bonding of fibers to the rubber matrix. The differences between the EPDM fiber filled composites with and without surface modification of fibers are investigated.

Especially hybrid surface modification of fibers to form an EPDM fiber filled composite brings an innovation to this study. Also basalt as a filler, and EPDM as a polymer had never been studied together before. Besides, the EPDM fiber filled composite is suitable for the applications for automotive industry in the production of a coolant hose which helps transferring water and ethylene glycol based fluids in the engine compartment of an automobile.

One of the motivations of this study is to prepare a rubber compound suitable to the specification SAE J20 Class E which is a coolant hose specification in automotive

industry. Class E of SAE J20 points out the requirement of a fiber filled EPDM composite. The hoses produced from EPDM fiber filled composites are mono-layer and usually can cover the demands of a multi-layer hose where the functional requirements are not very high. This situation brings the advantage of a cost reduction in rubber hoses, because when mono layer and multiple layer hose productions are considered, mono layer hose production is very advantageous in terms of costs.



CHAPTER 2

Materials and Method

2.1 Materials

2.1.1 Chemicals

- Arlanxeo Keltan 5470: Ethylene Propylene Diene Rubber (EPDM). Mooney Viscosity ML 1+4 (125 ° C) is between 51-59 MU. Ethylene content is between 63,9- 68,1 %. Volatile material is maximum 0,5 wt %. ENB content is between 4,1-5,1 %.
- Carbon black: N 762 SRF carbon (Purex HS-25 Orion Carbon, Germany). Iodine absorption number is between 23-33 g/kg. Oil absorption number is between 117-129 cc/100. Heating loss at 125 °C is max. 0,5 %. Sieve residue at 325 M is max. 50 ppm.
- Parafinic oil: SK-5 from Petrol Ofisi. Flash point is between 292-350 °C. Viscosity index is between 90-110 VI. Density is between 0,89-0,93 g/ml.
- Active zinc oxide: from Brüggemann. Zinc content as zinc oxide is minimum 92%. Specific surface area is minimum 57 m²/g.
- Stearic acid: from P.T Musim Mas, Indonesia.
- MBTS 80: Active content is 80% from Kettlitz (Polypowder)
- TMTD 80: Active content is 80% from Kettlitz (Polypowder)

- ZDBC 80: Active content is 80% from Kettlitz (Polypowder)
- S 80: Active content is 80% from Kettlitz (Polypowder)
- Glass fiber: PA2 (D) 4.5 from Cam Elyaf Sanayi. Filament diameter is between 10,5- 11,5 micron. Moisture content is max. 0,07 %. Size content is between 0,45- 0,75 %.
- Glass fiber: PP4- 4.5 from Cam Elyaf Sanayi. Filament diameter is between 12- 14 micron. Moisture content is max. 0,07 %. Size content is between 0,45- 0,75 %.
- Carbon fiber: is from Dow Aksa in the length of 6 mm.
- Basalt fiber: is from Spintex in the length of 24 mm. Melting point is around 1050 °C. Density is 2, 67 g/cm³.
- Aramid fiber: Trade name is Kevlar from Dupont. Fiber length is between 1,12- 1,25 mm. Moisture content is between 5,2- 10,8 %.

2.1.2 Instruments

- Rheometer tests are carried out in MDR 2000 test equipment of Alpha [1] (Figure 2.1 and Figure 2.2)



Figure 2.1: Alpha MDR 2000 Moving die Rheometer with computer

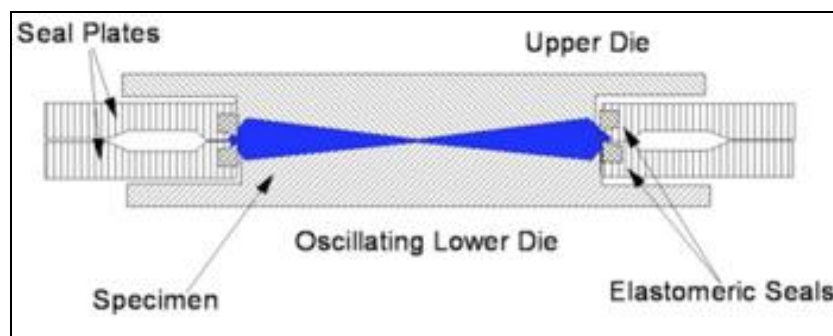


Figure 2.2: Die configuration of MDR 2000

- Tensile strength, elongation at break and tearing strength tests are made by using Zwick/Roell BDO-FB005TN testing machine [39] with computer (Figure 2.3).



Figure 2.3: Zwick/Roell test machine

- Hardness is measured with Zwick/Roell analogue hardness testing instrument to Shore A (Figure 2.4)



Figure 2.4: Zwick hardness test instrument [40]

- Compression set test is carried out at 125 °C for 70 hours. Compression ratio is 50 %.

- Heat ageing tests are carried out at 125 °C for 70 hours using a hot cabinet from Nuve [31] with forced air circulation. (Figure 2.5)



Figure 2.5: Hot cabinet from Nuve

- Coolant ageing test are carried out at boiling point of coolant for 70 hours. Mixing content is ethylene glycol to water in the ratio of 50:50. Reflux condenser, a heater and a volumetric flask is used.



Figure 2.6: Reflux condenser for coolant ageing

- RPA tests are carried out in RPA Premier of Alpha Technologies. Its frequency is between 0,1 to 3000 cpm. Temperature range is between ambient upto 230 °C. Strain is between $\pm 0,07\%$ to $\pm 1255\%$.



Figure 2.7: RPA test machine

- Raman Analyses are made with Renishaw Raman Spectrometer



Figure 2.8: Raman analysis test machine

- SEM analyses are carried out with Carl Zeiss 300VP model.

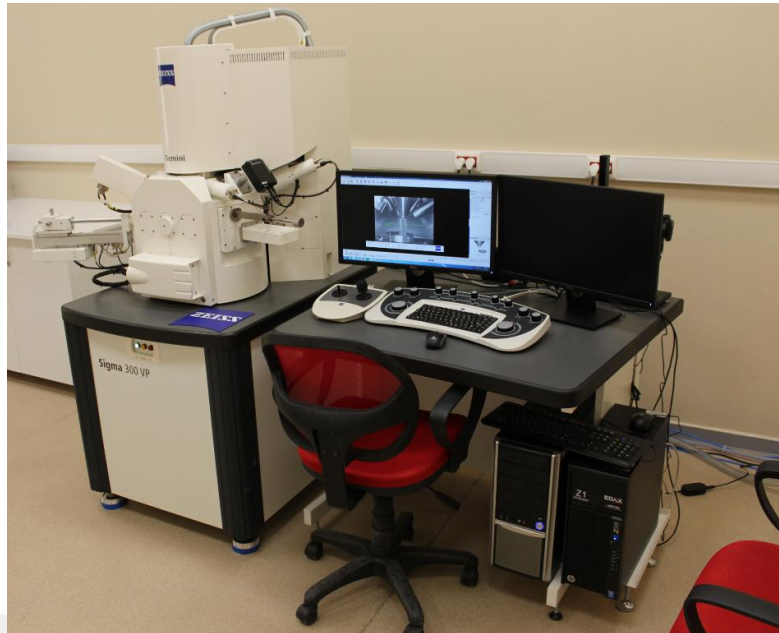


Figure 2.9: SEM analysis test machine

- FTIR analyses are carried out with Thermo Scientific Nicolet iS50 FT-IR Spectrometer



Figure 2.10: FTIR test machine

Surface tension and contact angle tests are carried out with Attension Theta camera system.

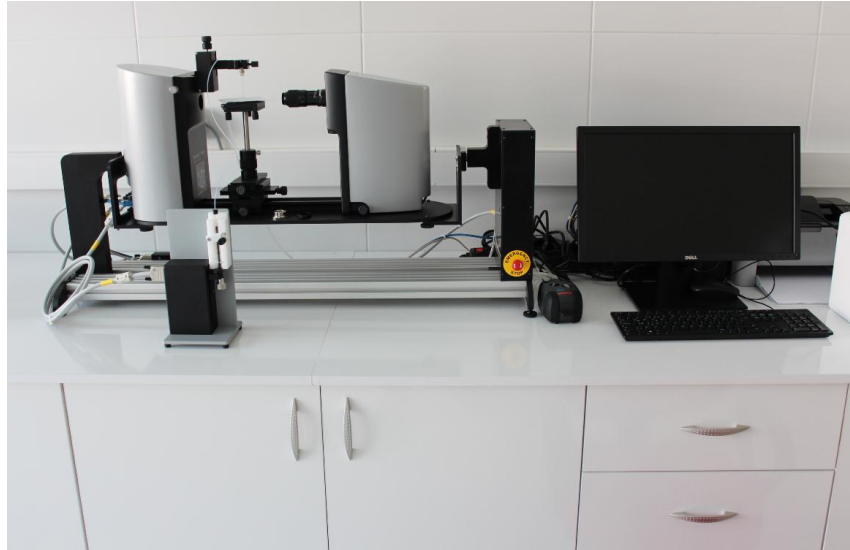


Figure 2.11: Surface tension and contact angle test device.

2.2 Method

2.2.1 Preparation of Semi-finished Product

Two main process is applied to produce rubber mixtures, closed chamber mixing and afterwards open mill mixing.

Closed Chamber Mixing (Internal Mixer): Consist of an enclosed chamber and two rotors with small clearance between them and enclosing wall. The rotor type is intermeshing rotor type which is well known in industry for the advantage of better homogeneity and dispersion [10]. The mixer is a laboratory scale one with 3 lt. capacity. It is fully automated and PLC controlled. Mixing programme of the machine has 5 steps, in each step mixing time or mixing temp. can be adjusted, also ram pressure and rotor speed needs to be set with a reasonable cooling water temperature. The number of the mixing steps that needs to be adjusted is upto the decision of the compounder. After mixing parameters are defined, they are recorded to the system and then mixing is run automatically. The PLC control prevents the worker to set a parameter wrongly to the system. Mixing parameters are listed in Table 2.1 [15]. First rubber is thrown to the the mixer, mixed for 45 seconds at a ram pressure of 35 bar and a rotor cycle of 20 rpm. After rubber is mixed at the defined parameters, chemicals except curatives are added to the mixer. These chemicals are carbon black, oil, and the other small ingredients. They are mixed for 120 seconds at

a ram pressure of 35 bar and a rotor cycle of 30 rpm. Then curatives are added to the mixer. Ram pressure and rotor cycle is decreased to prevent scorch issues. Curatives are mixed for 30 seconds at a ram pressure of 20 bar and a rotor cycle of 15 rpm. During whole mixing cycle cooling water temperature is set to 20 ± 5 °C.



Figure 2.12: Lab. Scale mixer

Table 2.1: Mixing parameters in each step in intermesh banbury

	Mixing time (sec.)	Mixing temperature (°C)	Ram pressure (bar)	Rotor speed (rpm)	Cooling water temp. (°C)
1 st step (rubber is mixed)	45	-	35	20	20 ± 5
2 nd step (carbon black, plasticizer, other small ingredients are added)	120	-	35	30	20 ± 5
3rd step (vulcanizing agents, accelerators are added)	30	-	20	15	20 ± 5
4 th step (empty)	-	-	-	-	
5 th step (empty)	-	-	-	-	

Two roll open mill mixer: Consist of two smooth, hardened-steel rolls set horizontally. They rotate in opposite directions. The back roll rotates faster than the front one in order to produce a friction or grinding.

The compound that is gained at the end of mixing cycle in closed mixer does not have a proper shape. Therefore an additional open mill mixing is applied t the compound in order to have a proper shape sheet.



Figure 2.13: Two roll open mixer

The formulations are listed in Table 2.2. Formulations are designed by the experience gained from the previous experiences and by examining the chemical ratios in a rubber recipe that exist in literature. Fifteen formulations are studied by changing the fiber percentages and types [19] twenty two formulations are arranged by applying different fiber modifications. Totally thirtyseven formulations are prepared. Then 3 formulation are mixed additionally with the same content, D009, D009/4 and D018 to run RPA tests. At the end 40 formulations are held.

Table 2.2: Formulations that are prepared by changing the fiber percentages and types									
Formulation Code	D005	D006	D007	D008	D009	D010	D011	D01	D013
EPDM Rubber	100	100	100	100	100	100	100	100	100
Carbon black	122	122	122	122	122	122	122	122	122
Plasticizer	73	73	73	73	73	73	73	73	73
Active ZnO	3	3	3	3	3	3	3	3	3
Stearic acid	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
MBTS 80	2,1	2,1	2,1	2,1	2,1	2,1	2,1	2,1	2,1
TMTD 80	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8
ZDBC 80	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8
S 80	2,1	2,1	2,1	2,1	2,1	2,1	2,1	2,1	2,1
Carbon fiber	2	5	10	0	0	0	0	0	0
Basalt fiber	0	0	0	2	5	10	0	0	0
PA2 Glass Fiber	0	0	0	0	0	0	2	5	10
PP4 Glass Fiber	0	0	0	0	0	0	0	0	0
Aramide fiber	0	0	0	0	0	0	0	0	0

Table 2.2: Formulations that are prepared by changing the fiber percentages and types						
Formulation Code	D014	D015	D016	D017	D018	D019
EPDM Rubber	100	100	100	100	100	100
Carbon black	122	122	122	122	122	122
Plasticizer	73	73	73	73	73	73
Active ZnO	3	3	3	3	3	3
Stearic acid	0,5	0,5	0,5	0,5	0,5	0,5
MBTS 80	2,1	2,1	2,1	2,1	2,1	2,1
TMTD 80	0,8	0,8	0,8	0,8	0,8	0,8
ZDBC 80	0,8	0,8	0,8	0,8	0,8	0,8
S 80	2,1	2,1	2,1	2,1	2,1	2,1
Carbon fiber	0	0	0	0	0	0
Basalt fiber	0	0	0	0	0	0
PA2 Glass Fiber	0	0	0	0	0	0
PP4 Glass Fiber	2	5	10	0	0	0
Aramide fiber	0	0	0	2	5	10

Table 2.2: Formulations that are prepared by fiber modification												
Formulation Code	D006	D006/2	D006/3	D006/4	D009	D009/2	D009/3	D009/4	D009/5	D009/6	D009/7	
EPDM Rubber Compound	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	
Carbon fiber	5	0	0	0	0	0	0	0	0	0	0	
NaOH modified Carbon fiber	0	5	0	0	0	0	0	0	0	0	0	
EPDM sol. modified Carbon fiber	0	0	5	0	0	0	0	0	0	0	0	
Hybrid modified Carbon fiber	0	0	0	5	0	0	0	0	0	0	0	
Basalt fiber	0	0	0	0	5	0	0	0	0	0	0	
NaOH (%10) Modified Basalt f.	0	0	0	0	0	5	0	0	0	0	0	
EPDM sol. modified Basalt fiber	0	0	0	0	0	0	5	0	0	0	0	
Hybrid modified Basalt fiber	0	0	0	0	0	0	0	5	0	0	0	
Silane Modified Basalt fiber	0	0	0	0	0	0	0	0	5	0	0	
NaOH (%2) Mod. Basalt fiber	0	0	0	0	0	0	0	0	0	5	0	
NaOH (%2) and Silane Mod. Basalt	0	0	0	0	0	0	0	0	0	0	0	5

Table 2.2: Formulations that are prepared by fiber modification										
Formulation Code	D012	D012-1	D012/2	D012/2-1	D012/2-2	D012/3	D012/3-1	D012/4	D012/4-2	
EPDM Rubber Compound	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	304,5	
Glass PA2 fiber	5	0	0	0	0	0	0	0	0	
Bare glass PA2 fiber dried in oven	0	5	0	0	0	0	0	0	0	
NaOH Mod. Glass PA2 fiber	0	0	5	0	0	0	0	0	0	
NaOH Mod. bare glass PA2 fiber - Oven	0	0	0	5	0	0	0	0	0	
NaOH Mod. bare glass PA2 fiber -Hot Water	0	0	0	0	5	0	0	0	0	
EPDM Solution mod. Glass PA2 Fiber	0	0	0	0	0	5	0	0	0	
EPDM Solution mod. bare Glass PA2 Fiber-Oven	0	0	0	0	0	0	5	0	0	
Hybrid modified Glass PA2 fiber	0	0	0	0	0	0	0	5	0	
Hybrid mod. bare Glass PA2 fiber oven	0	0	0	0	0	0	0	0	0	5

Table 2.2: Formulations that are prepared by fiber modification		
Formulation Code	D018	D018/2
EPDM Rubber Compound	304,5	304,5
Aramide fiber	5	0
NaOH Mod. Aramide fiber	0	5

Rheometer tests are applied to unvulcanized rubber to identify the vulcanization characteristics of semi-finished products.

2.2.2 Tests Applied to Semi-finished Products

2.2.2.1 Rheometer Test

Rheometers allow monitoring of stiffness changes as cure progress by measuring cure characteristics [8]. Rheometer test standard is ASTM D5289. Rheometer is a moving die rheometer (MDR). In MDR only bottom die moves, this creates advantage for better heat transfer.

5±0.5 gr sample is taken from the rubber mixture for rheometer test. It is run at 190°C for 3 minutes for all of the blends. It brings the advantage to see curing characteristics of the blends in a short time. Also, test is made from uncured rubber mixture so it does not require to cure the compound and prepare test samples from it. Therefore, it is a practical test. The test is run at isothermal conditions. There are several outputs of rheometer test which are listed below:

M_L: It is the minimum torque value at the test temperature. At this point cross links are not formed yet. Material is softened as heat is given up to the material and has plastic properties more than elastic properties at this point [8]. This value gives idea about the flow characteristics of the material in extrusion process or in the mould. Smaller minimum torque values mean easy and quick flowing of the material and large minimum torque values the opposite. Also it can be said that in small M_L values swelling of the material at the exit of the die in extrusion machine can be larger than that of in big M_L values. However cross linking is not formed yet this value can represent the hardness of the material.

M_H: It is the maximum torque value at test temperature and is the point where the compound is completely cured. All of the cross links are formed at this point and the material have completely elastic characteristics. This value gives idea about the hardness of the material, increasing of the M_H value means harder finished product. When the number of cross links increases maximum torque value increases.

t_{s2}: It is scorch time. It represents the required time that the material must pass from the extrusion process safely before being vulcanized. Above this point the material starts to gain elastic properties, plastic behaviour of material leaves its place to

elastic behaviour [8]. It is a term that is widely used in rubber industry. Short scorch times are not preferred because the cross links may begin to form at the time of extrusion. This is an unwanted situation because if cross linking starts shape can't be given to the semi-finished product. The surface of the semi finished product would not be smooth either. Also in the same manner long scorch times are not preferred because cross linking may not be formed in the desired density at this time. This means longer vulcanization times or unvulcanized (insufficiently cured) material. This creates weakness in physical properties of the material and the finished product can't be elastic as its desired, shape problems may arise. So by considering process requirements optimum scorch time must be tried to be gained.

Theoretically the time required for the state of cure to increase to two torque units above the minimum at the given cure temperature means scorch time.

t₁₀: The time required for the state of cure to reach 10 % of the full cure defined as $(M_H - M_L)$.

t₅₀: The time required for the state of cure to reach 50 % of the full cure defined as $(M_H - M_L)$.

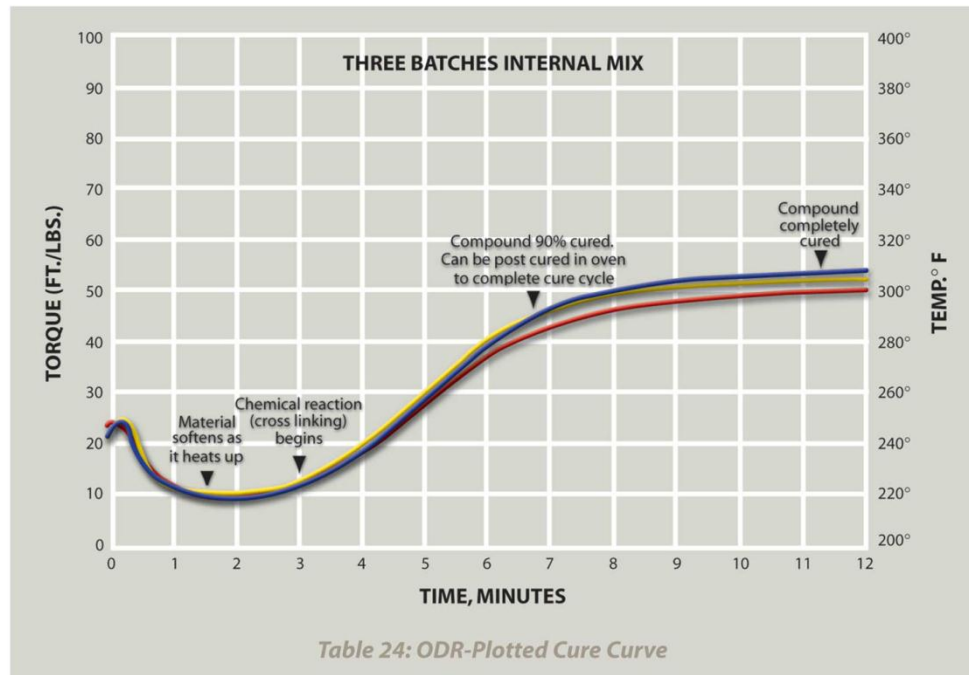
t₉₀: The time required to reach 90 % of full cure defined as $M_H - M_L$. t_{90} is generally the state of cure at which the most physical properties reach optimal results. This value is critical while determining the vulcanization times in different curing processes as whole rubber materials is vulcanized till they reach 90 % of full cure (t_{90} value). This time is enough for material to gain its physical properties because after taking the material out of any curing process the remained 10 % cure continues.

If t_{90} isn't considered and the vulcanization process is finished when the whole curing is completed, physical characteristics of the finished product would be affected negatively. Because after taking the product from the vulcanization process, curing would slowly continue, and reversion would be seen.

In the same manner if the material is taken out from the vulcanization process before it reaches t_{90} value, enough cross links would not be formed, and curing would not be sufficient enough for the material to have required physical properties.

So, by considering the situations above, it can be understood that t_{90} is a very important value and it is the optimum time for curing a rubber material.

A rheometer curve can be seen in the below Figure 2.14.



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Figure 2.14: A Rheometer curve

2.2.2.2 Rubber Process Analyzer (RPA) Test

RPA is used to determine the characteristics of rubber compounds before, during and after curing. RPA test is applied according to ASTM D6204 standard. The aim of this test is covering the use of a rotorless oscillating shear rheometer for the measurement of the flow properties of raw rubber and unvulcanized rubber compounds [9]. So, it runs test not only from unvulcanized rubber but also from raw rubber. RPA is a raw polymer tester, processability tester, advanced curemeter and a dynamic mechanical tester.

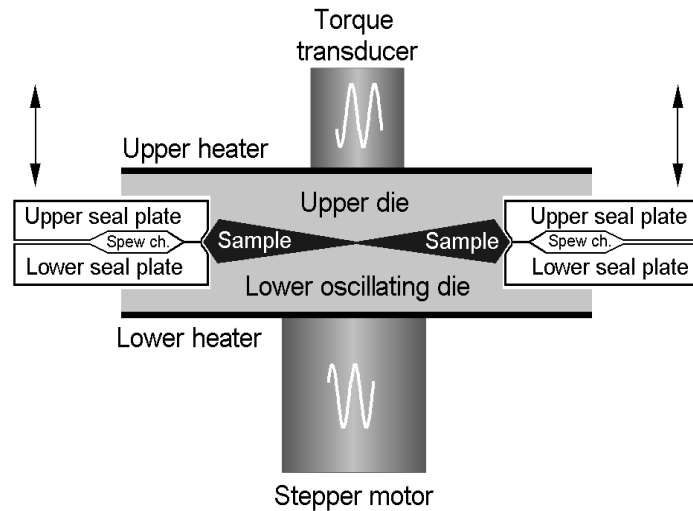


Figure 2.15: RPA mold

An unvulcanized rubber test specimen is loaded between the moulds. There are two moulds one of which is oscillating through a rotary amplitude. A sinusoidal torsion strain is produced in the test sample and this results in a sinusoidal torque which measures the viscoelastic quality of test specimen. These measurements can be gained under variable frequency conditions (frequency sweep) where strain and temperature are kept constant, under variable strain conditions (strain sweep) where frequency and temperature are kept constant or under variable temperature conditions (temperature sweep) where frequency and strain are kept constant. Also a timed test can be performed in a which sinusoidal strain is applied for a time period under constant strain, frequency and temperature conditions.

In each step of frequency, strain and temperature rheological properties are measured. The outputs are elastic torque S' , viscous torque S'' , storage shear modulus, G' , loss shear modulus G'' , $\tan \delta$, complex dynamic viscosity η^* , and real dynamic viscosity η' .

In our study cure test, frequency sweep and strain sweep tests are carried out. Cure test is run at 180 °C for 30 minutes.

In frequency sweep test, temperature is 80°C, Strain is %1, Frequency sweep is between 1 cpm to 100 cpm, $\tan \delta$ vs S' graph is plotted. It is run to check how the compound behaviour will be in extrusion process in terms of good surface quality, easy flow and easy processing.

In first strain sweep temperature is 100°C, frequency is 0,1 Hz., strain sweep is between 0,07° to 70,310°. Tan δ vs Strain graph is plotted. It evaluates extrusion die swell of the compounds.

In second strain sweep test, temperature is 80°C, Frequency is 0,1 Hz., Strain is between 0,035° to 0,1°. G' at %1 (0,07°) strain gives a correlation for the evaluation of hardness.

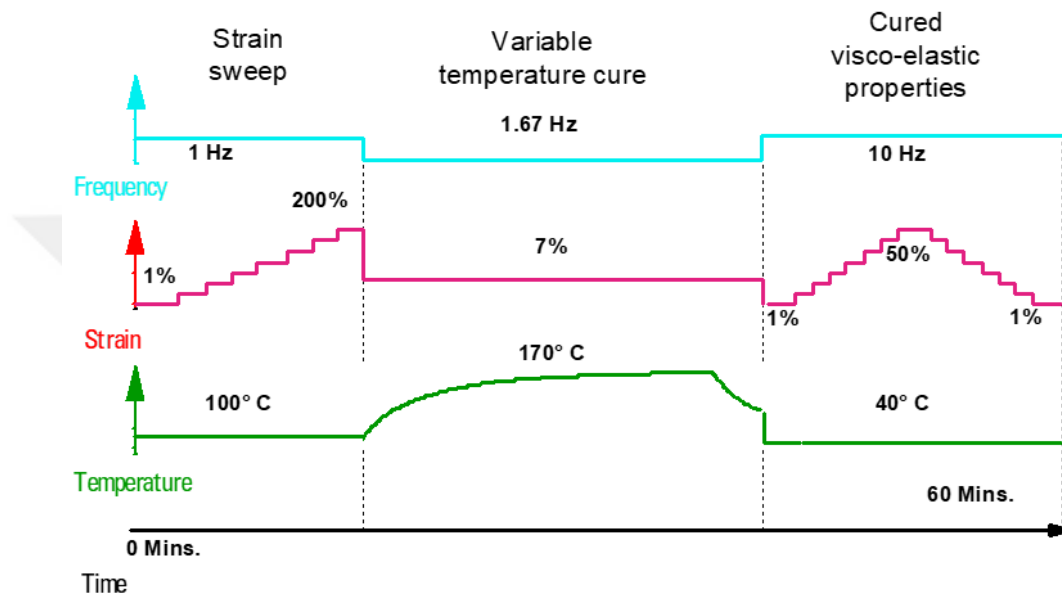


Figure 2.16: RPA before, during, after cure test curves

2.2.3 Preparation of Test Plates

Rubber mixtures are cured by rubber molding technology in laboratory scale press. The mould is in the thickness of 2 mm so the final product (test plate) would have 2 mm thickness. The length and width of the test plate is 20x20 cm.

The vulcanization parameters are defined mostly by considering the t_{90} value obtained in rheometer test. It is a well-known phenomenon that each 10 °C decrease equals to two times increase in t_{90} value. Rheometer tests were run at 190 °C and each rubber mixture has a t_{90} value around 2 minutes. Therefore, it is decided to cure the test samples at 170 °C for 8 minutes for all of the trials. 150 bar standard curing pressure is selected for piston pressure

2.2.4 Tests Applied to Finished Products

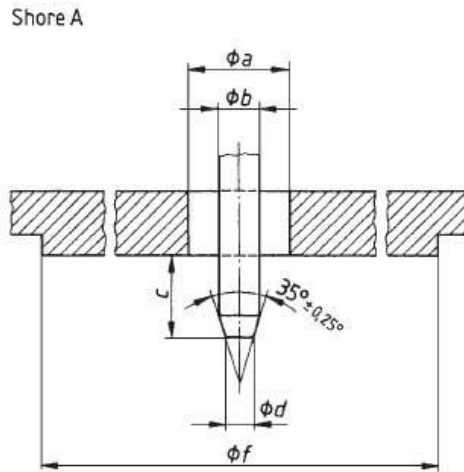
After the rubber blends are vulcanized at specific vulcanization parameters, finished products are gained. There are several tests applied to test plates which are carried out according to SAE J-20 Class E (Society of Automotive Engineers, Coolant Hoses, Fiber reinforced EPDM) [33]. The tests carried out from the finished product are listed below:

- Hardness test
- Tensile strength test
- Elongation at break test
- Tear strength test
- Compression set test
- Hot air ageing test
- Coolant Ageing test
- SEM Analysis
- Raman Analysis
- Surface Tension and Contact angle
- FTIR Analysis

2.2.4.1 Hardness Test

Standard DIN 53505 is used to measure hardness of the rubber pieces (Shore A and Shore D). Viscoelastic properties particularly elastic modulus determines the hardness of rubber. Type A durometer which measures the hardness range from 10 to 90 ShoreA is used. Shore hardness is defined as the indentation by a body of defined shape and under a specific load [14].

Scale, indenter and pressure foot (Figure 2.17), durometer stand composes durometer. Scale interval shows one Shore hardness unit, and the accuracy of the instrument shall be ± 1 Shore A unit [14]. 12.5 ± 0.5 N load shall be applied to the test piece while measuring hardness and the pressure foot shall be parallel to the surface of the test piece [14].



a	$\varnothing (3 \pm 0,10)$ mm	Indenter hardened and polished
b	$\varnothing (1,25 \pm 0,15)$ mm	
c	$(2,5 \pm 0,02)$ mm	
d	$(0,79 \pm 0,01)$ mm	
r	$(0,1 \pm 0,01)$ mm (spherical)	
f	$\varnothing (18 \pm 0,50)$ mm	

Figure 2.17: Indenter and pressure foot (see table below the figure 2.17 for dimensions) [14]

The diameter of the test piece shall be at least 35 mm in diameter and thickness shall be at least 6 mm, and the surface of the test piece shall be smooth. In our study, thickness of the test plates are 2 mm, therefore 3 layers of plates are put over each other to have a total thickness of 6 mm. Hardness is measured with this method. In this method any air should not be trapped between the layers not to effect measurement.

After vulcanizing test plates minimum 16 hours would pass to measure hardness. Measurement shall be done at a temperature of 23 ± 2 °C. Specimens shall be conditioned at 23 ± 2 °C at least for 30 minutes. When measuring hardness, once the

pressure foot touches test piece, at least 3 second should pass to measure true hardness.

2.2.4.2 Tensile Strength-Elongation at Break Test

ASTM 412 (Standard test methods for vulcanized rubber and Thermoplastic elastomers-tension) is used to measure tensile strength and elongation at break. Maximum tension strain applied to the test piece till it reaches breaking point is called tensile strength (T_S) [5]. The value recorded at breaking point (T_{Sb}) (Figure 2.18) is the tensile strength at breaking point. Elongation occurs between the marked points of the test piece at the breaking moment (Figure 2.18) is called Elongation at break (EAB). Units of T_S and T_{Sb} are MPa or N/mm^2 and elongation at break is %. The minimum value of tensile strength according to SAE J-20 Class E is 5 MPa and elongation at break is 100 % [33].

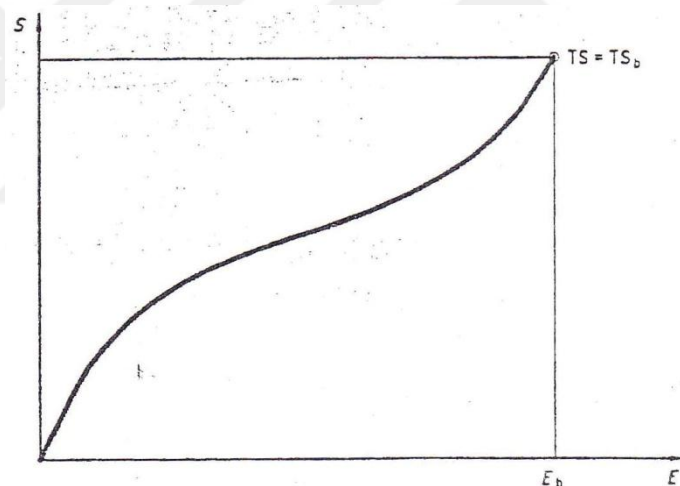


Figure 2.18: Presentation of T_S , T_{Sb} , EAB in a figure.

In tests dumbbell shaped test pieces are used. Test plates are cut by a pneumatic machine in the shape of dumbbell. Figure 2.19 shows the dimensions of dumbbell shaped test pieces.

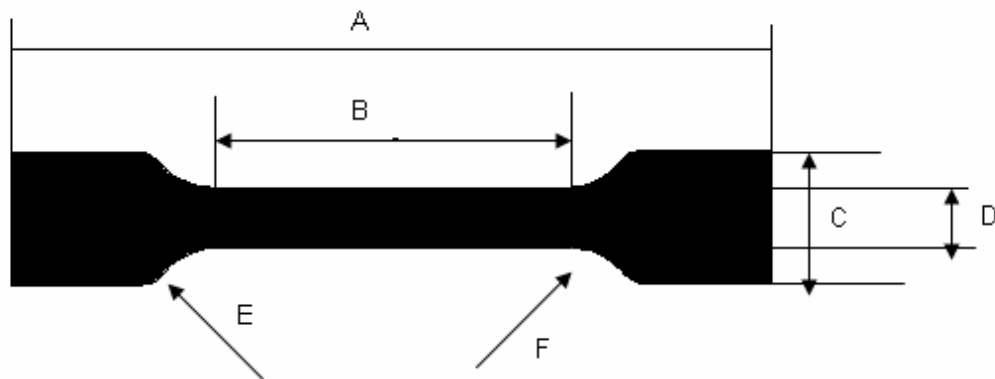


Figure 2.19: Dimensions of a dumbbell shaped test piece [5]

A: Total length: 75 mm

B: Length of narrow part: 25 mm

C: Width of the ends: 12.5 mm

D: Width of the narrow part: 4 mm

E: Curve radius (outer): 8 mm

F: Curve radius (inner): 12.5 mm

At area B of dumbbell shaped test piece (Figure 2.19), width and thickness is measured and recorded to the computer. Then test piece is placed between the grips. Attention should be paid while adjusting the test piece to distribute tension uniformly over the cross section. Speed of the test should be 500 ± 50 mm/min. There exists an extensometer in the machine to measure elongation. After the specimen is placed between the grips, test starts, machine pulls the specimen at the speed adjusted till the specimen breaks. Computer automatically shows the values of tensile strength and elongation at break numerically and graphically.

Test shall run at 23 ± 2 °C at least 16 hours after vulcanization. At least 3 hours should pass when the test temperature is 23 °C.

2.2.4.3 Compression Set Test

Compression set test is carried out according to ASTM D-395 (Standard Test Method for Rubber Property- Compression Set). Ability of rubber compounds to

retain elastic properties after prolonged action of compressive stresses are measured by compression set test [4]. Compression set test includes the maintenance of deflection, application of a force, repeated deformation, and recovery from compressive forces [4]. They simulate service conditions including static stresses. Test are carried out at elevated temperatures.

The test specimen is a cylindrical disc. It is gained directly from the laboratory press mould. Dimension of the test specimen is 29 mm in diameter and 13 mm in thickness. Test sample should be conditioned at room temperature at least 24 h after vulcanization. Conditioning time should not exceed 60 days.

Compression set apparatus consists of two steel plates between the parallel faces of which the specimens shall be compressed as shown in Figure 2.20. There are space bars to maintain constant deflection. Space bars should have a thickness of 9,5 mm. When it is thought that thickness of test specimen and space bars is 13 mm and 9,5 mm respectively, %25 compression is applied to the test sample. Oven is necessary to maintain 125 °C test temperature. Test is carried out at 15C for 70 hours.

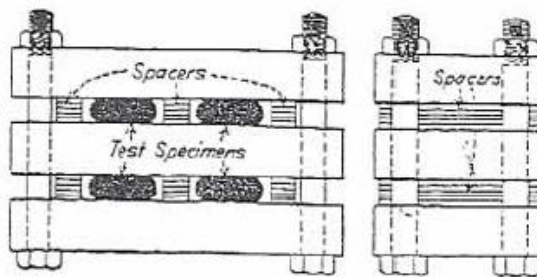


Figure 2.20: Device for compression set test under defined deflection [4]

At the beginning of test original thickness of the sample is measured. Samples are placed between the plates of the compression set device with the spacers on each side allowing sufficient clearance for the bulging of rubber when compressed. The bolts are tightened so that the plates meet with the spacers and sample is compressed by %25. Compression set apparatus with the samples inside is kept in oven for 70 hours at 125 °C. After test period is completed, apparatus is taken from the oven, test samples are removed immediately and left to cooling. Test samples should be cooled for 30 minutes on a non-conductive surface such as wood before measuring the final thickness. After cooling period passes thickness of the sample should be measured from the centre point. Calculation is made as follows.

t_0 : initial thickness of the sample

t_r : final thickness of the sample

t_s : thickness of the spacer

$$\text{Compression set } \% = \frac{t_0 - t_r}{t_0 - t_s} * 100$$

2.2.4.4 Tear Strength Test

Tear strength test is carried out in accordance with ISO 34-1 (Rubber, vulcanized or thermoplastic- determination of tear strength, Part 1, Trouser, angle and crescent test pieces). A special type of rupture called tear can lead to a failure in service of vulcanize rubbers. ISO 34-1 measures the resistance to tearing action. Stress distribution, strain rate and test piece size can affect tear strength [22].

There are several types of test methods for tear strength test even the specification is same. In our study method A is used. Also dimension of specimen is determined according to the method. Method A refers trouser type test specimen shown in Figure 2.21.

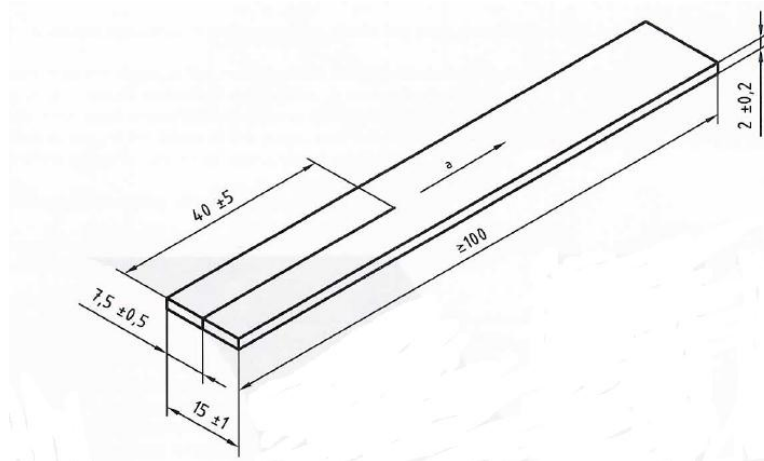


Figure 2.21: Trouser type test piece [22]

Firstly 2 mm thick test plate is cured in laboratory press by the help of a proper mould. Trouser shape test is cut by a die. The cutting edges of the die shall be sharp

and free from ragged edges. Test plates shall be kept in laboratory conditions for at least 3 hours before the test pieces are cut.

A tensometer is used for the test. The speed of the jaws should be 100 mm/min for trouser test piece. Grips which tighten the specimen as the tension increases should exist in the test machine.

Test needs to be carried out at a laboratory temperature of 23 ± 2 °C. Thickness of the sample where tearing is expected to occur is measured. Then test piece is mounted to the test machine. A steady increasing traction force is applied at a rate of 100 mm/min till the sample is broken. Tear strength is automatically taken from the machine numerically and graphically. It is expressed in newtons per mm of thickness.

2.2.4.5 Heat Ageing Test

ASTM D-573 (Standard Test Method for Rubber- Deterioration in an Air Oven) is used for heat ageing test. Influence of elevated temperature on the physical properties of vulcanized rubber is determined by heat ageing test. Oxidative and thermal ageing causes deterioration in the physical properties of rubber and rubber products. They must resist these kinds of deformations [7].

After test plates of 2 mm thickness are prepared, dumbbell shaped test pieces are gained. Hardness, tensile strength, and elongation at break values are measured at initial state before ageing. Then remained dumbbell shaped test pieces are used for heat ageing tests. They are exposed to deteriorating influence of air at specified elevated temperatures for known periods of time. After test period is finished, same tests with the initial state are carried out (hardness, tensile strength and elongation at break) and the change in these values are compared and recorded. Test conditions and results must be suitable with the requirements of SAE J-20 Class E standard. Heat ageing test must be carried out at 125 °C for 70 hours. The units of the change are ShoreA and %, respectively for hardness and tensile strength- elongation at break. The hardness change can't exceed +15 points, tensile strength change can't exceed -20 % and elongation at break change can't exceed -50 %.

Ovens can be used as a heating medium. Air is the heating medium for ageing chamber. The dumbbell shaped specimens shall be suspended vertically without touching each other. After vulcanizing samples at least 24 hours should pass before starting ageing test. When ageing period is completed, samples should be removed from oven, cooled down to room temperature on a flat surface and rest not less than 16 hours nor more than 96 hours before running tests. Test temperature for determining physical properties after heat ageing should be 23 ± 2 °C.

2.2.4.6 Coolant Ageing Test

ASTM D 471 (Standard Test Method for Rubber Property- Effect of Liquids) is used for this ageing test. Coolant ageing test is made to evaluate the comparative ability of rubber and rubber-like compositions to withstand the effect of coolant [6] as referred in SAE J-20 Class E standard. This test includes change in volume, change in tensile strength, change in hardness and change in elongation at break.

Test plates are cured and dumbbell shaped test pieces in 2 mm thickness are cut from the test plate. Before coolant ageing test, hardness, tensile strength, and elongation at break tests are run. Also, weight of the test piece in air and water are determined at initial conditions for volume change test. This method provides procedures for exposing test specimens to the influence of coolant under definite conditions of time and temperature. The resulting deterioration is determined by measuring the changes in physical properties before and after immersion to coolant. Test conditions and results must be suitable with the requirements of SAE J-20 Class E. Coolant ageing test must be carried out at the boiling point of the mixture of $\frac{1}{2}$ by volume distilled water and $\frac{1}{2}$ by volume ethylene glycol-based coolant for 70 hours. A water-cooled reflux condenser must be used for this test. After ageing period, hardness, tensile strength, elongation at break and weight of specimen in both air and water for volume change are recorded. They are compared with the original results. The unit of the change of physical properties is % except hardness. Hardness change is expressed in Shore A unit. Hardness change shall be between -10 to +10 Shore A. Tensile strength change shall not exceed -20 %, elongation at break shall not exceed -25 % and volume change shall be between -5 % and +20 %. The formulation of volume change is given below:

$$\Delta V, \% = \frac{(M_3 - M_4) - (M_2 - M_1)}{(M_2 - M_1)} \times 100$$

ΔV = change in volume, %

M_1 =initial mass of specimen in air, gr

M_2 = initial mass of specimen in water, gr

M_3 = mass of specimen in air after immersion, gr

M_4 = mass of specimen in water after immersion, gr

At the end of required immersion period, test specimens shall be removed from the reflux condenser and immediately cooled to room temperature in a fresh sample of the same fluid for 30 to 60 minutes. Then the samples shall be dipped in acetone quickly, blotted lightly with filter paper that is free of lint and foreign material. The time interval between dipping with acetone and testing for physical properties shall not be less than 1 hour nor more than 2 hours [6]. The temperature of test medium for determining the physical properties after coolant ageing test shall be 23 ± 2 °C.

Frostox HT-12 is used as a coolant and its properties are defined as follows.

PHYSICAL AND CHEMICAL PROPERTIES

	Value	Method
Density at 20°C [g/cm ³]	1.110–1.140	DIN 51757
Refractive index	1.425–1.438	DIN 53423
Boiling point [°C]	>170	ASTM D1120
Flash point [°C]	>110	ASTM D51758
pH value (33 % aqueous solution)	7.5–8.5	ASTM D1287
Reserve alkalinity [ml 0.1N HCl/10 g]	>10.0	ASTM D1121

Figure 2.22: Properties of Coolant

2.2.4.7 SEM Analysis

Scanning electron microscope with high magnification ratios is used to learn morphological, structural and elemental information, topographic composition and composition of specimen and to determine the interaction between the materials. 1000X and 500X is used for the measurements.

2.2.4.8 Raman Analysis

To identify the double, triple bonds and determine the number of bonds, measurement of internal molecular type is used.

2.2.4.9 Surface Tension and Contact Angle

This test is made for measuring surface energy. Each material has a specific surface structure. While blending different materials, the structure of the main material is effected and its energy changes. Surface tension affects polarity hence surface energy. If the polarity or surface energy of two different structures are close to each other, contact angles will be more similar.

2.2.4.10 FTIR Analysis

Detailed information about surface structure of fibers, bonding of specimen and functional groups will be gained by FTIR analysis.

2.3 Surface Treatment of Fibers with EPDM Solution

Short fibers are treated with a special type of solution. Solution consists of EPDM sticky rubber blend and toluen. EPDM sticky rubber blend to solution ratio is 1:4. Un cross-linked EPDM sticky rubber blend is melted in toluen homogenously. Solution is stirred manually in defined periods during 24 hours timeline. After 24 hours homogenous solution is gained. Short fibers are painted with this solution. Afterwards they are kept in an oven and dried at 70 °C for 24 hours. Drying helps to evaporate toluene in the mixture.



Figure 2.23: EPDM solution and Glass Fiber

2.4 Surface Treatment of Fibers with Alkali Solution

Fibers are kept in glass beaker in aqueous NaOH solution (%10 a/h) with a parafilm over it. It is washed with distilled water till NaOH is moved away. Then fibers are dried in an oven at 70 °C for 24 hours.



Figure 2.24: Glass fiber after alkali solution treatment

2.5 Surface Treatment of Fibers with Alkali and EPDM Solution (Hybrid)

In this treatment, fibers treated with alkali solution are mixed with EPDM-toluen solution. Firstly, fibers are kept in glass beaker in NaOH (%10) solution and water for 24 hours at room temperature with a parafilm over it. Afterwards they are kept in an oven for drying operation at 70 °C for 24 hours. Lastly fibers that are alkali treated are blended in EPDM- toluen solution. They are left to drying again at 70 °C for 24 hours.



Figure 2.25: Fibers in oven

Glass fiber+ NaOH

Glass fiber+ NaOH

Basalt fibers and PA2 glass fibers are selected to be candidates for applying further surface treatments.

2.6 Further Surface Treatments of Basalt Fiber

In this part of the study further surface treatments to basalt fiber are applied. 3 different kind of treatments are tried, silane, alkali and silane+alkali (hybride).

2.6.1 Silane Treatment

3-Triethoxysilylpropylamine, (APTES) is used as a silane bonding agent. Aqueous silane solution of %0,5 which PH value is adjusted to 4,5 with asetic acid is stirred for 15 minutes. Short basalt fibers are added to the solution and waited for 1 hour. After surface modification short basalt fibers are dried at 60 °C for 24 hours.



Figure 2. 26: Silane bonding agent solution with a Ph value of 4,5



Figure 2.27: Silane bonding agent applied, dried basalt fiber

2.6.2 NaOH (%2 cc.) treatement

Tekkim-Di-Sodium Hydrogen Phosphate Pure Grade (without water), TK170511.01002 numbered product is used in alkali treatment. Basalt fibers are added to %2 sodium hydroxide solution and kept at room temperature for 1 hour. Till

sodium hydroxide is completely moved away, they are washed with distilled water in which a few drops of acetic acid exist. Lastly, they are dried at 60°C for 24 hours.



Figure 2.28: NaOH applied, dried basalt fiber

2.6.3 NaOH (%2 cc.) + Alkali treatment (Hybrid)

In third type of surface treatment, silane coating is applied over sodium hydroxide alkali treated basalt fibers. Ratios and treatment process is similar with the processes applied for NaOH treatment and silane treatment.



Figure 2.29: Silane and NaOH treated basalt fiber.

2.7 Further Surface Treatments of PA2 Glass Fiber

2.7.1 Moving Silane Coating of PA2 Glass Fiber Away

Glass fibers produced by Şişecam which are coated with silane are treated with acetone and kept in glass beaker covered with parafilm at 24 °C for 24 hours to move the coating from the surface of the fibers. Acetone quantity is adjusted in such a way that all fibers in glass beaker contacts completely with acetone (Each separate fiber should contact acetone).

After 24 hours, fibers contacted with acetone are washed and rinsed with distilled water three times. With this method interaction of each fiber with water is provided. After rinsing operation, a part of fibers is kept in 2 lt glass beaker in which there exists water at 100 °C for 2 hours. Then it is left to drying at 70 °C for 24 hours in oven (Bare Glass Fiber- Processed in Hot Water)

The rest of fibers are directly dried at 70 °C for 24 hours in oven without an additional operation (Bare Glass Fiber- Processed in Oven)

Thus, it is aimed to move the silane coating away and have fibers which are not silane coated.

2.7.2 Alkali Treatment of Non-Silane Coated PA2 Glass Fiber

Similar process steps and laboratory conditions that are used to move silane coating away are applied to prepare sodium hydroxide (NaOH%10) solution with non-silane coated PA2 glass fibers. 100 ml of distilled water are added over 100 gram of glass fiber that exists in beaker till all glass fibers are covered with water. Ratio of sodium hydroxide to water is 1:9 (%10 NaOH solution). Solutions that are prepared are kept in beakers covered with parafilm at 24°C for 24 hours. Then fibers are dried and rinsed with water 3 times. After rinsing operation, a part of fibers is kept in 2 lt glass beaker in which there exists water at 100 °C for 2 hours. Then it is left to drying at 70 °C for 24 hours in oven (Bare Glass Fiber+ NaOH Processed in Hot Water)

The rest of fibers are directly dried at 70 °C for 24 hours in oven without an additional operation (Bare Glass Fiber+ NaOH- Processed in Oven)

2.7.3 EPDM Coating of Non-Silane Coated PA2 Glass Fiber

For EPDM treatment, non-silane coated PA2 glass fibers which are gained by following the previously used parameters and similar working steps (hot water and oven drying processes) are mixed with EPDM/toluene solution. EPDM/toluene solution is added enough to coat each fiber (<30 gr) and stirred manually. To move toluene in EPDM solution and to dry, it is kept in oven at 70°C for 24 hours. EPDM is in black colour because of carbon that exists in it, fibers gained at the end of drying are 2 types. First type is called “bare glass fiber+ EPDM- hot water processed”. And second type is called “bare glass fiber+ EPDM- oven processed”.

2.7.4 Alkali+ EPDM Coating of Non-Silane Coated PA2 Glass Fiber

Till now there are totally 6 different specimen types from 3 different groups. Glass fiber+ NaOH+ EPDM composite material is formed by adding EPDM to Glass fiber+ NaOH solution. Process steps of fibers differ from each other so it is divided into two as hot water processed and oven processed. First group is called “bare glass fiber+ NaOH+ EPDM- hot water processed” and second group is called “bare glass fiber+ NaOH+ EPDM- oven processed”.

At the end totally 8 different types of glass fibers are gained.

Table 2.3. Samples prepared by using hot water and oven

Processed in hot water	Processed in oven
Bare Glass Fiber PA2	Bare Glass Fiber PA2
NaOH Treated Bare Glass Fiber PA2	NaOH Treated Bare Glass Fiber PA2
EPDM Solution Treated Bare Glass Fiber PA2	EPDM Solution Treated Bare Glass Fiber PA2
Hybrid (NaOH+EPDM) Treated Glass Fiber PA2	Hybrid (NaOH+EPDM) Treated Glass Fiber PA2

CHAPTER 3

Results and Discussion

In this study the effect of different fibers, different fiber ratios and different surface treatment of fibers on cure characteristics, physico- mechanical properties, ageing properties, surface structure, functional groups and bonding properties of EPDM mixture is studied. The fiber ratio in EPDM mixture is increased by 2-5-10 phr respectively by using carbon, basalt, PA2 glass fiber, PP4 glass fiber and aramide fiber. The obtained results are evaluated by considering an international coolant hose specification called SAE J-20 Class E. Class E part of this specification covers the demands of fiber filled EPDM rubber. The blends that contain 5 phr fiber is determined as the most succesfull ratio for all fiber types by rheological analysis, physico-mechanical tests and agein tests. Further trials continued with 5 phr ratio. Then effect of different fiber surface treatment methods such as surface treatment with EPDM solution, alkali solution, EPDM and alkali solution (hybrid) are studied. Rheological analysis, physico- mechanical tests, ageing tests, SEM analysis, FTIR tests, surface tension and contact angle and Raman analysis are carried out. According to the result of surface treated EDPM fibers, further trials are decided to be made with basalt and PA2 glass fibers. Again all tests are repeated with specially tretaed basalt and PA2 glass fibers and results are evaluated seperately.

3.1 Test Results According to Changed Fiber Types and Ratios

3.1.1 Rheometer Test Results according to Changed Fiber Types and Ratios

Extrusion and vulcanization characteristics of rubber blends are determined by rheometer tests which have great importance in rubber industry. It is widely used to evaluate extrusion and moulding properties, scorch safety or rubber blends, curing characteristics, cross linking density and vulcanization parameters. Shortly they give information for process characteristics. The results of rubber blends by changing the fiber types and fiber ratios are given in Table 3.1. Rheometer tests are carried out for 3 minutes at 190 °C.

Table 3.1: Rheometer test results according to the changed fiber type and ratio

Rheometer tests at 190 °C for 3 minutes									
Formulation Code	Carbon Fiber Ratio (PHR)	Basalt Fiber Ratio (PHR)	PA2 Glass Fiber Ratio (PHR)	PP4 Glass Fiber Ratio (PHR)	Aramide Fiber Raito (PHR)	M _L (dNm)	M _H (dNm)	T _S (min.)	T ₉₀ (min.)
D005	2	0	0	0	0	1,01	12,01	0,79	2,06
D006	5	0	0	0	0	1,06	13,15	0,79	2,06
D007	7	0	0	0	0	1,09	12,95	0,77	2,05
D008	0	2	0	0	0	1,04	11,68	0,76	1,98
D009	0	5	0	0	0	1,05	11,91	0,76	1,99
D010	0	7	0	0	0	1,08	12,37	0,74	1,91
D011	0	0	2	0	0	1,01	13,54	0,76	2,07
D012	0	0	5	0	0	1,03	13,01	0,75	2,08
D013	0	0	7	0	0	1	14,16	0,74	2,06
D014	0	0	0	2	0	0,85	12,18	0,82	2,13
D015	0	0	0	5	0	0,97	12,95	0,79	2,1
D016	0	0	0	7	0	0,95	12,49	0,79	2,09
D017	0	0	0	0	2	0,89	13,12	0,77	2,1
D018	0	0	0	0	5	1,01	15,31	0,74	2,1
D019	0	0	0	0	7	1,03	14,36	0,76	2,13

The table above gives the most used values in rubber industry that are taken from a rheometer test such as M_L (minimum torque), M_H (maximum torque), t_s (scorch time) and t_{90} (time required to reach 90 % of full cure).

M_L is the minimum torque value at the test temperature. At this point cross links are not formed yet. Material is softened as heat is given up to the material and has plastic properties more than elastic properties at this point. The decrease in minimum torque value is due to the softening of the matrix. As fiber ratio in mixtures increase it is seen that minimum torque value increases except glass fiber filled rubber blends. It can be seen in Figure 3.1. This means that the flow of material will be easier in the blends where fiber ratio is low. When fiber ratio increases, the flow will be more difficult, and the machine process parameters need to be adjusted for an easy flow.

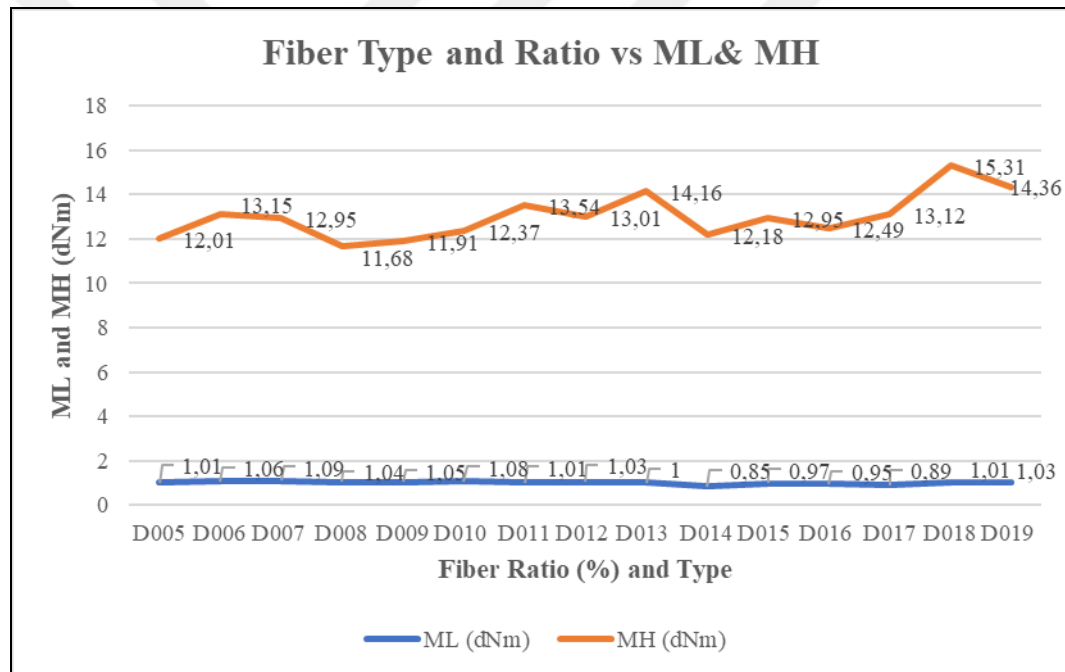


Figure 3.1: Fiber Ratio (%) and Type versus ML - MH graph

M_H is the maximum torque value at test temperature and is the point where the compound is completely cured. All of the cross links are formed at this point and the material have completely elastic characteristics. It gives idea about the hardness of the material directly. If the polymer matrix has ability to make more cross links than the maximum torque value will be higher. The stability between cross links will be stronger. Softer materials will have lower maximum torque values. In each group related to fiber type except glass fiber PA2, it is obviously seen that maximum torque value is the lowest for the blends filled with minimum fiber ratio. In most fiber type

groups, it is observed that blends with 5 phr fiber ratio gives maximum cross linking. Especially the blend with aramide fiber with 5 phr fiber ratio gives the highest maximum torque value. Among all fiber types, aramid fiber and glass PP4 fiber filled EPDM blends give higher maximum torque values than the other fiber types. Additionally, EPDM blend filled with basalt fiber type gives the lowest maximum torque values. These observations are supported by Figure 3.1. It indicates that aramide and glass PP4 fiber types can accelerate curing activity as well as 5 phr fiber ratio. Also, it is understood that basalt fiber type has the less active curing function on EPDM rubber blends when compared to other fiber types.

t_s is the time required for the state of cure to increase to two torque units above the minimum at the given cure temperature. It means scorch time. It is a measure of the premature vulcanization of the material. Above this point the material starts to gain elastic properties, plastic behaviour of material leaves its place to elastic behaviour. The materials that have lower scorch times create risk in extrusion and molding processes because the material must be processed in extrusion and must fill the cavities of the mold before it reaches scorch time. Even if few cross linking is started in extrusion or at the time of filling cavities of the mold this can create problems to give the required shape to the material. Surface failures may occur. In blends prepared with different fibers and different fiber ratios, it is observed that nearly all of them have similar scorch times. It is important to have optimum scorch time because blends with high scorch times may lead uncuring or insufficient curing whereas blends with short scorch times may lead to pre-curing. In Figure 3.2 it is seen that the blend with the highest scorch time is glass PP4 filled EPDM mixture. This trial also has the lowest minimum torque. There is an inverse proportion between minimum torque and scorch time, the material with easier flow properties has the safest scorch time. This relation is supported by the evidence found out in glass PP4 filled EPDM blend. In general, it is seen from Figure 3.2 that all the blends have very similar scorch times. This is an advantageous finding that all the fiber filled blends will not have any pre curing or insufficient curing problems.

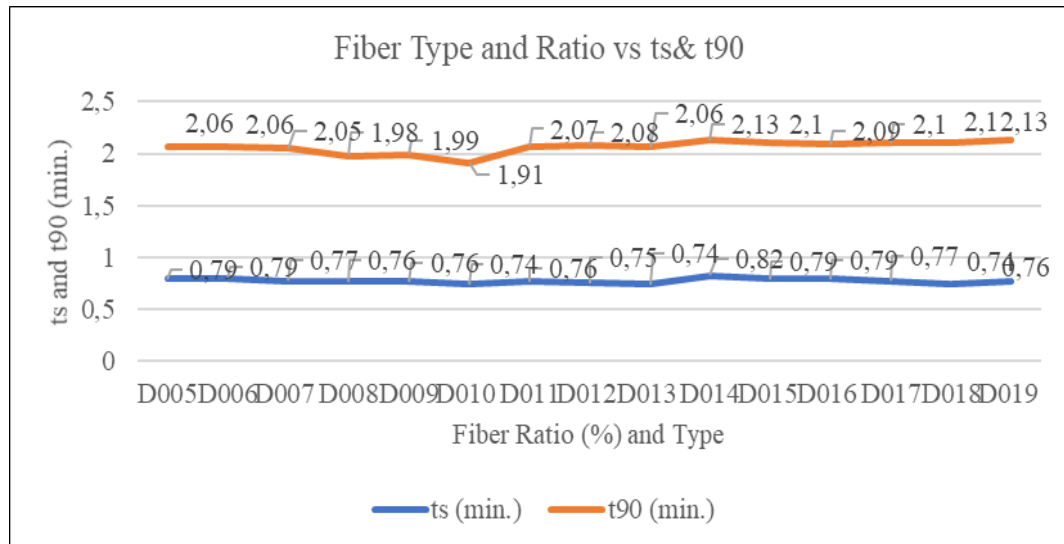


Figure 3.2: Fiber Ratio (%) and Type versus t_s – t_{90} graph

t_{90} , optimum cure time is the time required to reach 90 % of full cure defined as $M_H - M_L$. t_{90} is generally the state of cure at which the most physical properties reach optimal results. It is important to gain t_{90} at the end of rheometer test because optimum curing time is determined by considering this value. In the mixtures prepared by different fiber types and ratios, it is seen that 10 phr basalt fiber filled EPDM rubber blend has the minimum t_{90} value that it can be cured in shorter curing times. 2 phr glass PP4 fiber filled EPDM rubber blend and 10 phr aramide fiber filled EPDM rubber blend give the highest t_{90} values that they can be cured in longer curing times. It is observed from Figure 3.2. If curing finishes before t_{90} is reached then lack in physical properties, surface smoothness will occur.

3.1.2 Physico-mechanical Tests and Ageing Tests according to Changed Fiber Types and Ratios

Physico-mechanical tests of the vulcanized products include hardness, tensile strength, elongation at break, tear strength and compression set tests. They have great importance in rubber industry. They give idea about the finished product properties and how they will behave at the time of working on the engine. Ageing tests include hot air ageing and ageing in coolant. They are carried out at 125° for 70 hours and at boiling point for 70 hours respectively according to SAE J20 Class E. Physico-mechanical tests before and after ageing are compared including volume swell of the material. Ageing tests are of big importance in rubber industry because rubber

materials may work by exposing to hot air and coolant contact according to the place they work. So the effects of these conditions to the material must be observed not to have problems in the later times.

All of the results of physico-mechanical and ageing tests are evaluated according to SAE J20 Class E standard. In this section physico-mechanical and ageing tests will be investigated due to different fiber types and ratios used in EPDM rubber blends.

By changing the fiber types and fiber ratios in the mixture, at first physico-mechanical properties like hardness, tensile strength, elongation at break, tear strength and compression set values are investigated. Fiber ratio is increased in the ratios of 2-5-10 PHR's and fiber types are changed from carbon black, basalt, glass PA2, glass PP4 and aramide fiber. The obtained results can be seen in Table 3.2.

Table 3.2: Physico-mechanical test results according to the changed fiber type and ratio

Formulation Code	Rheometer tests at 190 °C for 3 minutes									
	Carbon Fiber Ratio (PHR)	Basalt Fiber Ratio (PHR)	PA2 Glass Fiber Ratio (PHR)	PP4 Glass Fiber Ratio (PHR)	Aramide Fiber Ratio (PHR)	Hardness (ShoreA)	Tensile Strength (MPa)	Elongation at break (%)	Tear Strength (N/mm)	Compression Set (%)
SAE J20 E	-	-	-	-	-	65-75	min. 5	min. 100	-	max. 85
D005	2	0	0	0	0	68	11,28	453	11,9	66,9
D006	5	0	0	0	0	70	10,7	428	12,9	66,6
D007	7	0	0	0	0	74	9,47	420	13	69,1
D008	0	2	0	0	0	66	11,18	442	11,6	62,2
D009	0	5	0	0	0	68	10,72	412	11,2	63,6
D010	0	7	0	0	0	70	11,07	448	10,8	62,5
D011	0	0	2	0	0	68	12,75	433	11	62,2
D012	0	0	5	0	0	69	12,36	426	10,8	61,5
D013	0	0	7	0	0	70	11,96	411	11,6	62,6
D014	0	0	0	2	0	68	11,67	403	9,3	64,8
D015	0	0	0	5	0	69	11,78	417	9,1	64,2
D016	0	0	0	7	0	70	11,67	384	11,6	62,7
D017	0	0	0	0	2	70	12,15	366	10,7	63
D018	0	0	0	0	5	77	10,74	329	12,9	64,2
D019	0	0	0	0	7	83	9,86	302	15,1	61,3

A well-defined penetrating body is pressed into the material under defined conditions stated in international specifications with the aim of measuring hardness which correlates to a certain degree with the determination of stress value. Shore A is the unit of hardness measurement. It is obviously seen that in each fiber type, with increasing fiber ratio that exists in EPDM rubber blend, hardness increases. It is in Figure 3.3. Hardness also correlates strongly with cross linking density. This means that blends with higher fiber ratio hves higher cross-linking density. Also, it means as the fiber ratio in the rubber blend increases, fibers tend to act as an accelerator or activator for the blend. Also, it is seen that 10 phr aramid filled EPDM rubber blend has the highest hardness. So, it can be said that aramid fiber is the most active fiber type in terms of hardness. While observing the results, SAE J20 Class E (fiber filled EPDM section) should be taken into consideration. It is indicated in this specification that desired hardness should be between 65- 75 ShoreA. For this reason, it can be said that the blends with a hardness higher than 75 ShoreA is above the limits such as 5 and 10 phr aramid fiber filled EPDM rubber mixtures. These fiber type and ratios activated the blend more than they must do. When the remaining results of other trials are evaluated, it is understood that they are inside the limits of SAE J20 Class E. If the hardness was below the limits, then it could be evaluated as the fiber content and type prevent full activation of the curatives. But this kind of a situation is not faced in any trial type.

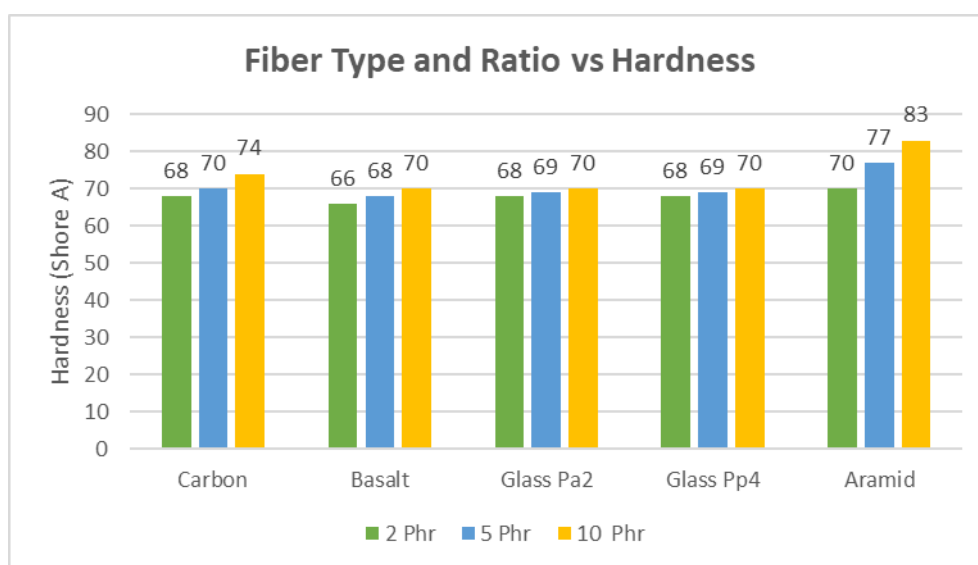


Figure 3.3: Fiber type and ratio vs hardness

The nature of deformation of the blends under an applied load can be understood from the stress strain curves. The stress or tensile strength values according to the

fiber type and ratio are given in Figure 3.4. It can be seen from the figure that in each fiber type study, with increasing ratio of related fiber type, tensile strength decreases. This finding is only not valid for basalt fiber, there exists a slight increase while passing from 5 phr to 10 phr in this fiber type. It is well known that hardness is increased with increasing fiber ratio independent from the fiber type. Therefore, it is waited to have higher tensile strength values with increasing fiber ratio. But the results showed a contrary situation. Especially 10 phr aramid fiber filled EPDM rubber blend which has the highest hardness value with 83 ShoreA, unexpectedly has the lowest tensile strength value. However, in the study of Natali M., EPDM based heat shielding materials for solid rocket motors: A comparative study of different fibrous reinforcements [29], it is stated that aramid fiber ratio reaches upto 30 phr and for 10 phr tensile strength gives the best result. In our study the finding is that it would be arising from the lack of synergy between the molecules of the rubber matrix and the fibers. It is found out that the fibers cannot be uniformly distributed and homogenously mixed in the rubber matrix, so that these fluctuations prevent the desired result to be reached. On the other hand when the results are checked in terms of SAE J20 Class E requirements, it is definitely obvious that all the different fiber types with different fiber ratios can meet the desired value of minimum 5 MPa tensile strength value.

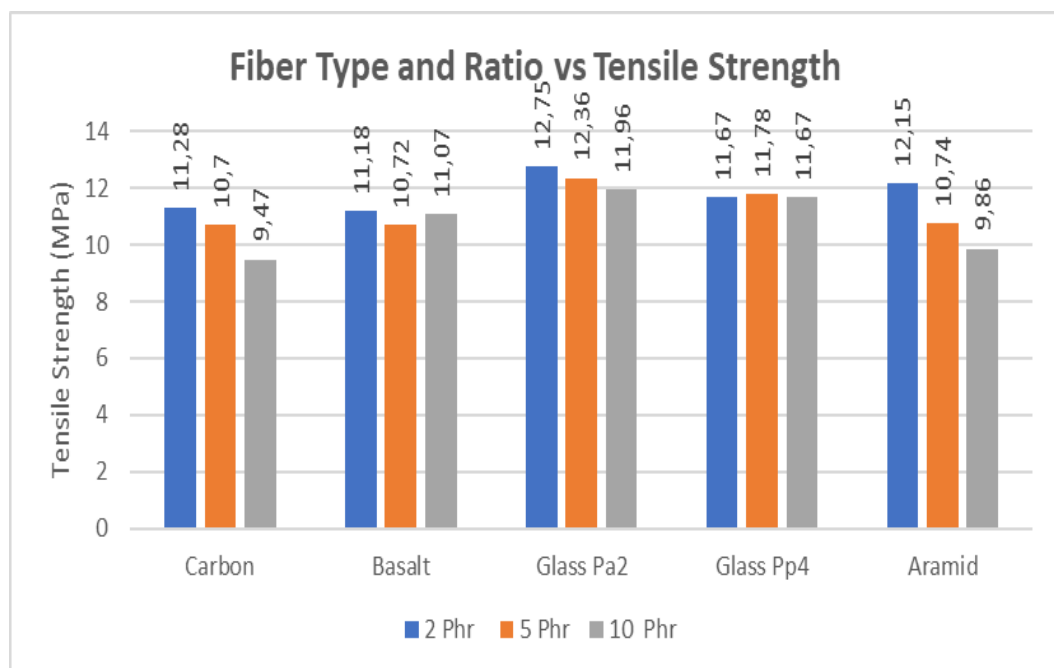


Figure 3.4: Fiber type and ratio versus tensile strength

Elongation at break and tensile strength have an opposite relationship. This means higher tensile strength values mean stronger bonds between the polymer chains that would lead lack of elasticity. Elongation at break value shows a decreasing trend with the increasing fiber ratio in EPDM- carbon fiber blend. For basalt fiber filled EPDM rubber blends, firstly with the increasing ratio of basalt fiber, elongation at break value decreased, then surprisingly an increase occurred at EAB. This result is thought to be related with the non- uniform distribution of basalt fiber in EPDM rubber matrix and weak compatibility of fibers within the polymer structure. A surface modification would be helpful to reach more linear and stable results. When EAB results of Glass PA2 fiber filled EPDM rubber mixtures are observed, it is seen that there exists a decreasing trend with the increasing fiber ratio. Glass PP4 fiber filled EPDM mixtures firstly showed an increasing trend at EAB, then a decreasing trend is held while fiber ratio is increased. This fluctuating results are also related with poor compatibility of fibers with polymer chains and a surface modification is needed. Lastly, aramid fiber ratio effect is investigated in terms of EAB for EPDM fiber filled mixtures. There exists a decreasing trend with increasing ratio of aramid fiber as expected. When requirements of SAE J 20 Class E international specification is taken into consideration, we can say that all the results can meet min. 100% EAB value. All results are above the minimum limit.

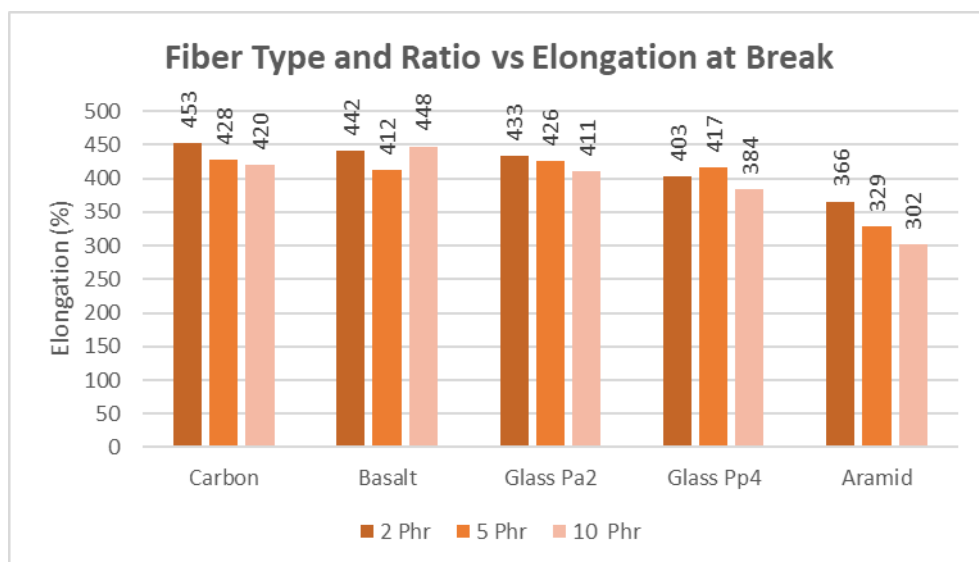


Figure 3.5: Fiber type and ratio versus elongation at break

At higher cross link densities such properties as tear strength, plateau or begin to decrease. So, it means that increasing hardness or cross link density makes the tear strength increase till a point, then makes a plateau and starts to decrease. Carbon

fiber filled EPDM rubber mixture tends to show an increase with the increasing fiber ratio. When basalt fiber filled EPDM rubber mixtures are investigated, it can be said that increasing ratio of basalt fiber leads to a decrease in tear strength. There is a slight difference between the values with increasing ratio, but care should be taken while deciding the optimum basalt PHR. The maximum cross-linking availability of EPDM rubber matrix with basalt fiber would be in between 2 and 10 phr. Glass PA2 filled EPDM rubber mixtures firstly shows a slight decrease while passing from 2 to 5 PHR and then shows an increase while passing from 5 to 10 PHR. It can be evaluated as 2 and 5 PHR Glass PA2 filled EPDM rubber mixtures have similar values. So, with increasing ratio from 5 to 10 PHR, there exist an increase in tear strength value as expected. Glass PP4 fiber filled EPDM rubber mixtures shows an increasing trend in terms of tear strength with increasing fiber ratio. In this conclusion, 2 PHR and 5 PHR filled mixtures are evaluated to have the similar values. When aramid fiber filled EPDM rubber mixtures are observed, it can be said that increasing ratio of aramid fiber also increases the tear strength. SAE J20 Class E specification states that minimum tear strength needs to be 4 N/mm. All the results are successful and above the limits when this value is considered.

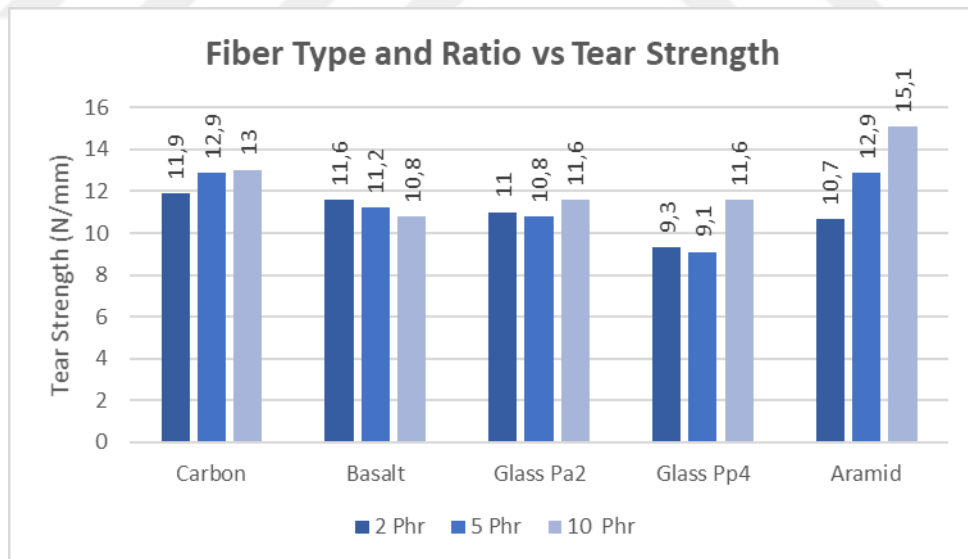


Figure 3.6: Fiber type and ratio versus tear strength

Compression set is an indicator for cross linking density and curing ratio of the elastomers. Compounds with higher cross-linking densities and curing ratios, give better compression set, numerically lower values. Compression set value is gained by compressing the elastomers under a defined period and defined temperature. The ratio of turning back to its starting position is measured. The elastomer which can

turn to its original starting position with more success is evaluated to have better polymer-curative interaction, whereas a better curing rate. Carbon black filled EPDM rubber mixtures shows an increasing compression set value with increasing fiber ratio. In this approach, 2 and 5 PHR filled EPDM mixtures are considered to have the similar compression set values. For basalt fiber reinforced EPDM rubber mixtures firstly increasing fiber ratio tends to increase compression set and then tends to decrease it. This fluctuation would occur because of the less-homogenous rubber compound. Fibers are distributed within the compound non-homogenously and do not form a good surface bonding with the polymer chains. Glass PA2 filled rubber compound firstly shows a decrease in compression set but then an increase is observed with increasing fiber ratio. It is a finding opposite with the expectation. This observation also points out that surface modification needs to be carried out for more compatible fiber-polymer interactions. Glass PP4 filled EPDM rubber mixtures show a decrease in compression set with increasing fiber ratio. Decrease in compression set values indicate that cross linking density and curing degree is higher in more fiber filled mixtures. Lastly, when aramid fiber filler EPDM rubber mixtures are investigated it is found out that with increasing fiber ratio, firstly compression set value increased and then decreased. There is not a linear correlation between compression set value and fiber ratio.

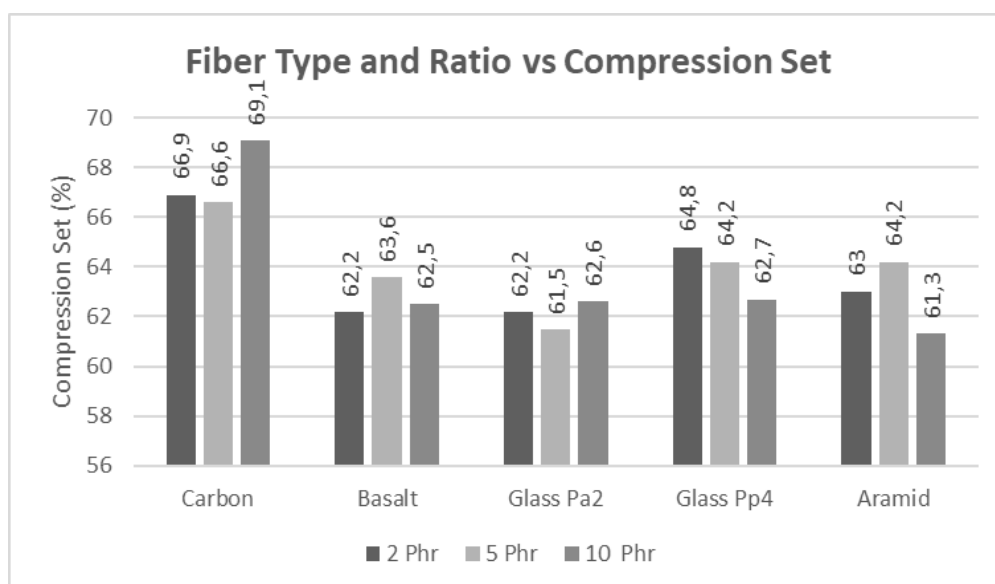


Figure 3.7: Fiber type and ratio versus compression set

After physico-mechanical tests are investigated then ageing test are carried out and the results are discussed. The results of hot air ageing test according to changed fiber

type and ratios is given in Table 3.3, coolant ageing test according to changed fiber type and ratios is given in Table 3.4. All of the test results are estimated by considering SAE J20 Class E [33]. By changing the fiber type and ratio and investigating all of the test results including both physico-mechanical and ageing tests, the most proper fiber ratio according to the standard will be selected. This blend then will be investigated for the effect of surface modifications respectively.



Table 3.3: Hot air ageing test results according to changed fiber type and ratio										
Formulation code	Fiber Type	Fiber ratio (%)	BEFORE HOT AIR AGEING			AFTER HOT AIR AGEING (125C, 70 h)				
			Hardness (Shore A)	Tensile Strength (MPa)	Elongation at break (%)	Hardness Change (Shore A)	Tensile Strength (MPa)	Tensile Strength Change (%)	Elongation at break (%)	Elongation at break change (%)
SAE J20 Class E			65-75	min. 5	min. 100	+15		max. -20		max. -50
02-HH-D005	Carbon	2	68	11,28	453	7	11,83	4,86	227	-50
02-HH-D006	Carbon	5	70	10,7	428	8	12,41	15,94	231	-46
02-HH-D007	Carbon	10	74	9,47	420	8	11,95	26,22	219	-48
02-HH-D008	Basalt	2	66	11,18	442	9	12,21	9,14	225	-49
02-HH-D009	Basalt	5	68	10,72	412	9	11,75	9,61	201	-51
02-HH-D010	Basalt	10	70	11,07	448	10	11,79	6,54	209	-53
02-HH-D011	Glass PA2	2	68	12,75	433	7	13,27	4,06	228	-47
02-HH-D012	Glass PA2	5	69	12,36	426	8	13,25	7,17	202	-53
02-HH-D013	Glass PA2	10	70	11,96	411	7	12,78	6,87	209	-49
02-HH-D014	Glass PP4	2	68	11,67	403	8	12,91	10,61	220	-46
02-HH-D015	Glass PP4	5	69	11,78	417	9	12,58	6,79	196	-53
02-HH-D016	Glass PP4	10	70	11,67	384	9	12,54	7,47	200	-48
02-HH-D017	Aramid	2	70	12,15	366	7	13,09	7,72	209	-43
02-HH-D018	Aramid	5	77	10,74	329	6	11,51	7,17	184	-44
02-HH-D019	Aramid	10	83	9,86	302	4	10,26	4,06	149	-51

Table 3.4: Coolant ageing test results according to changed fiber type and ratio											
Formulation code	Fiber Type	Fiber ratio (%)	BEFORE COOLANT AGEING			AFTER COOLANT AGEING (boiling point, 70 h)					
			Hardness (Shore A)	Tensile Strength (MPa)	Elongation at break (%)	Hardness Change (Shore A)	Tensile Strength (MPa)	Tensile Strength Change (%)	Elongation at break (%)	Elongation at break change (%)	Volume Change (%)
SAE J20 Class E			65-75	min. 5	min. 100	±10		max. -20		max. -25	-5; +20
02-HH-D005	Carbon	2	68	11,28	453	3	11,92	5,64	364	-20	0,4
02-HH-D006	Carbon	5	70	10,7	428	4	11,01	2,90	337	-21	0,1
02-HH-D007	Carbon	10	74	9,47	420	3	10,66	12,66	318	-24	0,2
02-HH-D008	Basalt	2	66	11,18	442	2	11,69	4,52	339	-23	0,3
02-HH-D009	Basalt	5	68	10,72	412	4	11,64	8,56	298	-28	0,4
02-HH-D010	Basalt	10	70	11,07	448	4	10,55	-4,68	270	-40	1,6
02-HH-D011	Glass PA2	2	68	12,75	433	4	12,86	0,86	315	-27	0,3
02-HH-D012	Glass PA2	5	69	12,36	426	4	12,48	0,97	293	-31	-1
02-HH-D013	Glass PA2	10	70	11,96	411	3	12,28	2,71	296	-28	0,4
02-HH-D014	Glass PP4	2	68	11,67	403	3	12,22	4,70	350	-13	0,4
02-HH-D015	Glass PP4	5	69	11,78	417	3	12,23	3,78	310	-26	0,8
02-HH-D016	Glass PP4	10	70	11,67	384	4	11,51	-1,35	285	-26	0,1
02-HH-D017	Aramid	2	70	12,15	366	2	12,69	4,41	274	-25	-0,9
02-HH-D018	Aramid	5	77	10,74	329	0	11,12	3,50	243	-26	0,2
02-HH-D019	Aramid	10	83	9,86	302	-2	10,64	7,87	231	-24	-0,9

Hardness change after ageing tests is given in Figure 3.8. Firstly, results of hardness change after hot air ageing are examined. For carbon fiber, with increasing ratio of carbon fiber in EPDM rubber mixture, hardness change is increased then it is stabilized. Basalt fiber filled EPDM rubber mixture results show that increasing ratio of basalt fiber firstly kept the hardness change same but then it increased. For glass PA2 fiber, increasing fiber ratio first increased hardness change then a small decrease occurred. Glass PP4 fiber filled EPDM rubber mixture trials gave a similar finding with carbon fiber, as follows; hardness change first increased then remained same with increasing fiber ratio. For aramide fiber, increase in fiber ratio effected hardness change oppositely which is desired. Low hardness change means the rubber compound can withstand the hot air ageing better and it will not loose its properties under engine working conditions. Secondly hardness change test results after coolant ageing is investigated. For carbon fiber, with increasing fiber ratio, hardness change increased and then decreased slightly. Increasing basalt fiber ratio increased hardness change and hardness change remained constant with increasing ratio. Increasing ratio of glass PA2 kept hardness change same and then a decrease in hardness change is observed. Glass PP4 fiber increase did not affect hardness change at the beginning but then an increase is held. For aramid fiber, increasing ratio of fiber decreased hardness change linearly but lastly with a negative value. It can be evaluated as increasing ratio of fiber helped the rubber material to be more resistant to hot air ageing in terms of hardness change, more fiber leads high hot air resistant material. But there exists an optimum value, when fiber ratio is increased over the optimum ratio then negative change in hardness is gained hence having a softer material than its original form. On the other hand, when all the values after hot air and coolant ageing are evaluated according to SAE J20 Class E, all the results are within the limits which are max. +15 ShoreA and ± 10 ShoreA respectively.

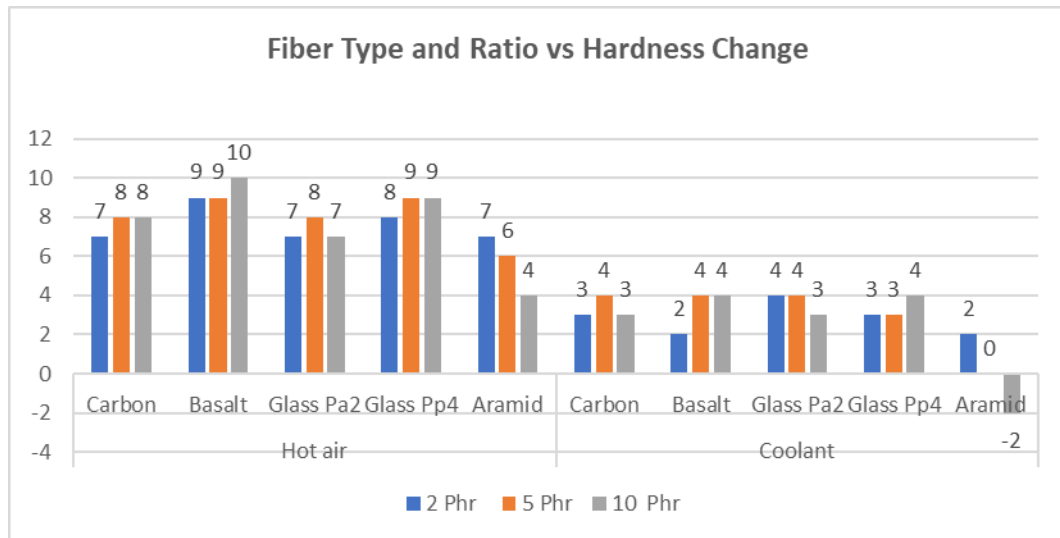


Figure 3.8: Fiber type and ratio versus Hardness change

Tensile strength changes after ageing tests is given in Figure 3.9. Tensile strength changes after hot air and coolant ageing tests show fluctuation due to the changed fiber type and ratio. This gives the idea that surface bonding of the fibers to polymer matrix is not so compatible that they do not form a homogenous structure to have meaningful results. After hot air ageing, EPDM rubber mixtures filled with aramid fiber gives most successful results in terms of tensile strength change, it is observed that with increasing fiber type and ratio tensile strength change decreases. This is due to the structure of aramid because an industry type aramid grade is selected to be worked with and it has the most proper surface structure suitable to be blended with polymers in the most homogeneous way compared to the other fibers. Also, this points out the importance of surface modification of fibers. When carbon fiber results are checked, it is seen that with increasing carbon fiber ratio, change in tensile strength increases. Increase in the ratio of basalt fiber firstly increases the change in tensile strength, then decreases the value similar with the finding in glass PA2. Increase in Glass PP4 ratio gives a decrease and then an increase in the tensile strength change. All the test results dependent on different fiber types are within the limits of SAE J20 Class E specification for tensile strength change after hot air ageing. When tensile change results after coolant ageing are observed, it is seen that with increasing ratio of carbon fiber and aramid fiber, change in tensile strength first decreases and then increases. For basalt fiber, an increase in tensile strength change is held with increasing fiber ratio. When the ratio is basalt fiber is increased again, a decrease in tensile strength is gained. Glass PA2 fiber studies showed that with increasing fiber ratio, change in tensile strength increased linearly. Increase in the

ratio of glass PP4 decreased tensile strength change. All the test results dependent on different fiber types are within the limits of SAE J20 Class E specification for tensile strength change after coolant ageing.

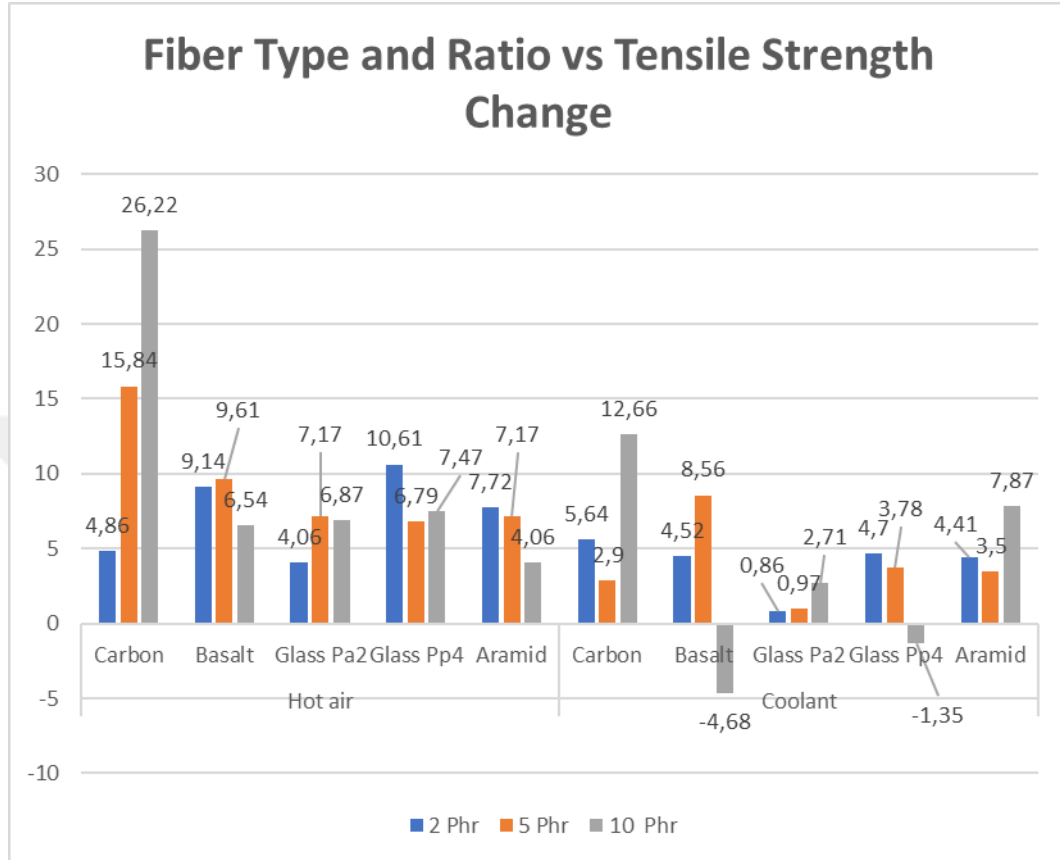


Figure 3.9: Fiber Type and Ratio vs Tensile Strength Change

Elongation at break change after ageing tests is given in Figure 3.10. Firstly, elongation at break changes after hot air ageing are observed. For carbon fiber, there exists a fluctuation with the increasing fiber ratio. Firstly, EAB change decreases and then increases with increasing fiber ratio. For basalt and aramid fiber, linear results are obtained. When fiber ratio increases, an increase in EAB change is gained meaning that lower EAB values are obtained thus change between initial state and after ageing state increases. Increase in fiber ratio in EPDM mixture makes the compound less resistant to hot air ageing in terms of EAB. For Glass PA2 and Glass PP4 fibers, with the increasing fiber ratio, an increase in EAB change is obtained, then by increasing the fiber ratio from 5 to 10 PHR gave a decreasing EAB change. When the results are evaluated according to SAE J20 Class E, there exists some deviating results. Secondly, elongation at break changes after coolant ageing are observed. For carbon and basalt fiber filled EPDM mixture studies, it is seen that

increasing fiber ratio increased the change in EAB. Increase in the ratio of Glass PA2 and aramid fiber in EPDM rubber mixture firstly increased the change in EAB and then decreased the value. For Glass PP4, when the ratio of fiber increased from 2 to 5 PHR, EAB change increased and then from 5 to 10 PHR it remained constant. When the results are evaluated according to SAE J20 Class E, there exists some deviating results also after coolant ageing in terms of EAB change.

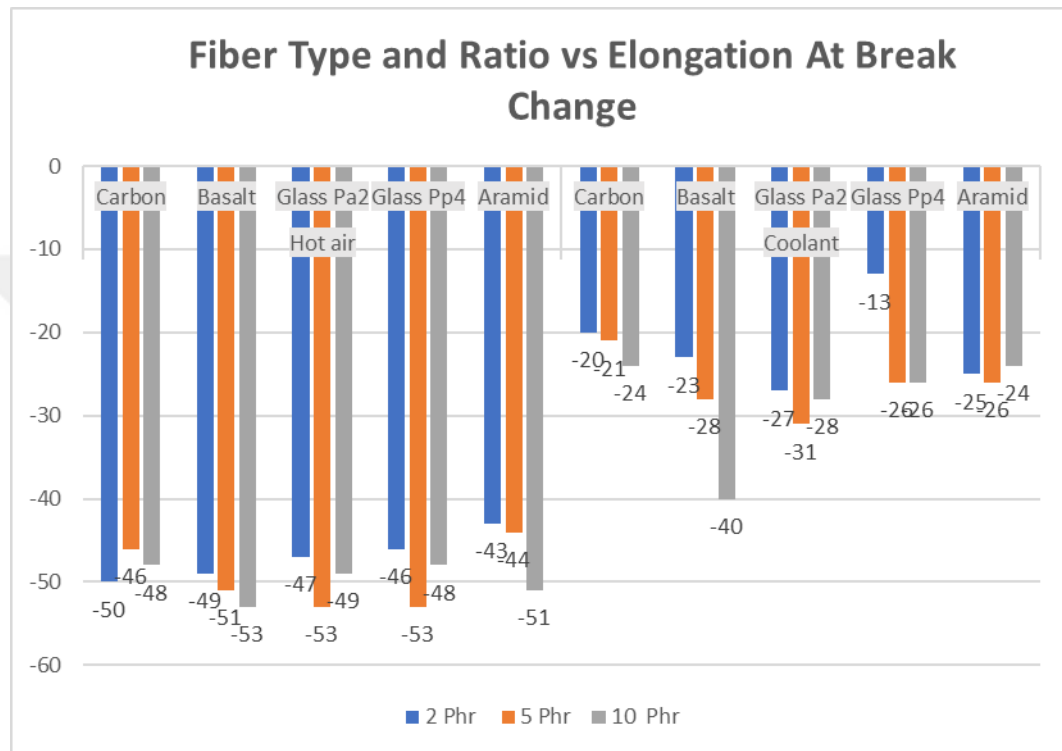


Figure 3.10: Fiber Type and Ratio vs Elongation At Break Change

Coolant effect on the rubber mixture tend to degrade it. For this reason, volume change after coolant ageing is measured. Sometimes rubber compound tends to swell and sometimes tends to shrink. Swelling of rubber compound is related to the chemicals in the coolant that is transferred to the compound hence the compound volume increases and swells. Shrinking of the rubber compound is related with the chemicals that is transferred from the compound to the coolant hence the compound loses weight and gets shrunk. After coolant ageing, when volume change is observed, a fluctuation is seen. For carbon and glass PA2 fibers, with increasing fiber ratio, first a decrease in volume change is seen, then by increasing from 5 to 10 PHR, an increase in volume change is gained. When the fiber ratio is increased in basalt fiber filled EPDM rubber mixtures, an increase in volume change is observed clearly. For Glass PP4 and aramide fiber studies, an increase in fiber ratio resulted an increase

and then a decrease in volume change. When we evaluate the results according to SAE J20 Class E, it is seen clearly that all the results are within the limits of the specification.

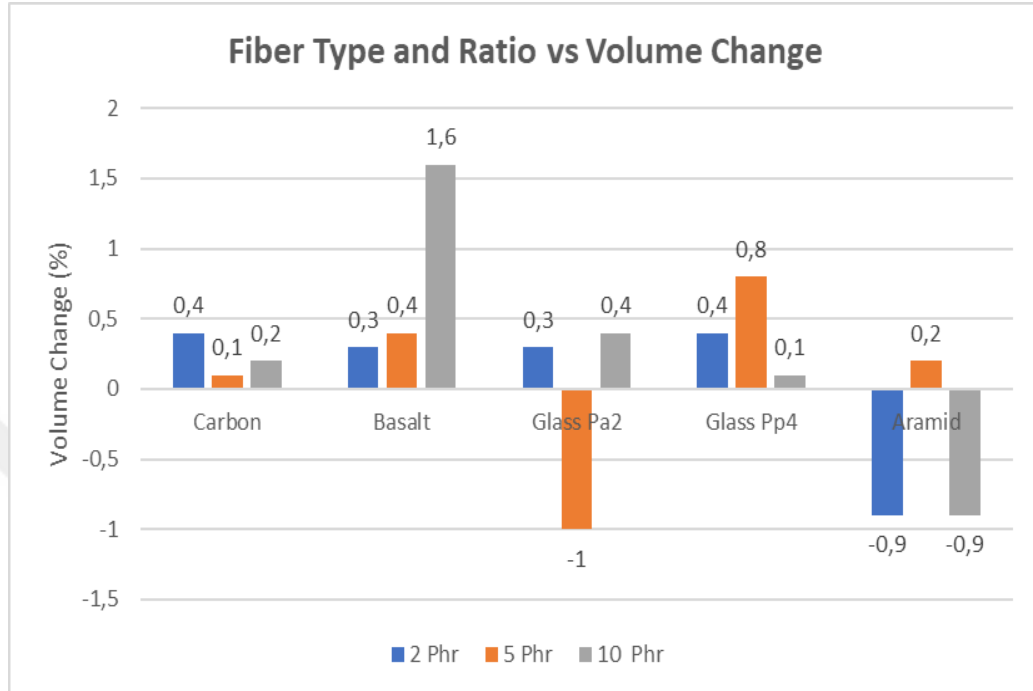


Figure 3.11: Fiber Type and Ratio vs Volume Change

When all rheometer tests, physico-mechanical tests and ageing test results are checked, it is seen that fiber ratio 5 PHR gives the optimum results. When the ratio is increased to 10 PHR some properties are lost. If it remained at 2 PHR some properties are not improved as desired. Also there are some fluctuating results with increasing fiber ratio. This is related to the poor surface bonding of fibers to the polymer matrix. Therefore surface structure of fibers is decided to be improved with different surface modification methods.

3.2 Test Results According to Surface Treatment of Fibers

3.2.1 Rheometer Test Results According to Surface Treatment of Fibers

The most suitable fiber ratio is selected by evaluating the results of fiber filled EPDM rubber mixtures. It is decided to proceed with 5 PHR fiber ratio for all the fiber types that are planned to be studied with. In first phase of study, carbon, basalt, PA2 glass, PP4 glass and aramid fiber are used in EPDM rubber mixtures. In this part of the study one of the glass fiber type is substituted from the study because effect of glass fiber and different glass fiber types are searched and it would be enough to continue with only one glass fiber type. For this reason, PA2 glass fiber is selected to work with. So, carbon, basalt, PA2 glass and aramid fiber filled EPDM mixtures with 5 PHR ratio is studied in this section. Also, an output of the previous phase of the study is that a fiber modification needs to be done. Fiber modification methods are surface treatment of fibers with EPDM solution, with alkali and with both EPDM solution and alkali (hybrid). In aramid fiber filled EPDM rubber mixture studies, only effect of surface treatment with alkali is investigated as aramid is an industrial grade and does not require surface modification like the other fiber types. All of the formulations are blended in internal mixer. Even results of 5 PHR fiber ratio without surface treatment was held in the previous phase of the study, it is again prepared to have a consistence between the blends. The details of the formulations are given in Table 3.5 as follows.

Table 3.5: Formulations prepared by surface treatment of fibers

Formulation Code	Fiber Type	Fiber Ratio (PHR)	Surface Treatment Method
D006	Carbon	5	Without
D006/2	Carbon	5	Alkali
D006/3	Carbon	5	EPDM sol.
D006/4	Carbon	5	Alkali+EPDM sol.
D009	Basalt	5	Without
D009/2	Basalt	5	Alkali
D009/3	Basalt	5	EPDM sol.
D009/4	Basalt	5	Alkali+EPDM sol.
D012	PA2 Glass	5	Without
D012/2	PA2 Glass	5	Alkali
D012/3	PA2 Glass	5	EPDM sol.
D012/4	PA2 Glass	5	Alkali+EPDM sol.
D018	Aramid	5	Without
D018/2	Aramid	5	Alkali

Firstly, rheometer tests are run, then physico- mechanical and ageing tests are carried out as well as SEM analysis, Raman analysis, surface tension and contact angle. Results are evaluated both according to the interactions between surface treated fibers with polymer matrix and requirements of SAE J20 Class E.

Table 3.6: Rheometer test results according to different surface treatment methods of fibers at 5 PHR

Formulation Code	Surface Treatment Method	ML (dNm)	MH (dNm)	Ts (min.)	T90 (min.)
D006	Without	1,08	12,08	0,7	1,7
D006/2	Alkali	1,08	12,86	0,72	1,86
D006/3	EPDM sol.	1,16	13,34	0,71	1,77
D006/4	Alkali+EPDM sol.	1,16	12,24	0,7	1,73
D009	Without	1,15	12,23	0,72	1,91
D009/2	Alkali	1,21	12,51	0,75	1,84
D009/3	EPDM sol.	1,19	13,44	0,73	1,85
D009/4	Alkali+EPDM sol.	1,24	12,92	0,72	1,84
D012	Without	1,26	12,99	0,73	1,81
D012/2	Alkali	1,27	13,46	0,84	1,82
D012/3	EPDM sol.	1,12	12,67	0,72	1,82
D012/4	Alkali+EPDM sol.	1,3	12,42	0,73	1,88
D018	Without	1,32	14,27	0,71	1,84
D018/2	Alkali	1,23	11,27	0,66	1,74

Minimum torque (ML) and maximum torque (MH) values related with the surface treatment method of fibers at 5 phr fiber ratio can be seen from Figure 3.12. For carbon fiber, it is seen clearly from graph that the EPDM mixture that contain alkali treated carbon fiber has the similar ML value when compared to carbon fiber without treatment. When surface treatment is applied with EPDM solution and hybrid form of alkali and EPDM solution it is observed that ML values increase. It can be said that alkali treatment helps to keep ML value same hence viscosity remains same, and flow of material do not get more difficult. For basalt fiber, different treatment method of fibers increase ML value of the EPDM rubber mixture. But the closest result to the non- treated fiber is the treated fiber with EPDM solution. The rubber mixture prepared with this surface treatment method is evaluated to give the similar

flow properties with the non- treated basalt fiber. When results of PA2 glass fiber is observed, it is seen that ML value that belongs to EPDM rubber mixture with the treatment of EPDM solution gives the lowest ML value between the others. It is understood that faster and easier flow characteristics in extrusion or molding can be reached with this treatment method in case PA2 glass fiber is used. For aramid fiber, alkali treated aramid fiber filler EPDM rubber mixture has a lower ML value than the non-treated aramid fiber filled EPDM rubber mixture. Alkali treatment helped to decrease ML value. When MH values are investigated, it is seen from the Figure 3.12 clearly that for carbon and basal fibers, treatment with alkali and treatment with EPDM solution increases MH value hence cross-linking density. More cross links are waited to be formed with the treatments of fibers hence more stiff materials are gained. When hybrid treatment of these fiber types is observed, it is seen that the MH values are still higher than the original forms but a little bit lower than the alkali or EPDM solution treated fibers separately. For PA2 glass fiber studies, it is seen that EPDM rubber mixture filled with alkali treated fibers give the highest MH value among the other trials. EPDM mixtures filled with PA2 glass fibers treated with EPDM solution has a lower ML value than the original form of the fiber. It means that state of cure is decreased with this treatment method and connecting bridges and cross links between the polymer chain and curatives are prevented. When aramide fiber studies are observed, similar with the finding in ML value is also gained for MH value, a significant decrease in MH value occurs with the treatment of aramid fiber with alkali.

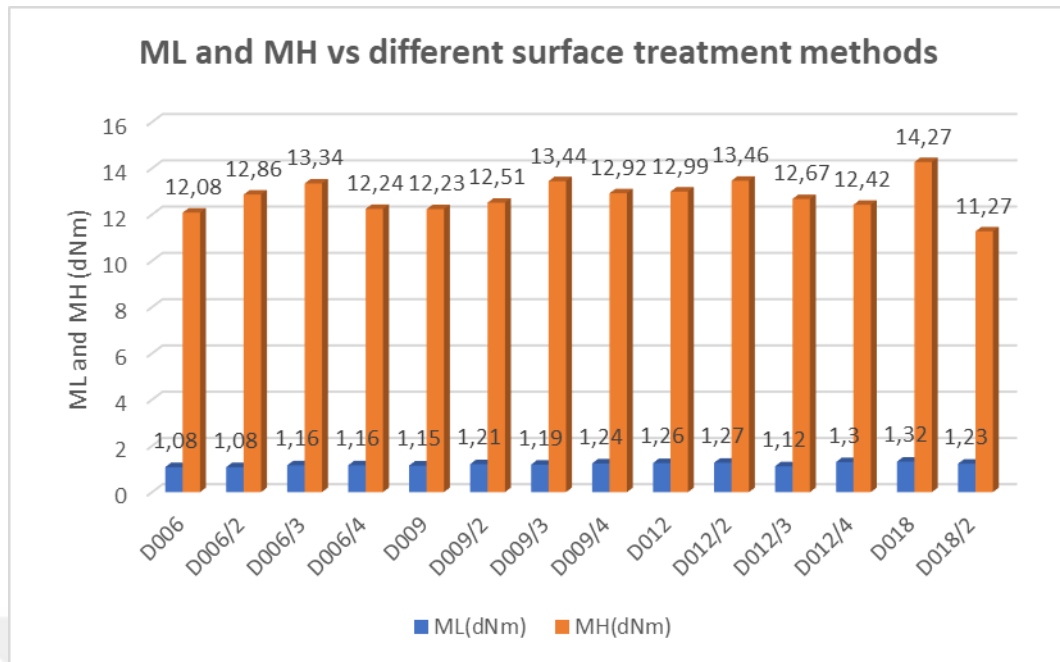


Figure 3.12: ML and MH vs different surface treatment methods

Scorch time, ts2 and t90 values related with the surface treatment method of fibers at 5 phr fiber ratio can be seen from Figure 3.13. Firstly, results of ts2 values are evaluated. When carbon fiber and aramid fiber results are observed, it is seen clearly that ts2 values remained nearly same with different surface treatment method of fibers. The results gained with the surface treated fibers are very close to the results that are obtained without treatment. It is seen that ts2 is not affected from surface treatment of fibers in carbon and basalt fiber studies. For PA2 glass fiber studies, it is understood that alkali treated fiber increases the ts2 value more than the other trials meaning that the starting time needed to pass from plastic state to elastic state is broader and safer. For EPDM solution treated fibers and hybrid fiber studies, ts2 values remained same. When aramid fiber treatment is investigated it is seen that alkali treatment of aramid fiber led the ts2 value to decrease. If EPDM rubber mixture filled with alkali treated fiber needs to be processed, it should be kept in mind that start of curing operation will be faster than the mixture filled with non-treated aramid fiber. Secondly t90 values are evaluated. When carbon fiber trials are observed, it is seen clearly that alkali treated fiber extended t90 more than the non-treated fibers or other surface treatment methods. Comment can be made as more time is needed to finish curing operation or cross-linking operation with alkali treated carbon fiber. The other surface treatment methods do not change t90 value. For basalt fiber, a decrease is observed in t90 values with the all surface treatment

methods which can be evaluated as a faster cure is reached. On the other hand, it is seen that despite the surface treatment methods decreased t90 they have all very close results with each other. When PA2 glass fiber studies are checked, it is understood that only hybrid fiber treatment increased t90 value whereas other treatment methods kept t90 value same with the non-treated fiber. It can be evaluated as hybrid treatment of PA2 glass fiber prevents curing speed arising from the interactions between the bonding of fibers to the rubber matrix. For aramid fiber studies, it is seen clearly that t90 decreases with alkali treatment similar with the finding gained for ts2.

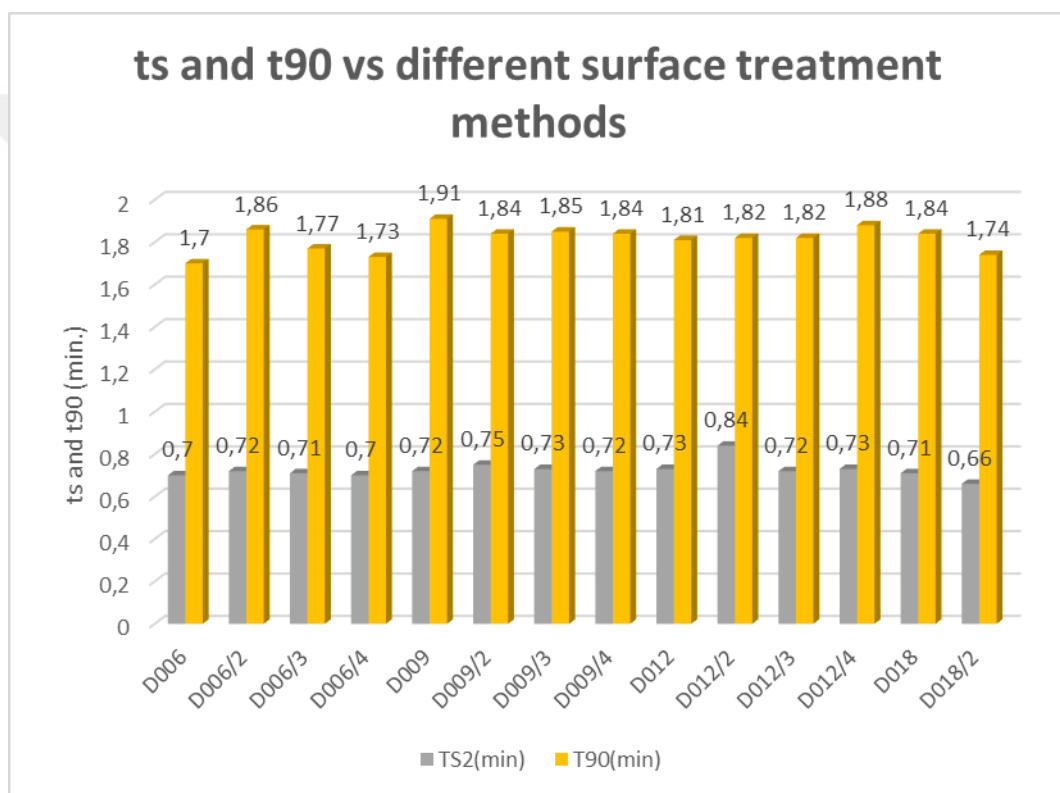


Figure 3.13: ts and t90 vs different surface treatment methods

3.2.2 Physico-mechanical and Ageing Test Results According to Surface Treatment of Fibers

Hardness test results at initial state, after hot air ageing and coolant ageing are given in Table 3.7. It is studied on the effect of surface modification method of fibers at 5 PHR usage ratio on hardness properties before and after ageing.

Table 3.7: Hardness vs different surface treatment methods of fibers at 5 PHR

Formulation Code	Surface Treatment Method	Hardness Initial (ShoreA)	Hardness After Hot Air Ageing (ShoreA)	Hardness After Coolant Ageing (ShoreaA)
SAE J20 E	-	65-75	+15	±10
D006	Without	71	9	5
D006/2	Alkali	72	6	1
D006/3	EPDM sol.	73	6	3
D006/4	Alkali+EPDM sol.	72	6	4
D009	Without	71	6	2
D009/2	Alkali	71	7	3
D009/3	EPDM sol.	72	5	1
D009/4	Alkali+EPDM sol.	70	8	3
D012	Without	72	7	3
D012/2	Alkali	71	7	3
D012/3	EPDM sol.	72	4	2
D012/4	Alkali+EPDM sol.	71	7	4
D018	Without	80	4	-2
D018/2	Alkali	72	6	5

Initial hardness results for various surface treatment methods can be seen clearly from Figure 3.14. It is observed that surface treatment of fibers helped to decrease the hardness slightly or at least kept the value at the same limits compared to the non-treated fiber. Most significant change is gained in aramid fiber that has a surface treatment with alkali. Hardness is decreased 8 points in the EPDM rubber mixture filled with alkali treated aramid fibers. Generally, it is evaluated that surface treated fibers form better surface bonding within the polymer matrix, resulting in a more homogenous structure hence well mixed compounds with desired hardness values. Besides when the results are considered according to the demands of SAE J20 Class

E, it is seen that EPDM rubber mixtures filled with surface treated fibers remain inside the limits, despite non-treated fibers sometimes can not catch the limits between 65-75 ShoreA.

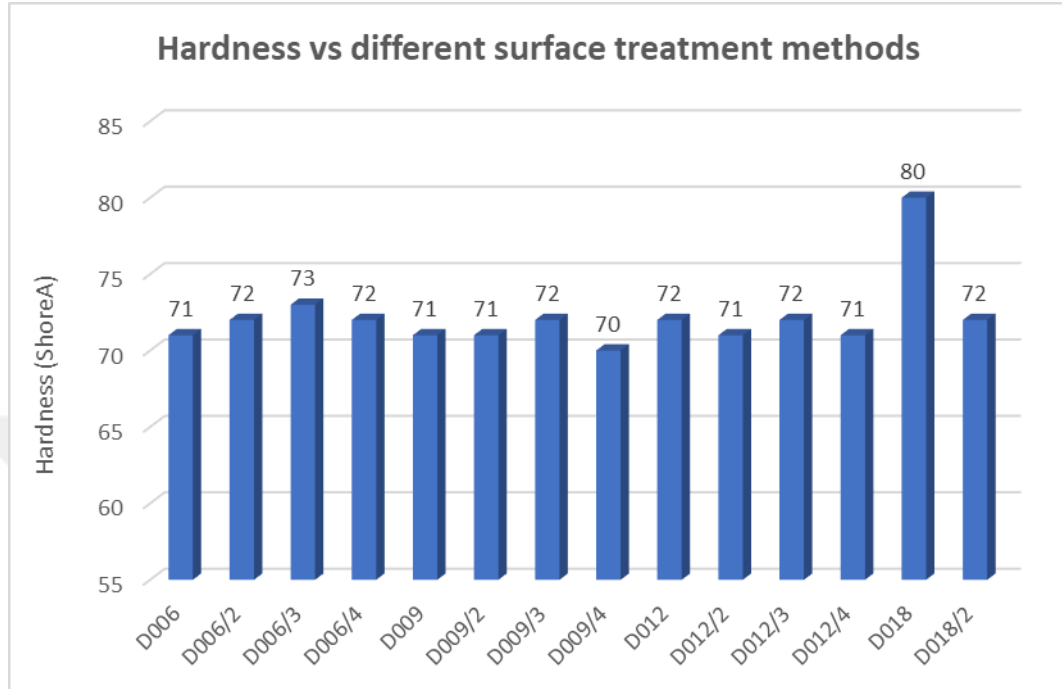


Figure 3.14: Hardness vs different surface treatment methods

Hardness change after hot air ageing and coolant ageing due to the effect of different surface modification methods can be seen clearly from Figure 3.15. Firstly, hardness change after hot air ageing is investigated. When carbon fiber results are examined, it is seen that surface treatment of carbon fiber helped to decrease hardness change after hot air ageing, meaning that material gets more resistant to ageing in hot medium. Surface treated carbon fibers are more compatible to the structure that they exist inside. For basalt fiber results, it can be said that surface treatment of basalt fiber with EPDM solution decreased the hardness change after hot air ageing whereas the other surface modification methods increase hardness change after hot air ageing which means making the blend less resistant to hot air contact. Further surface modification methods need to be studied related to basalt fiber. When PA2 glass fiber surface treatment is investigated, it is seen that similar to the finding in basalt fiber, most successful result in terms of hardness change after hot air ageing is held with surface treatment with EPDM solution. The other surface treatment methods kept the hardness change value same with the non-treated fiber. PA2 glass fiber surface treatment needs to be studied with further trials. For aramid fiber, it is

seen from the Figure 3.15 that hardness change is increased after hot air ageing with alkali surface treatment. In terms of the requirements of SAE J20 Class E, all trials can meet the specification with all surface treatment methods after hot air ageing for hardness change. Secondly, hardness change after coolant ageing for different surface treatment methods are evaluated. When carbon fiber results are observed, it is understood that hardness change decreases after coolant ageing by the help of surface treatment with alkali, EPDM solution and hybrid. It is a desired result because lower hardness change means the rubber material is more resistant to coolant which it has a contact with. Coolant cannot deform the rubber material easily. For basalt fiber studies, a finding similar to hot air ageing is gained with coolant ageing. Basalt fiber which has a surface treatment with EPDM solution led the hardness change after coolant ageing to decrease. But oppositely other surface treatment methods increased hardness change which is not an expected result. Therefore, further trials need to be carried out on the surface treatment methods of PA2 glass fiber. When aramid fiber results are observed, it is seen that surface treatment with alkali increased the hardness change. When result is checked from a different point of view, it is understood that without surface treated fiber there occurred a softening after coolant ageing meaning that some fillers migrated to coolant. But with alkali treated fibers a hardening occurred after coolant ageing, which is an expected situation with the effect of hot coolant that is in contact with the rubber material. So, surface modification of fiber also helped aramid fiber to have a meaningful result after coolant ageing. When hardness change after coolant ageing results are evaluated according to SAE J20 Class E, it can be easily said that all results meet the requirement.

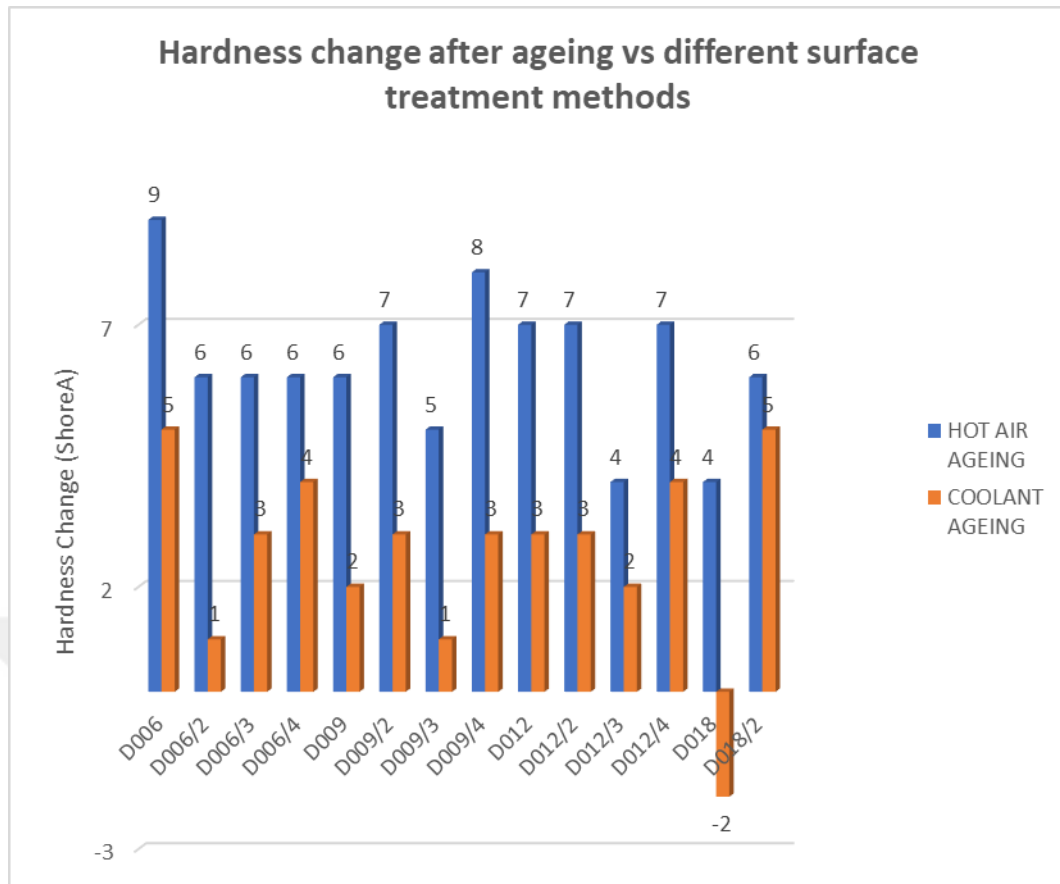


Figure 3.15: Hardness change after ageing vs different surface treatment methods

Tensile strength test results at initial state, after hot air ageing and coolant ageing are given in Table 3.8. It is studied on the effect of surface modification method of fibers at 5 PHR usage ratio on tensile strength properties before and after ageing.

Table 3.8: Tensile strength vs different surface treatment methods of fibers at 5 PHR

Formulation Code	Surface Treatment Method	Tensile Strength, Initial (Mpa)	Tensile Strength Change After Hot Air Ageing (%)	Tensile Strength Change After Coolant Ageing (%)
SAE j20 E	-	min.5	max. -20	max. -20
D006	Without	9,98	6,34	-1,33
D006/2	Alkali	10,11	3,54	-4,95
D006/3	EPDM sol.	8,79	9,76	1,48
D006/4	Alkali+EPDM sol.	10,04	14,31	-1,10
D009	Without	10,61	6,48	-0,75
D009/2	Alkali	10,46	8,75	0,67
D009/3	EPDM sol.	10,54	5,17	0,19
D009/4	Alkali+EPDM sol.	10,2	6,76	0,78
D012	Without	10,63	5,37	-3,20
D012/2	Alkali	10,33	9,34	-0,10
D012/3	EPDM sol.	10,14	8,73	-4,83
D012/4	Alkali+EPDM sol.	9,21	12,53	-8,69
D018	Without	9,82	9,69	-3,56
D018/2	Alkali	9,91	10,07	-1,61

Tensile strength results due to different surface treatment methods of various fibers are seen from Figure 3.16. When carbon fiber results are evaluated, it is understood that close results are gained with all different surface treatment methods except EPDM solution method. With this method the result decreased significantly. Surface treatment with EPDM solution is not suitable and compatible for carbon fiber as it creates a loss in tensile strength value. When basalt fiber studies are investigated, it is

seen that surface treatments of basalt fiber kept the tensile strength values at the same limits with the non-treated fiber. For PA2 glass fiber, surface treatment of fiber decreased the tensile strength value linearly which points out a lower strength between the polymer chains. Thus, further surface treatment methods need to be searched for PA2 glass fiber. When aramide fiber results are observed, it is seen that surface treatment with alkali remained the tensile strength value same with the non-treated form. On the other hand, if it is needed to evaluate the results according to SAE J20 Class E specification, it is clear that all the results can meet the demands of the specification in terms of tensile strength.

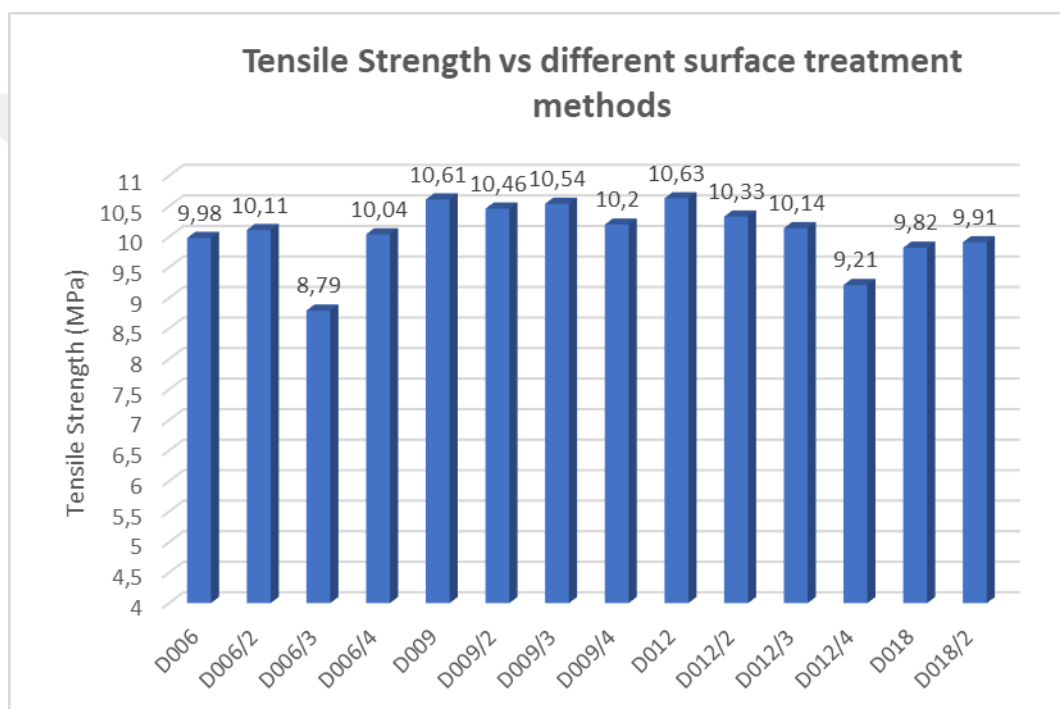


Figure 3.16: Tensile strength vs different surface treatment methods

Change in tensile strength after hot air and coolant ageing dependent on the different surface modification methods can be evaluated from Figure 3.17. Hot air ageing and coolant ageing makes some effects on mechanical properties like tensile strength, and it is needed to be discussed. Firstly, effect of surface treatment of fibers on tensile strength change after hot air ageing is investigated. When carbon fiber results are checked, it is seen that surface treatment of fiber with alkali decreased change in tensile strength. Other treatment methods like EPDM solution and hybrid increased tensile strength change. For basalt fiber studies, it is seen that most successful results for tensile strength change after hot air ageing is gained with surface treatment of fiber with EPDM solution. It decreased the value more than the others hence

providing the material to be more resistant to hot air ageing. When PA2 glass fiber studies are observed, it is understood that surface treatment of fibers did not help to decrease tensile strength change after hot air ageing when compared to the non-treated fiber. Further surface treatment methods would be better to try for PA2 glass fiber. For aramid fiber, it can be said that surface treatment with alkali kept the tensile strength change same with non-treated fiber. According to the requirement of SAE J20 Class E, all the results of EPDM rubber mixture filled with surface treated fibers are within the limits of specification. Secondly, tensile strength change after coolant ageing is investigated. When carbon fiber surface treatment results are observed, it is seen that alkali treatment increased tensile strength change, whereas EPDM solution treatment made a positive change effect by having a same numerical value. After hybrid treatment of fiber tensile strength change remained same with the non-treated fiber. From these results, it can be said that only EPDM solution treatment method provided an increase in tensile strength hence a positive change is held while the other treatment methods provided a decrease in tensile strength meaning a negative change in tensile strength. Also, alkali treatment has the highest change after coolant ageing therefore it is not evaluated as a suitable treatment method for carbon fiber. When basalt fiber results are investigated it is seen that all surface treatment methods converted the negative change of tensile after coolant ageing to a positive change and they are all close to each other. The change of tensile strength are very similar for all four trials so that it can be evaluated as surface treatment of basalt fibers did not create significant difference in terms of tensile strength. For PA2 glass fiber results, alkali treatment gave the most successful improvement in tensile change while other treatment methods increase the tensile change. Hybrid treatment created a negative synergetic effect on this property. Some more treatment methods need to be studied. When aramid fiber results are checked, it is seen that alkali treatment helped to decrease tensile strength change. If the results are evaluated according to the limits of SAE J20 Class E, it can be said that all EPDM rubber mixtures with different surface treatment methods can meet the specification.

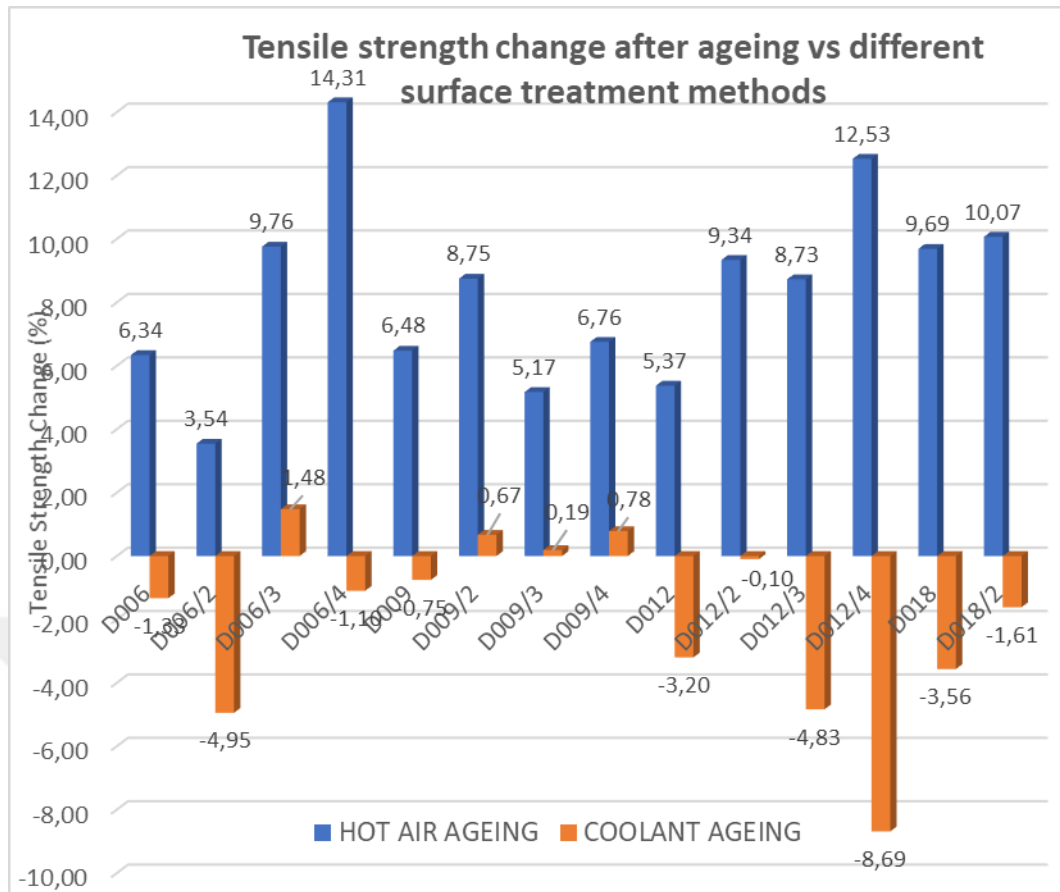


Figure 3.17: Tensile strength change after ageing vs different surface treatment methods

Elongation at break test results at initial state, after hot air ageing and coolant ageing are given in Table 3.9. Effect of different surface modification methods of fibers at 5 PHR fiber usage ratio on elongation at break properties before and after ageing is studied.

Table 3.9: Elongation at break vs different surface treatment methods of fibers at 5 PHR

Formulation Code	Surface Treatment Method	Elongation at break, Initial (Mpa)	Elongation at Break Change After Hot Air Ageing (%)	Elongation at Break Change After Coolant Ageing (%)
SAE J20 E	-	min. 100	max. -50	max. -25
D006	Without	352,8	-49,3	-29,4
D006/2	Alkali	311,6	-34,3	-14,4
D006/3	EPDM sol.	260,0	-38,8	-18,7
D006/4	Alkali+EPDM sol.	352,4	-42,6	-21,4
D009	Without	359,3	-46,8	-22,8
D009/2	Alkali	358,3	-44,4	-15,6
D009/3	EPDM sol.	350,4	-54,6	-19,9
D009/4	Alkali+EPDM sol.	359,8	-49,0	-18,8
D012	Without	353,9	-46,6	-16,8
D012/2	Alkali	370,2	-43,7	-35,9
D012/3	EPDM sol.	354,7	-47,2	-18,4
D012/4	Alkali+EPDM sol.	345,7	-46,8	-34,3
D018	Without	326,9	-51,5	-29,3
D018/2	Alkali	385,5	-48,7	-23,1

Elongation at break results due to different surface treatment methods of various fibers are seen from Figure 3.18. When carbon fiber results are observed, surface modification of fibers with alkali and EPDM solution decreased EAB linearly whereas hybrid treatment created a synergetic effect arising from the combination of

alkali and EPDM solution and increased the EAB value to the same value with the non-treated fiber. For basalt fiber, it is seen clearly from Figure 3.18 that surface modification of fibers did not change EAB value at the initial state. The results are very similar and close to each other. When PA2 glass fiber studies are observed, it can be said that similar with the finding in basalt fiber, mostly surface treatment methods kept EAB value same with the non-treated fiber except alkali treatment. Alkali treatment provided an increase in EAB hence making the material more elastic than the others. Alkali treatment led a better surface bonding for the fiber in the polymer matrix. For aramid fiber results, it is seen that alkali treatment made a significant increase in EAB value which gives the idea that surface treatment is successful, and a more homogenous and well dispersed compound is held. On the other hand, according to SAE J20 Class E demands, it is seen clearly that all surface modification methods led the EPDM rubber mixture to have results inside the limits of specification.

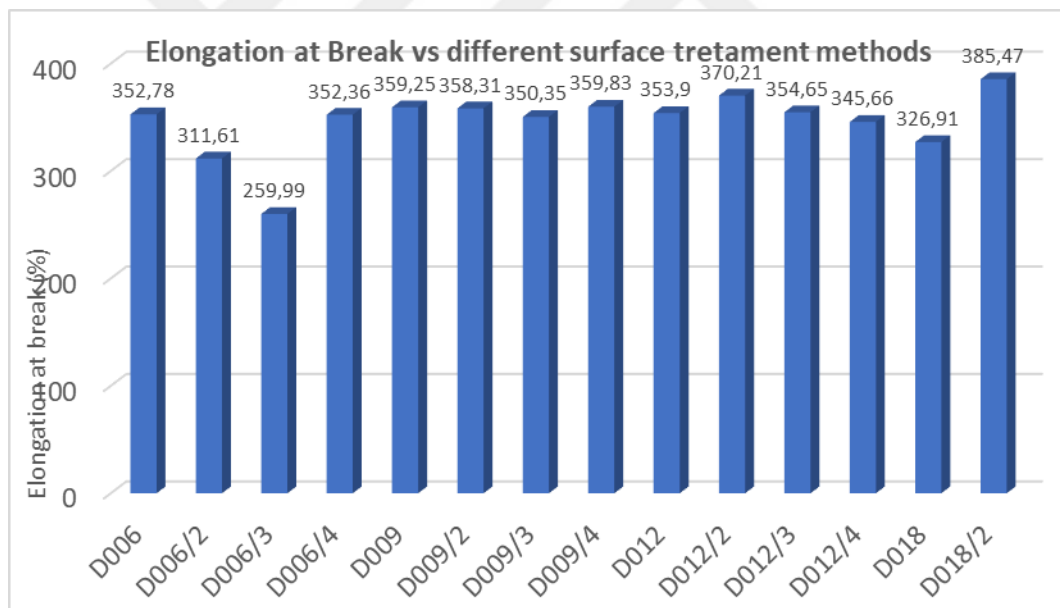


Figure 3.18: Elongation at break vs different surface treatment methods

Elongation at break change after hot air and coolant ageing due to the different surface modification methods are given in Figure 3.19. Hot air and coolant ageing create a deformation on rubber compounds also on elastic properties so EAB change is an important characteristics that needs to be evaluated to see how much rubber compound is deformed and how the compound's elasticity on the working conditions of engine is affected. Firstly, EAB change after hot air ageing dependent on the different surface modification methods are checked. When carbon black results are

observed, it is seen that all surface modifications decreased the change at EAB value, especially alkali treatment method. Surface modification of fibers help the rubber compound to retain its elastic properties after hot air ageing better when compared to non-treated fiber. This result is resulting from better surface bonding of fibers to the rubber matrix after being surface treated creating a more compatible structure in the matrix. When basalt fiber results are observed, it is understood that most of the surface modification methods kept the EAB change at the same value with the non-treated fiber except EPDM solution treatment. EPDM solution treatment created a significant difference at EAB change result and it is not an expected result. Therefore, further surface treatment methods need to be studied for basalt fiber. When PA2 glass fiber results are observed, it is seen that EPDM rubber mixtures filled with surface treated fibers have similar EAB change values with the non-treated fiber. Only alkali treatment created a slight improvement in EAB change. For aramid fiber, it is seen that alkali treatment led the EAB change to decrease by having a lower value. It is understood that surface treatment is helpful to have an improved elastic property after hot air ageing. From the SAE J20 Class E point of view, only 2 results can not catch the limits, basalt fiber treated with EPDM solution and non-treated aramid fiber. The other can meet the specification requirements. Surface modification of fibers is usually helpful to resist hot air and keep elastic properties after ageing. Secondly, EAB change after coolant ageing due to the different surface modification methods are discussed. When carbon fiber results are investigated, it is seen that surface modification of all kinds improved EAB change after coolant ageing significantly with the best result belonging to alkali treatment. Carbon fibers with surface treatment are better bonded to the rubber matrix and give more homogenous structure. For basalt fiber, again the benefits of surface treatment can be seen for EAB change after coolant ageing with improved results. EAB change is smaller with surface treated fibers, again the best result gained by alkali treatment. When PA2 glass fiber trials are checked, fluctuation between the results of EAB change is seen. Alkali treatment gave better EAB change whereas EPDM solution and hybrid treatment gave higher EAB change after coolant ageing which means that compounds' elasticity is decreased when compared to non- treated fiber. This is not a usual or expected situation that more trials need to be done on surface treatment of PA2 glass fibers. When aramid fiber results are controlled, alkali treatment helped to

decrease EAB change and improved the elastic property of EPDM rubber mixture after coolant ageing by forming a more compatible fiber. Additionally, when the requirements of SAE J20 Class E is taken into consideration, it is seen that only 4 results are out of the limits and 2 of them is coming from non-treated fibers and the rest coming from PA2 glass fiber studies. It is already understood that PA2 glass fiber treatments need to be verified. And surface treatment of fibers play an important role to improve ageing properties.

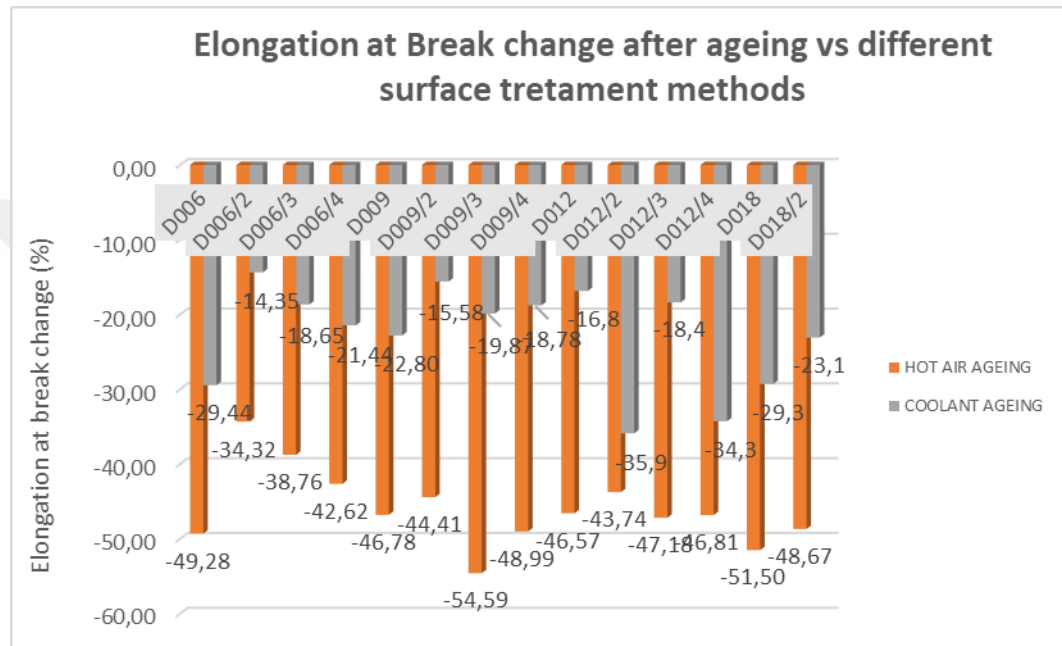


Figure 3.19: Elongation at break change after ageing vs different surface treatment methods

Volume change of EPDM rubber mixtures after coolant ageing due to the different surface treatment methods are listed in Table 3.10. Coolant ageing leads to swelling or shrinking of rubber material dependent on the chemicals migrating from one direction to the other. The aim is to see the effect of surface modification of fibers on the volume change results.

Table 3.10: Volume change after coolant ageing vs different surface modifications of fibers at 5 PHR

Formulation Code	Surface Treatment Method	Volume Change (%)
SAE J20 E	-	-5; +20
D006	Without	1,1
D006/2	Alkali	0
D006/3	EPDM sol.	0
D006/4	Alkali+EPDM sol.	0,1
D009	Without	0,1
D009/2	Alkali	0,1
D009/3	EPDM sol.	-0,5
D009/4	Alkali+EPDM sol.	-0,9
D012	Without	-0,4
D012/2	Alkali	2,5
D012/3	EPDM sol.	-0,5
D012/4	Alkali+EPDM sol.	0,4
D018	Without	3,6
D018/2	Alkali	0,2

The effect of coolant ageing on volume change of EPDM rubber mixture filled with fibers which have different surface treatments can be seen in Figure 3.20. When carbon fiber results are observed, it is seen that different surface treatments of fibers decreased volume change after coolant ageing. An improvement is gained with surface treatment of fibers. The result is evaluated as treated fibers can form better

homogeneity in the rubber matrix by supporting the cross links formed between the polymer chains hence preventing the damage coming from the coolant effect. For basalt and PA2 glass fiber studies, EPDM solution, hybrid treatment and alkali treatment respectively give fluctuating results opposite to what expected. Detailed surface treatment studies need to be done with these fibers. For aramid fiber a significant decrease is gained with alkali treatment parallel with the finding held from carbon fiber. When requirements of SAE J20 Class E is taken into consideration, all the results can meet the specification.

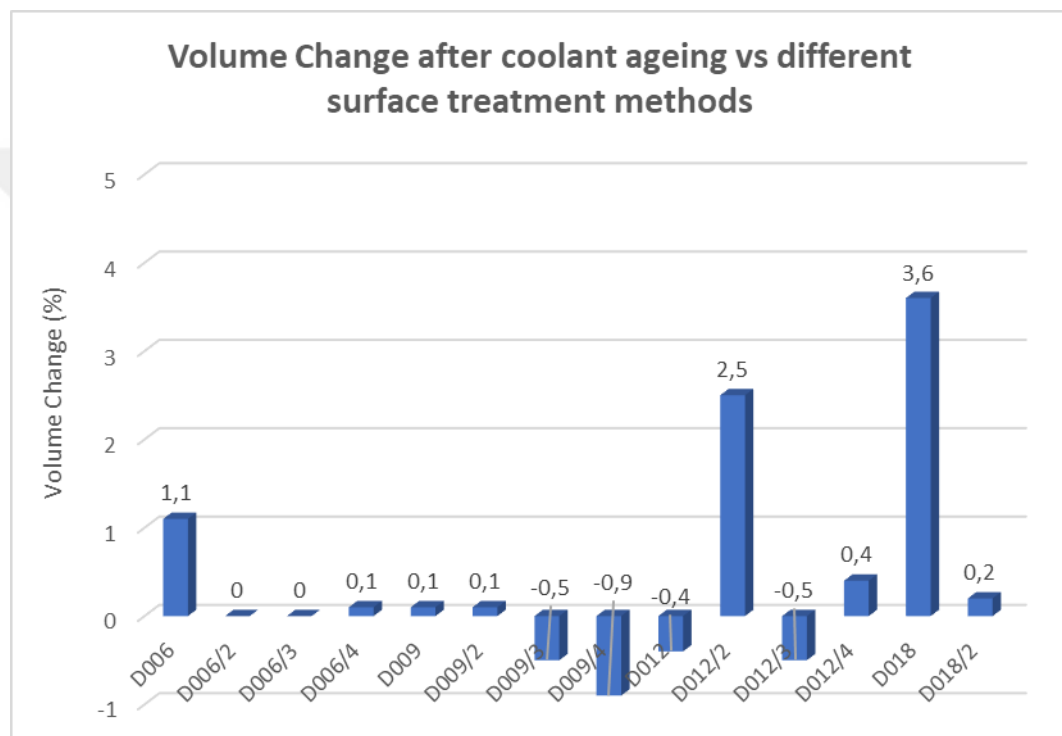


Figure 3.20: Volume change after coolant ageing vs different surface treatment methods

Tearing strength at the initial state is tested for EPDM rubber mixtures that are filled with various type of fibers at 5 PHR ratio with different surface treatment methods. Results can be seen clearly from Figure 3.21. Results that are gained for carbon fiber studies revealed that tearing strength decreases with surface modification of fibers but still in the limits of SAE J20 Class E specification which has to be minimum 4 N/mm. For basalt fiber an increase and a slight improvement in tear strength is gained but still values are very close to each other by meeting SAE J20 Class E. When PA2 glass fiber is observed, it is seen that an increase in tear strength is held with the surface modifications except EPDM solution treatment. Further surface modifications of fibers need to be discussed. All the results can meet SAE J20 Class

E. For aramid fiber, it can be said that alkali surface treatment of fiber decreased tear strength but still can meet easily the demand of specification.

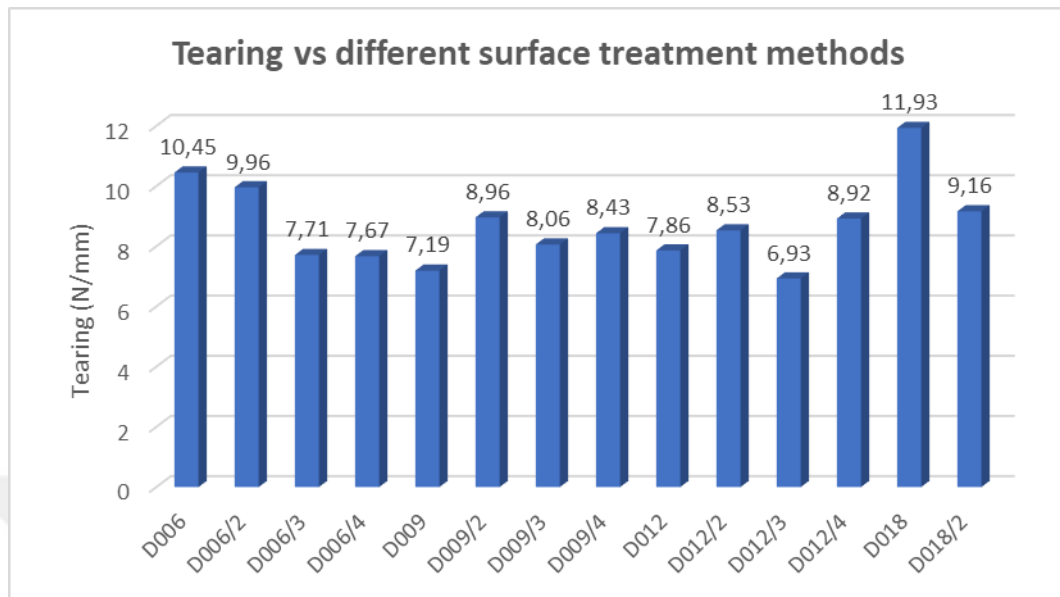


Figure 3.21: Tearing strength vs different surface treatment methods

Compression set test is run at the initial state from different EPDM rubber mixtures filled with fibers at 5 PHR ratio with different surface treatment methods. Results can be seen from Figure 3.22. Compression set is a key indicator for the cross linking density and the behaviour of the material when exposed to hot air under a definite load. The lower the compression set value is desired for better operating conditions. When carbon fiber results are checked it is seen that surface treated fibers do not change compression set test value. For basalt fiber trials the same finding is gained. When glass fiber results are observed, it is seen that alkali treatment of fiber improved the result slightly but the rest results belonging the other modification remained same. When aramid fiber studies are investigated, it is seen that fiber surface treatment do not affect compression set. On the other hand when the results are evaluated according to the requirements of SAE J20 Class E, it is seen that all the mixtures are successful.

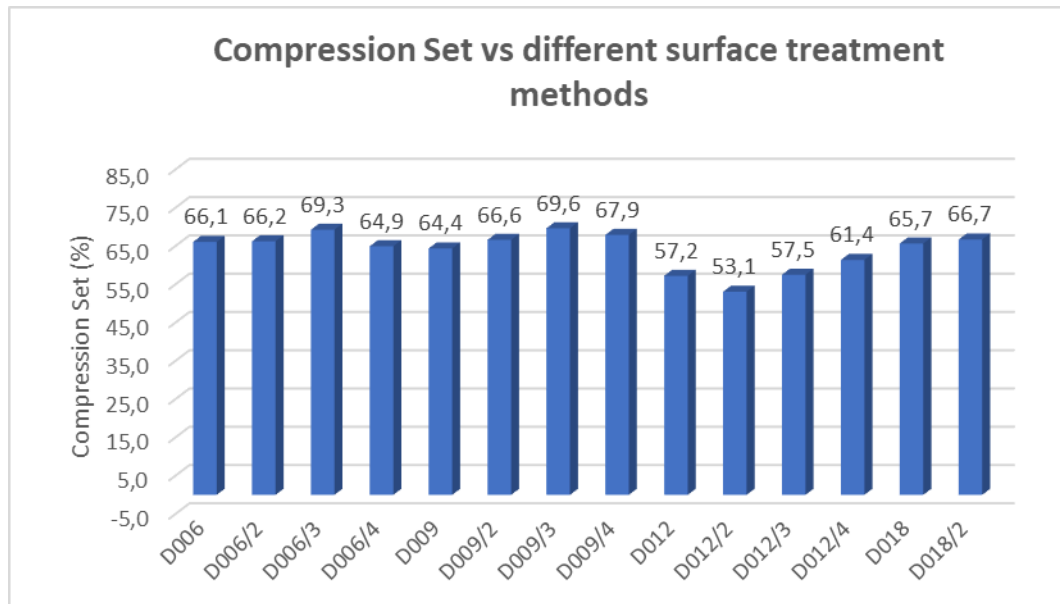


Figure 3.22: Compression set vs different surface treatment methods

3.2.3 Surface Analysis Results According to Surface Treatment of Fibers

After rheological, physico-mechanical and ageing tests are carried out, some more tests which indicates the surface bonding quality of fibers in the rubber compound are run. These analyses include SEM, Raman and surface tension and contact angle measurements. Tests are done from EPDM rubber mixtures filled with 5 PHR fiber ratio with EPDM solution treatment method. Even rheological- physico-mechanical and ageing tests of EPDM solution treated aramid fiber and reference EPDM mixture (without fiber, called E002) do not exist in this part of the study, SEM analyses, surface tension and contact angle measurements and Raman analyses are made to see the surface treatment effect and to form an integrity with the other trials.

SEM analysis is carried out from the EPDM rubber mixtures filled with 5 phr fiber ratio with EPDM solution surface treatment method. Results can be seen from the images as follows.

Surface modification brings the advantage of well dispersed short fibers among the rubber matrix. The improvement in surface quality and surface bonding of fibers to the polymer can be seen very clearly and easily from the figures below.

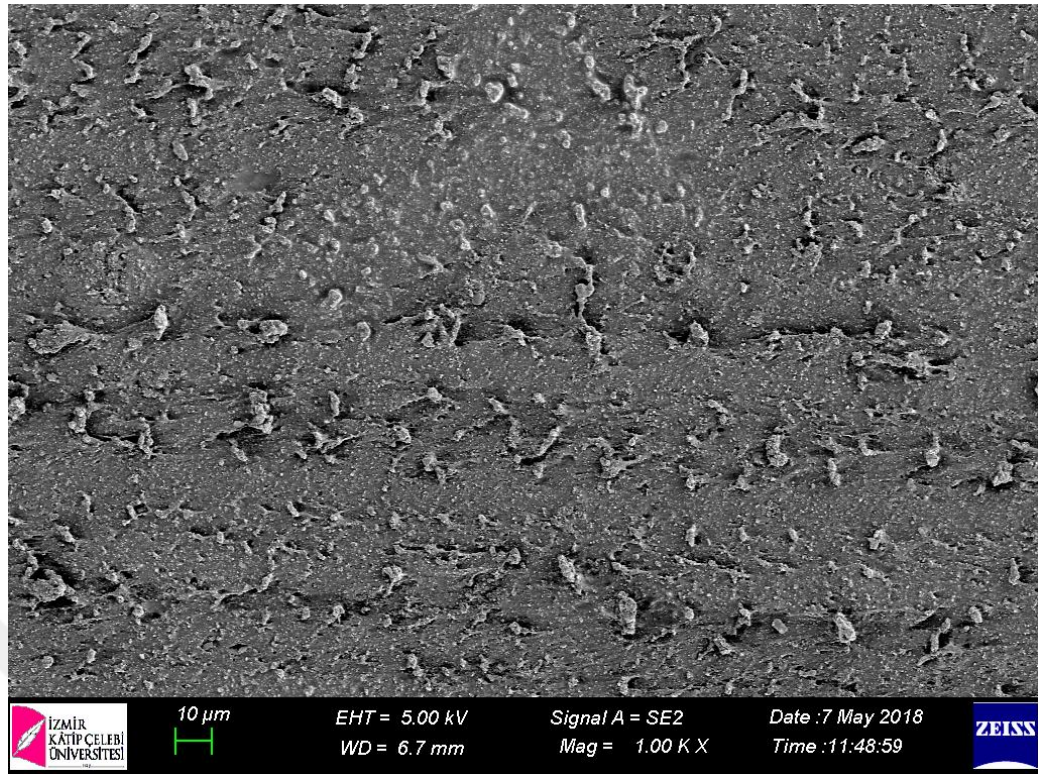


Figure 3.23: SEM analysis of EPDM rubber mixture without fiber (reference mixture)

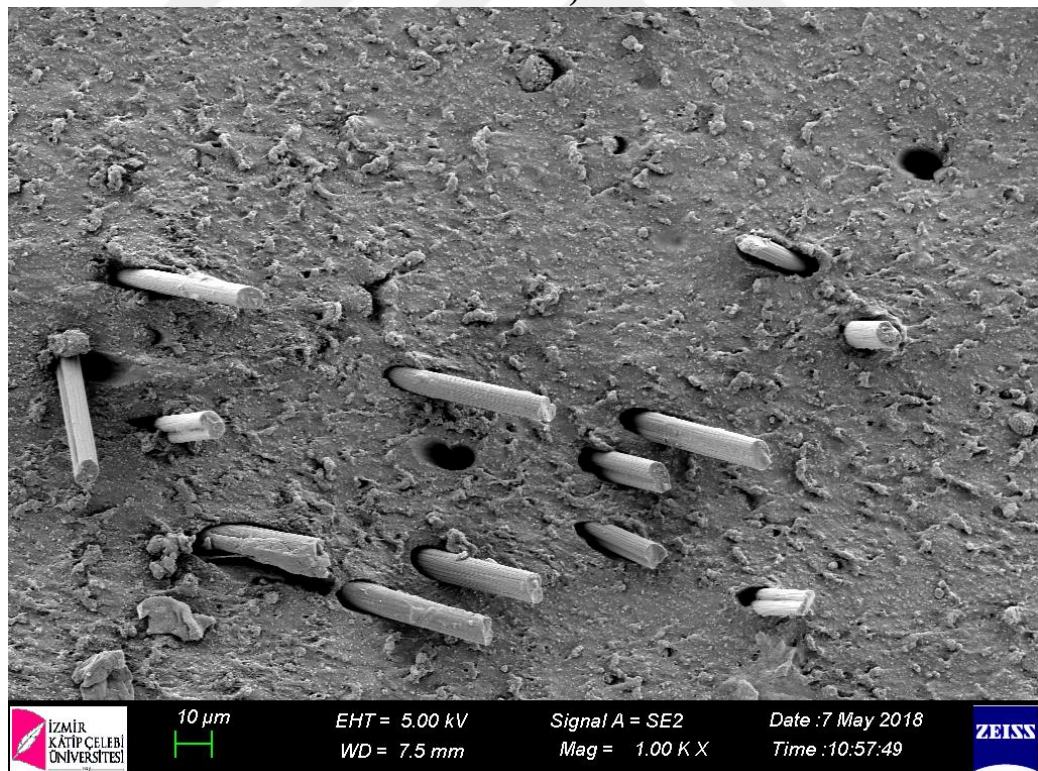


Figure 3.24: SEM analysis of EPDM rubber mixture with non-treated carbon fiber

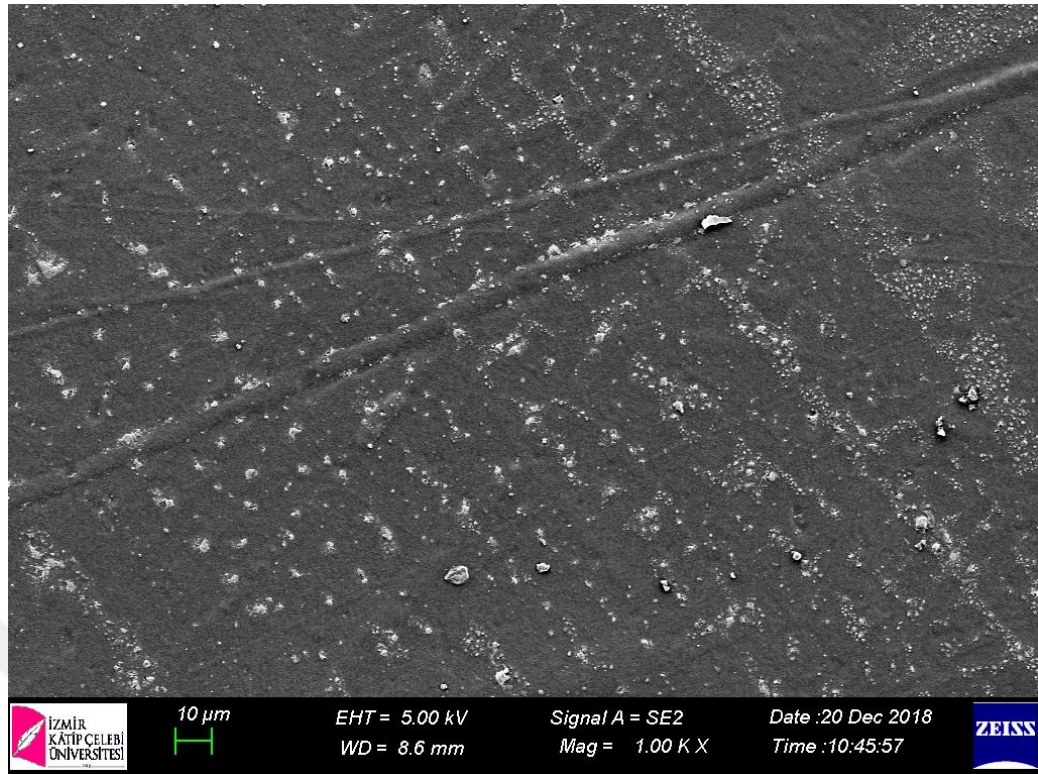


Figure 3.25: SEM analysis of EPDM rubber mixture with EPDM solution treated carbon fiber

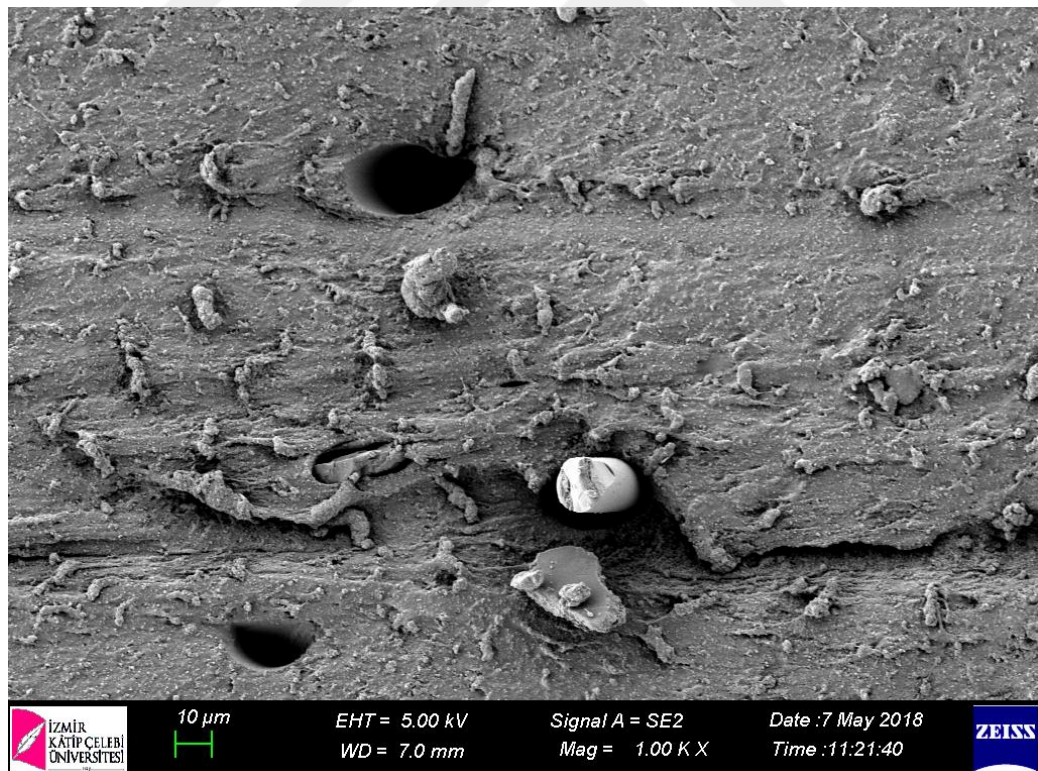


Figure 3.26: SEM analysis of EPDM rubber mixture with non-treated basalt fiber

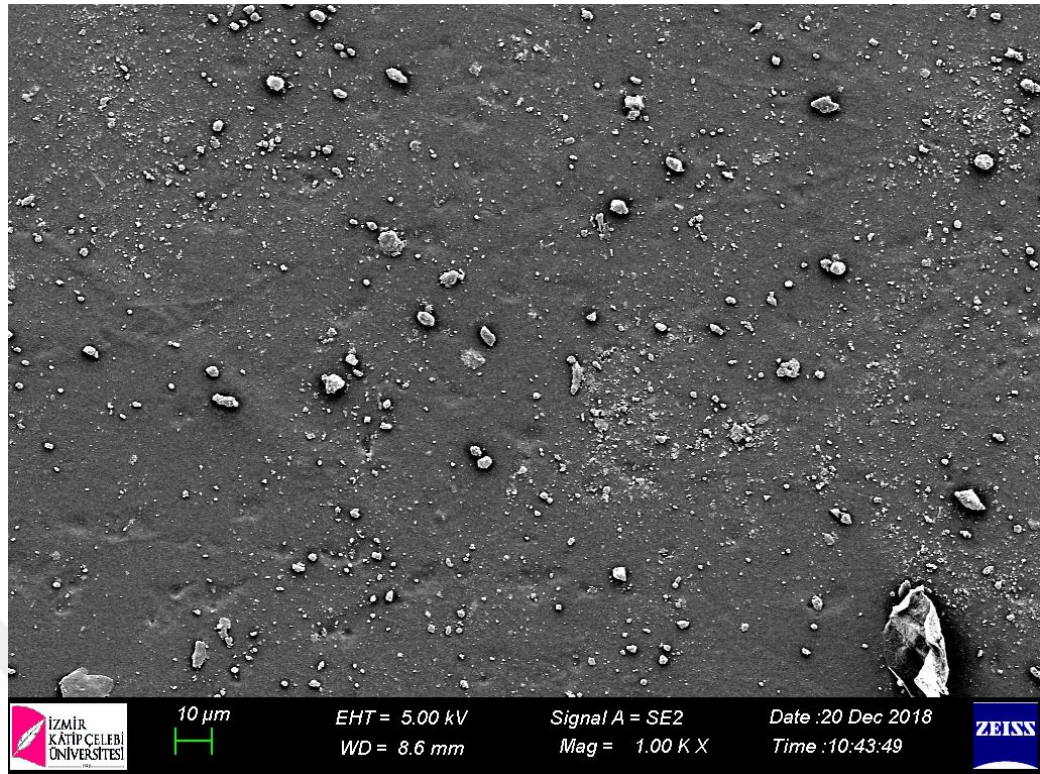


Figure 3.27: SEM analysis of EPDM rubber mixture with EPDM solution treated basalt fiber

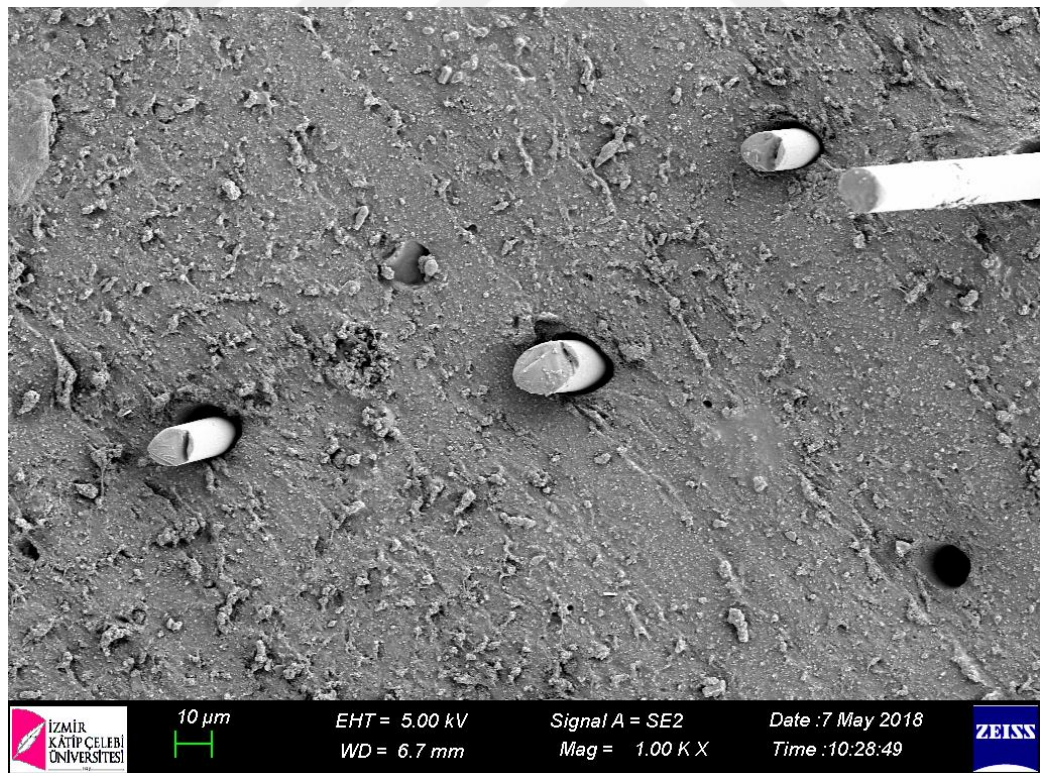


Figure 3.28: SEM analysis of EPDM rubber mixture with non-treated PA2 glass fiber

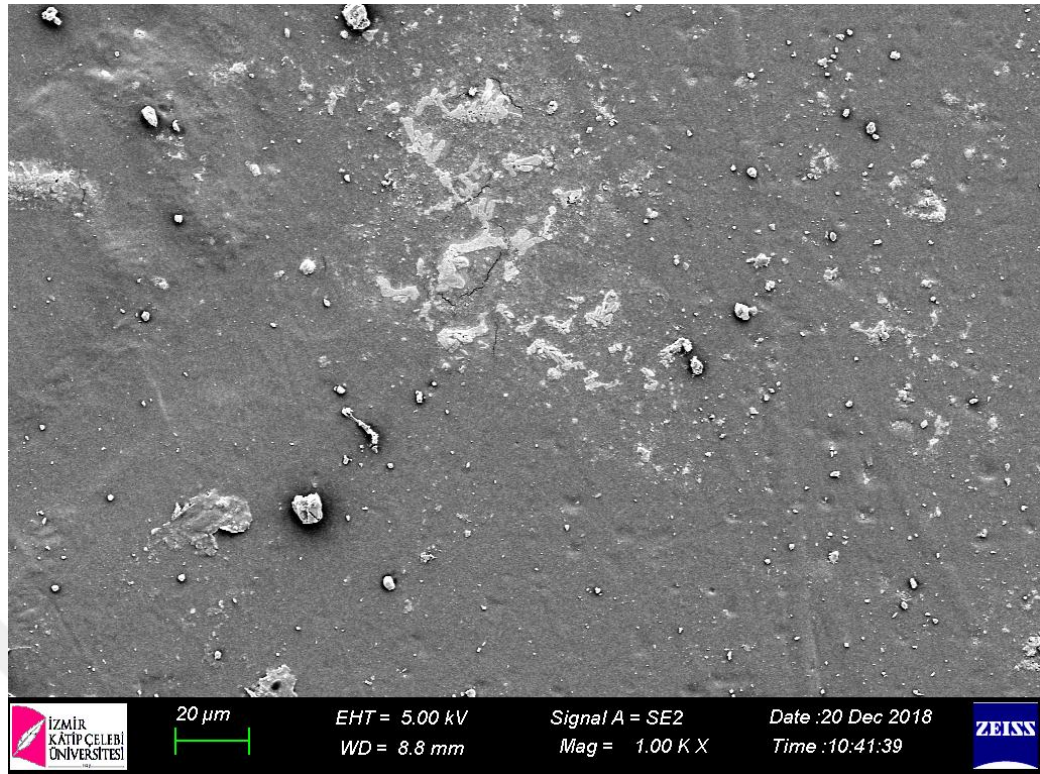


Figure 3.29: SEM analysis of EPDM rubber mixture with EPDM solution treated PA2 glass fiber



Figure 3.30: SEM analysis of EPDM rubber mixture with non-treated aramid fiber

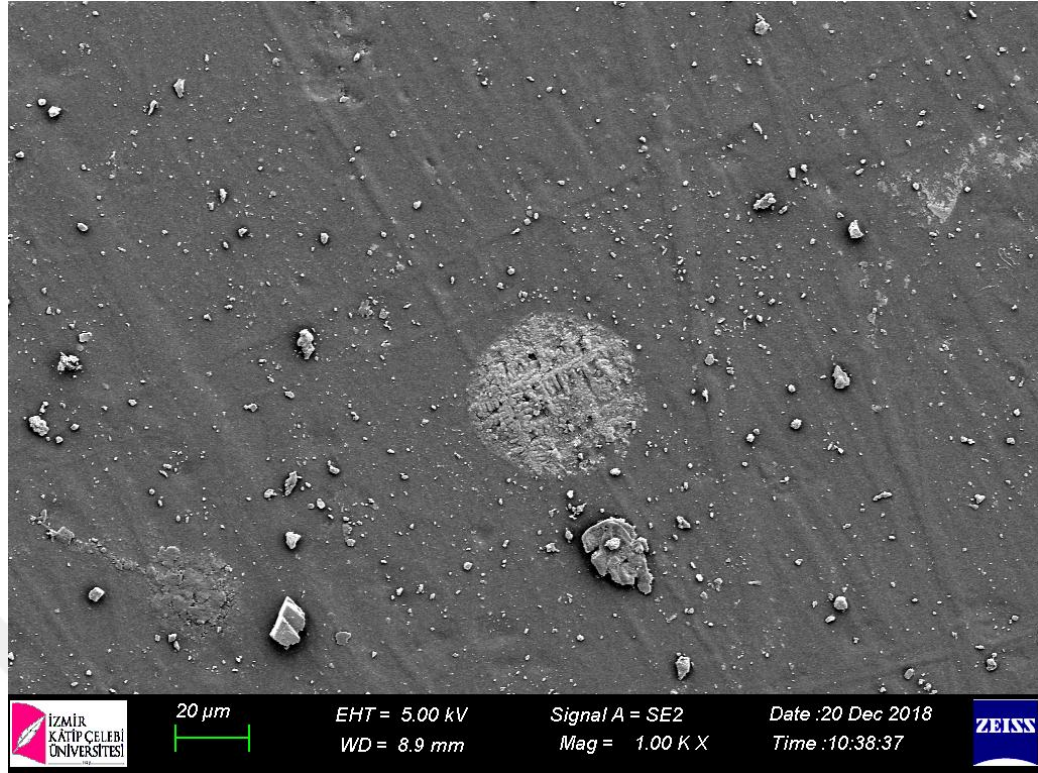


Figure 3.31: SEM analysis of EPDM rubber mixture with EPDM treated aramid fiber

Surface tension and contact angle is measured from EPDM rubber mixtures filled with fibers whose surfaces are treated with EPDM solution method at 5 PHR fiber ratio. The results are given in Figure 3.32. It is seen from the results that EPDM rubber mixtures with EPDM solution treated fibers give higher contact angles when compared to the mixtures with non- treated fibers. This also gives the idea that bonding quality of fibers inside the rubber mixture is better with EPDM solution treatment. However, any mixture cannot reach the result of reference mixture, it is seen obviously that treatment gives a positive effect for more successful compatibility.

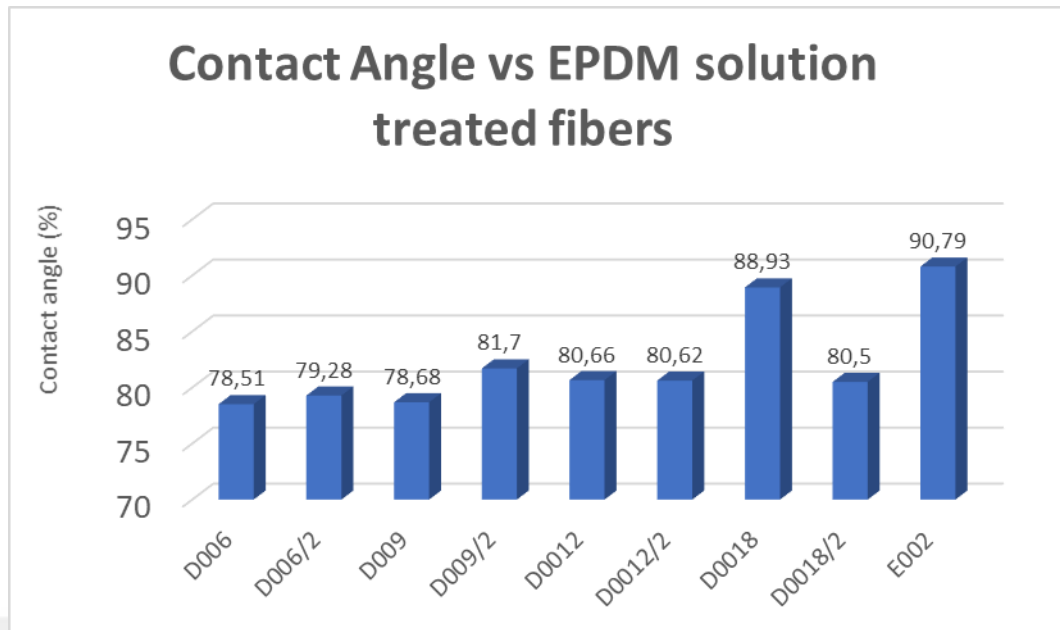


Figure 3.32: Contact angle vs EPDM solution treated fibers

Lastly Raman analysis is carried out from EPDM rubber mixture filled with carbon fiber which is treated with EPDM solution and exist at the mixture with 5 PHR. Images of Raman analysis are given in the figures as follows. In Raman analysis, carbon signals cover polymer signals. This is the handicap of raman analysis. Molecular connection of interface area do not seem very succesful. From figures, fiber orientation in rubber matrix is located both radially and axially. This is an expected situation, fibers will be oriented in extrusion.

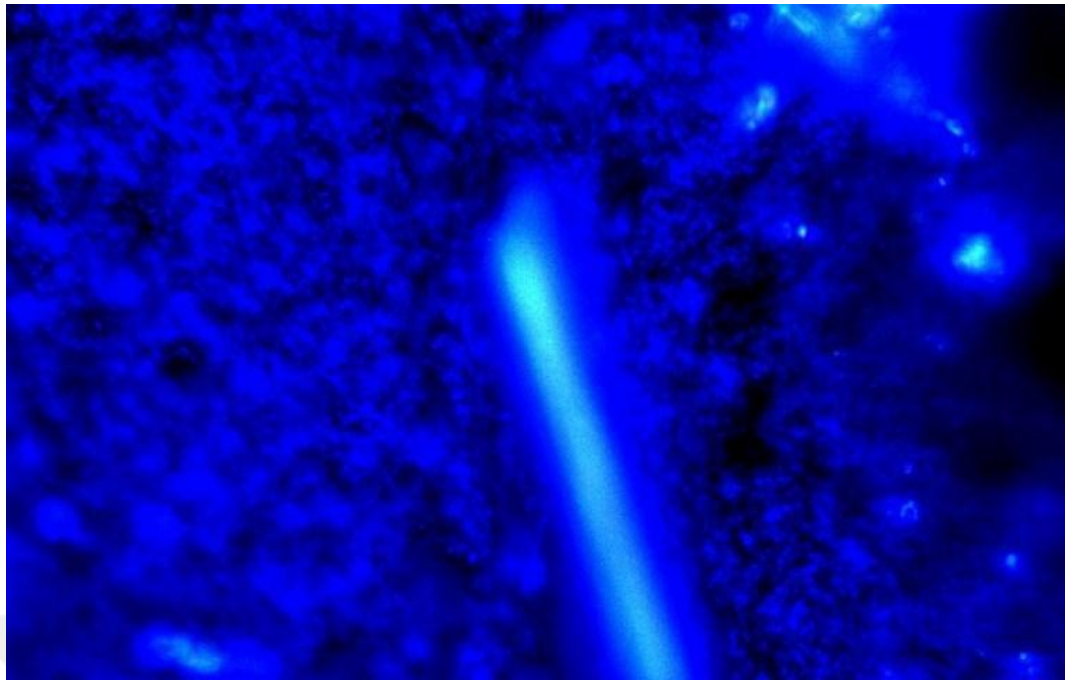


Figure 3.33: Bright light image of Sample under the 100x optic zoom

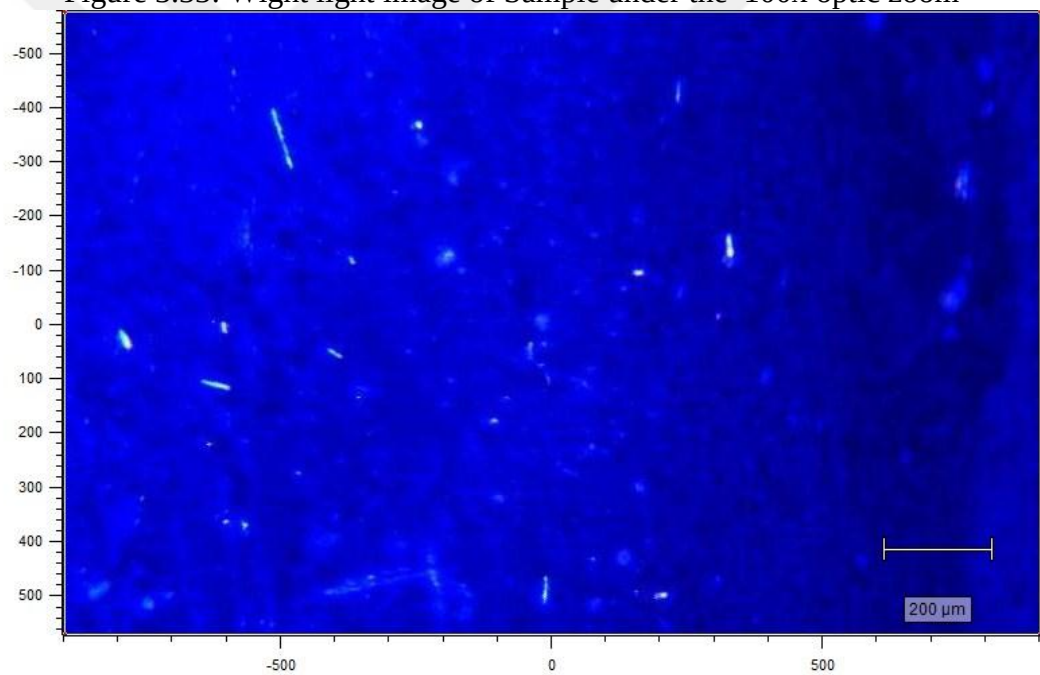


Figure 3.34: 5x optical magnification

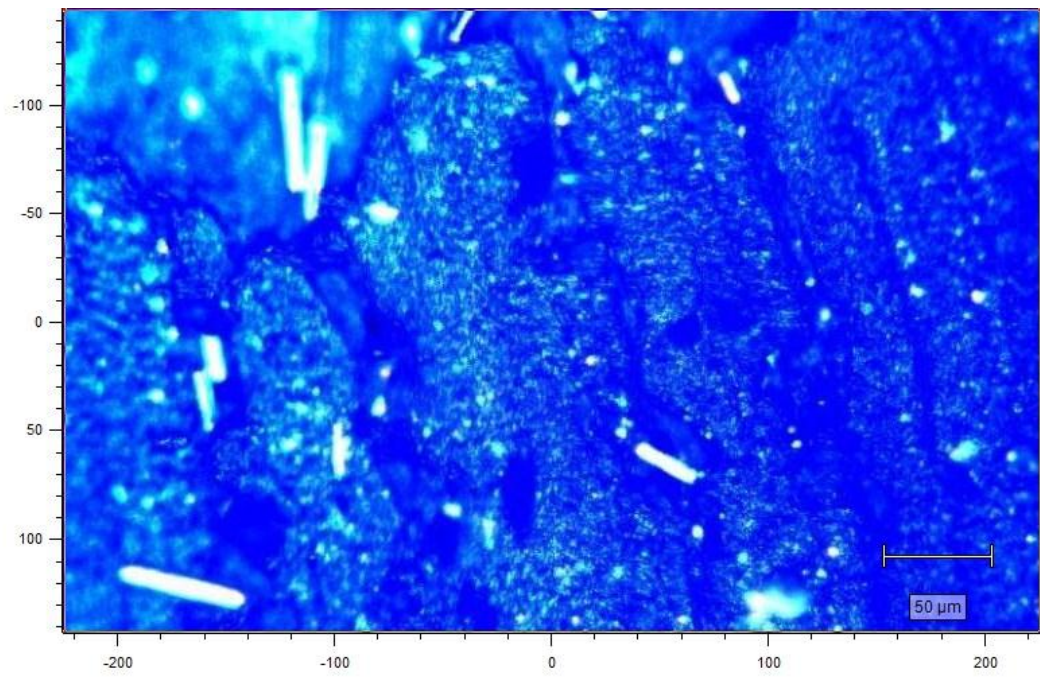


Figure 3.35: 20x optical magnification

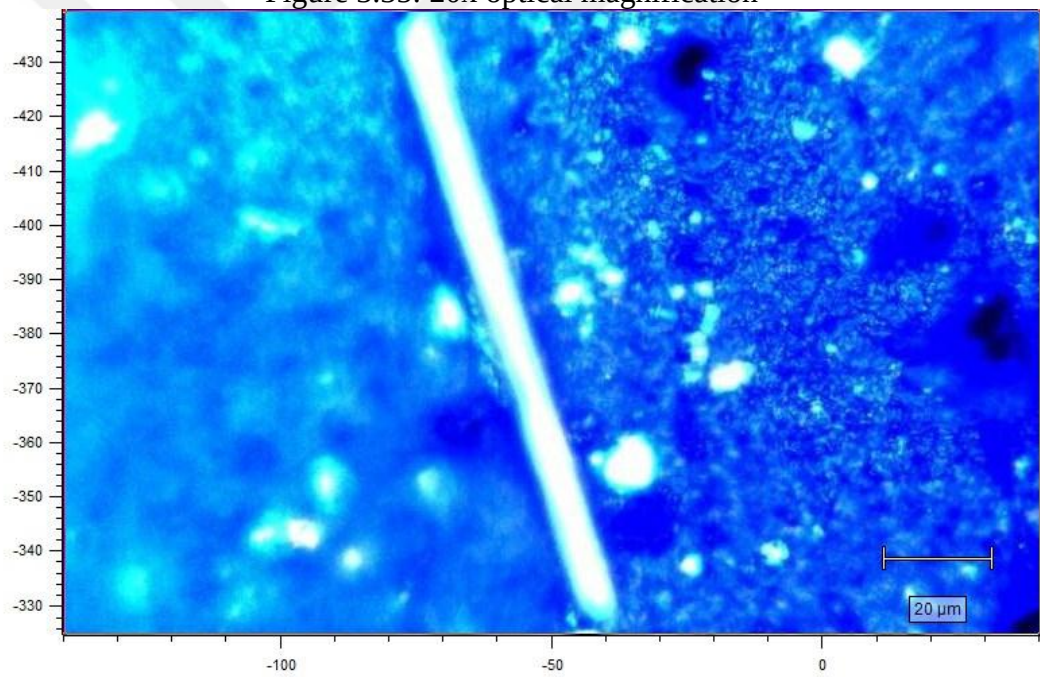


Figure 3.36: 50x optical magnification

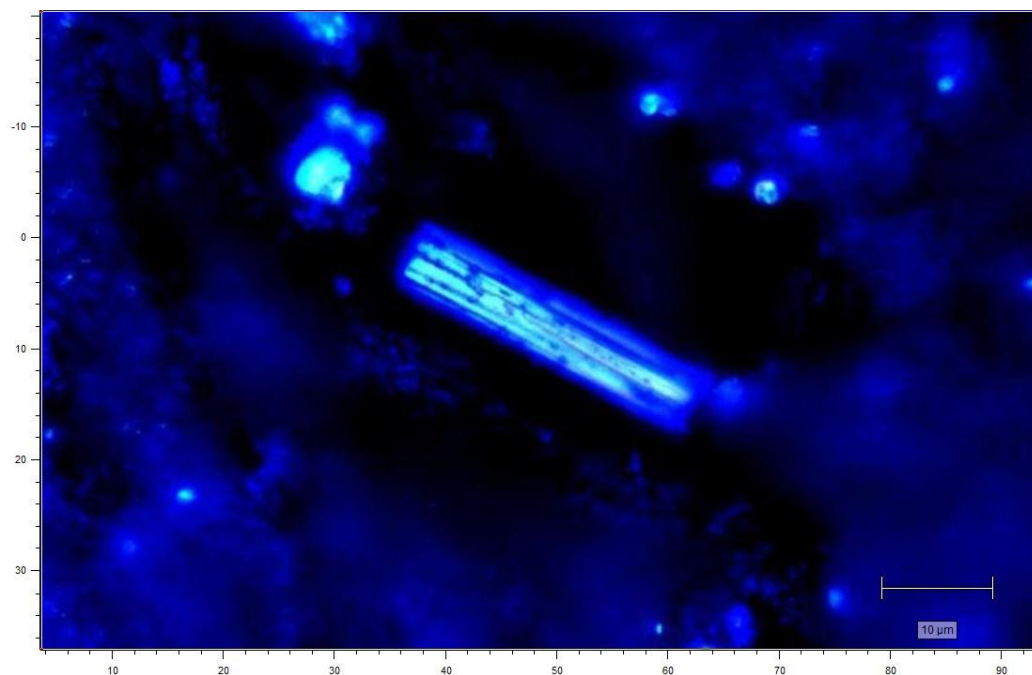


Figure 3.37: 100x optical magnification

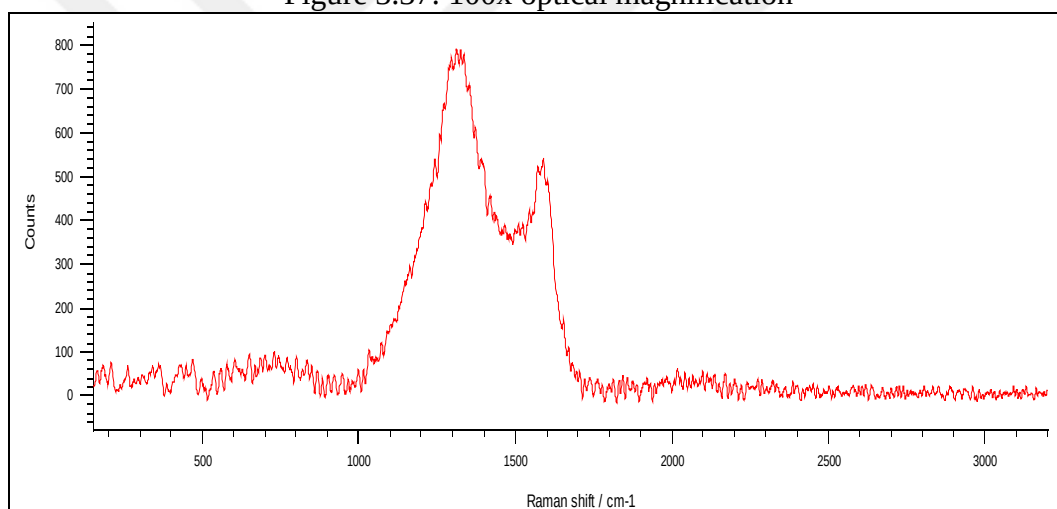


Figure 3.38: Polymer side of Raman spectrum between 150-3200 cm^{-1}

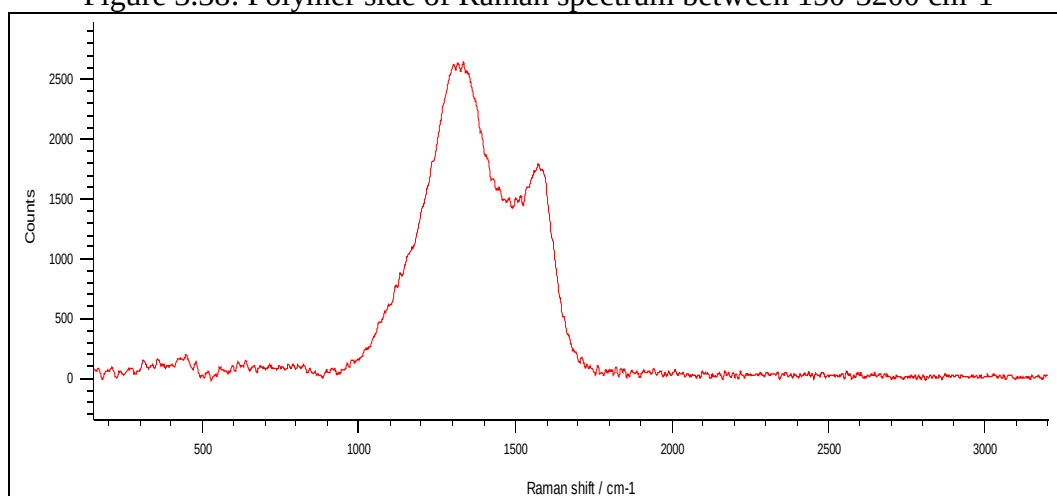


Figure 3.39: CF side of Raman spectrum between 150-3200 cm^{-1}

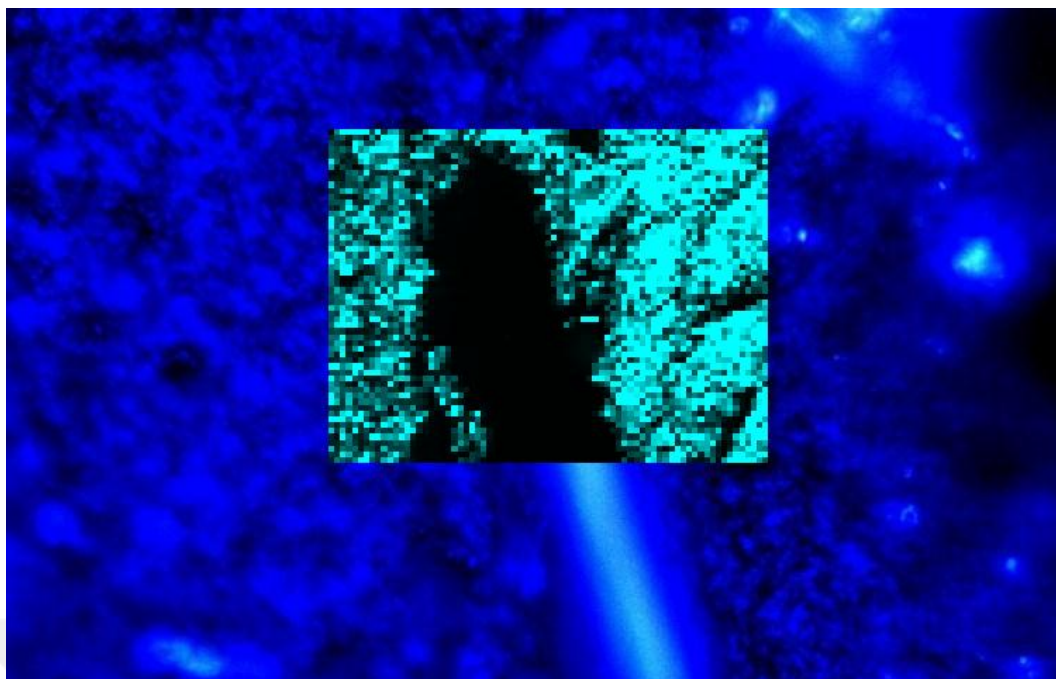


Figure 3.40: Signal to axis from 392-604 cm^{-1} (signals from polymer)

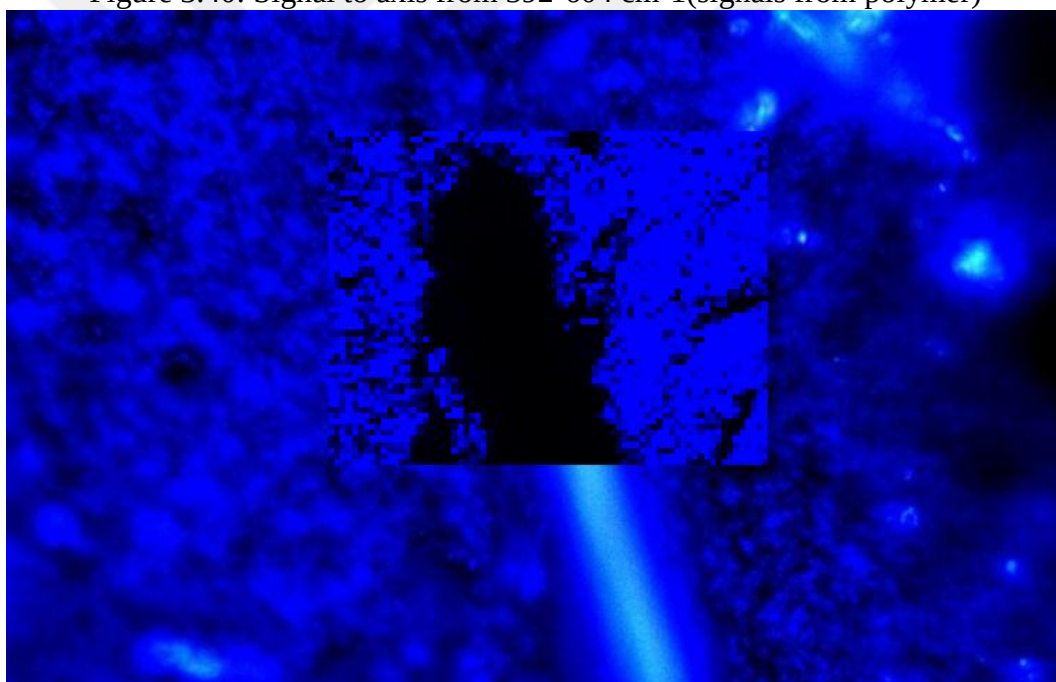


Figure 3.41: Intensity at point 987 cm^{-1} (Unknown Peak)

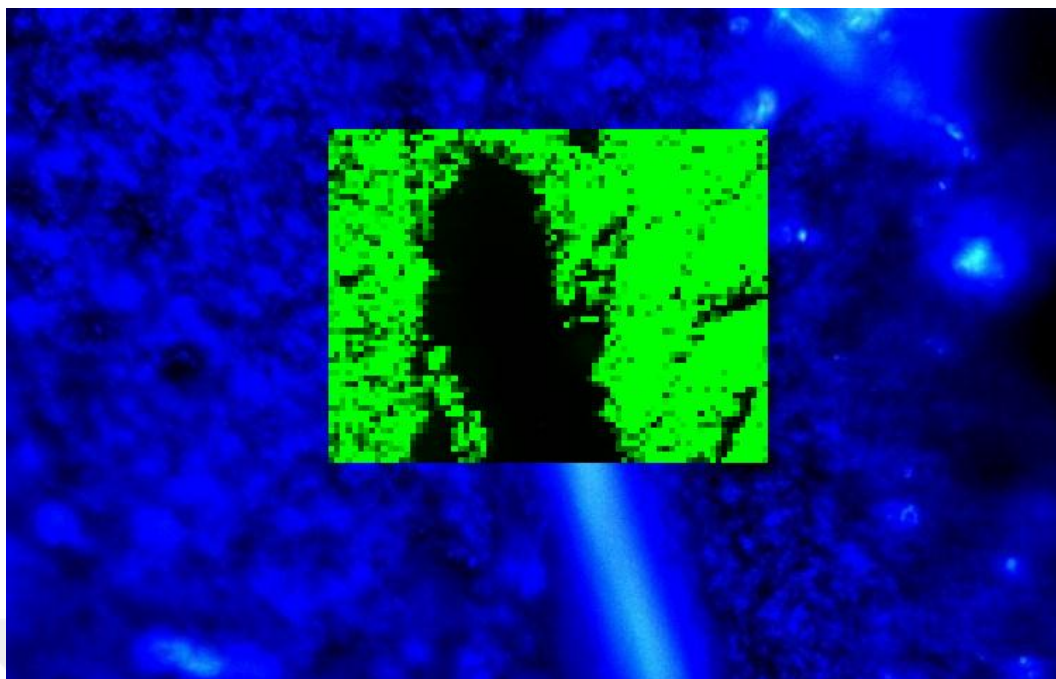


Figure 3.42: Signal to axis from 1198-1449 cm^{-1} (carbon fiber)

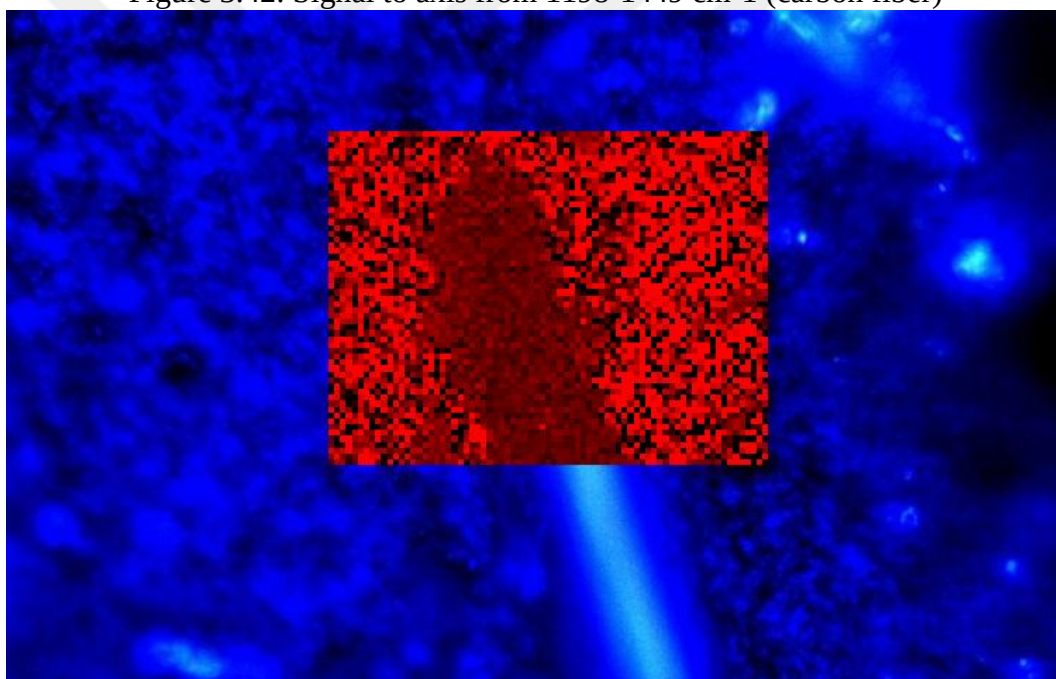


Figure 3.43: Signal to baseline 1181-1447 (CF Raman Peaks) (coming from rubber mixture or carbon fiber, carbon fiber area)

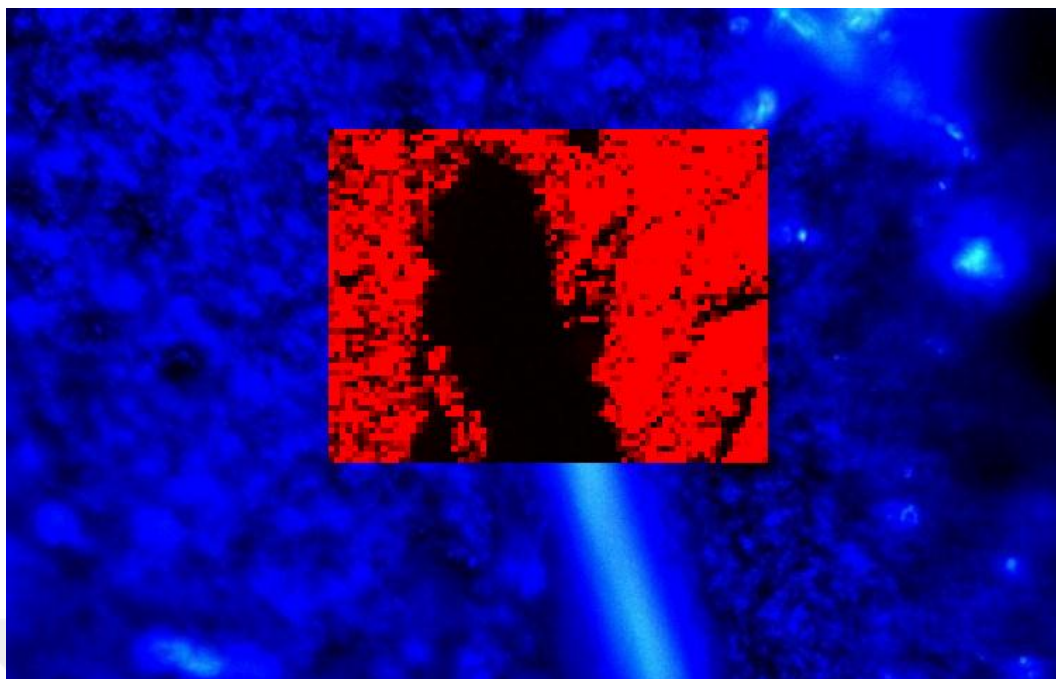


Figure 3.44: Intensity at point 897 cm⁻¹ (Unknown Peak)

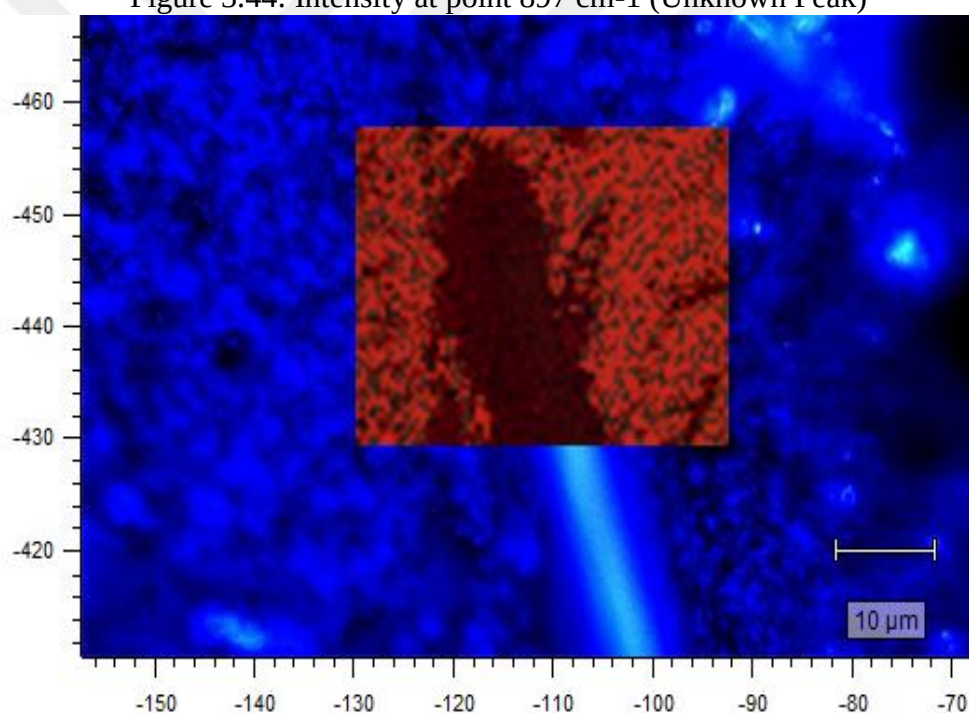


Figure 3.45: Combination of 5 different parts of Raman spectrum

When all the results including rheological tests, initial physico-mechanical tests, ageing tests, SEM analysis, contact angle measurements, Raman analysis are taken into consideration for different kind of treated fiber filled EPDM rubber mixtures, it is seen obviously that treatment of fibers improved properties of blends. Especially treatment brought a better surface bonding of fibers inside the rubber matrix, more homogenous and well dispersed mixture as well improved interface. In studies of

basalt and PA2 glass fiber, fluctuations in the results are seen. They are selected to be studied in more details in the next section. Further surface treatments will be carried out with these fiber types.

3.3 Test Results According to Further Surface Treatments of Basalt and PA2 Glass fibers

3.3.1 Rheometer Test Results According to Further Surface Treatments of Basalt and PA2 Glass fibers

The further surface treatments of fibers are selected by evaluating the results of EPDM rubber mixtures that are filled with fibers with different surface treatment methods. It is decided to continue studies with basalt fiber and PA2 glass fiber because of some fluctuating results that they have. Also, basalt fiber would be a good option to bring the EPDM rubber mixture some improved characteristics like hot air resistance, mechanical properties and acoustic properties. Although 8 type of surface treatments are applied to PA2 glass fiber, including both oven and hot water processed for bare type, alkali treated type, EPDM solution treated type and hybrid treated type, only 5 of them are used in EPDM rubber mixtures. In this part of the study the EPDM rubber mixtures that are prepared with further surface treatment methods of basalt and PA2 glass fiber at 5 PHR ratio are mentioned in the Table 3.11 as follows.

Table 3.11: Formulations according to further surface treatments of basalt and PA2 glass fiber

Formulation Code	Fiber Type	Fiber Ratio (PHR)	Surface Treatment Method
D009/5	Basalt	5	Silane
D009/6	Basalt	5	NaOH (%2)
D009/7	Basalt	5	NaOH (%2)+ Silane (hybrid)
D012-1	PA2 Glass	5	Bare type, processed in oven
D012/2-1	PA2 Glass	5	Bare type, alkali treated, processed in oven
D012/2-2	PA2 Glass	5	Bare type, alkali treated, processed in hot water
D012/3-1	PA2 Glass	5	Bare type, EPDM solution treated, processed in oven
D012/4-2	PA2 Glass	5	Bare type, alkali+EPDM solution treated, processed in oven

From the EPDM rubber mixtures rheometer tests are run, then physico- mechanical and ageing tests are carried out. From the surface treated fibers, SEM analysis, Raman analysis and FTIR analysis are made. Results are evaluated both according to the interactions between surface treated fibers with polymer matrix and requirements of SAE J20 Class E.

Rheometer test results are given in Table 3.12. To be able to compare the further surface treatments of basalt and PA2 glass fiber with the non-treated form of fibers, the results of non-treated fibers are also shown in the table.

Table 3.12: Rheometer test results of basalt and PA2 glass fiber filled EPDM rubber mixtures

Formulation Code	Fiber/ Surface Treatment Method	ML (dNm)	MH (dNm)	Ts (min.)	T90 (min.)
D009	Basalt/ Non-treated	1,15	12,23	0,72	1,91
D009/5	Basalt/ Silane	0,98	12,03	0,71	1,79
D009/6	Basalt/ NaOH (%2)	1,03	12,76	0,73	1,77
D009/7	Basalt/ NaOH (%2)+ Silane (hybrid)	0,82	13,01	0,73	1,8
D0012	PA2 Glass/ Non-treated	1,26	12,99	0,73	1,81
D012-1	PA2 Glass/ Bare type, processed in oven	1,11	13,68	0,75	2,05
D012/2-1	PA2 Glass/ Bare type, alkali treated, processed in oven	1,17	12,76	0,74	1,91
D012/2-2	PA2 Glass/ Bare type, alkali treated, processed in hot water	1,18	12,52	0,77	1,97
D012/3-1	PA2 Glass/ Bare type, EPDM solution treated, processed in oven	1,12	12,52	0,77	2,05
D012/4-2	PA2 Glass/ Bare type, alkali+EPDM solution treated, processed in oven	1,18	12,82	0,73	1,93

Minimum torque (ML) and maximum torque (MH) values related with the further surface treatment methods of basalt and PA2 glass fibers at 5 phr fiber ratio can be seen from Figure 3.46. When ML values for basalt fiber and PA2 glass fiber studies are observed, it is seen that all of further treatments gave lower results which indicates easier flow properties and lower energy consumption in different process conditions like mixing, extrusion, molding etc. and better dispersed compounds. %2 NaOH and silane modified basalt fiber (hybrid fiber), D009/7 and bare PA2 glass fiber processed in oven, D012-1 gives the lowest ML values when compared to other trials. When MH values of EPDM rubber mixtures filled with basalt fibers and PA2

glass fibers are observed, it is seen that highest cross-linking density with the highest MH value belongs to %2 NaOH and silane modified basalt fiber (hybrid fiber), D009/7 among basalt fiber trials and bare PA2 glass fiber processed in oven, D012-1 among PA2 glass fiber trials respectively.

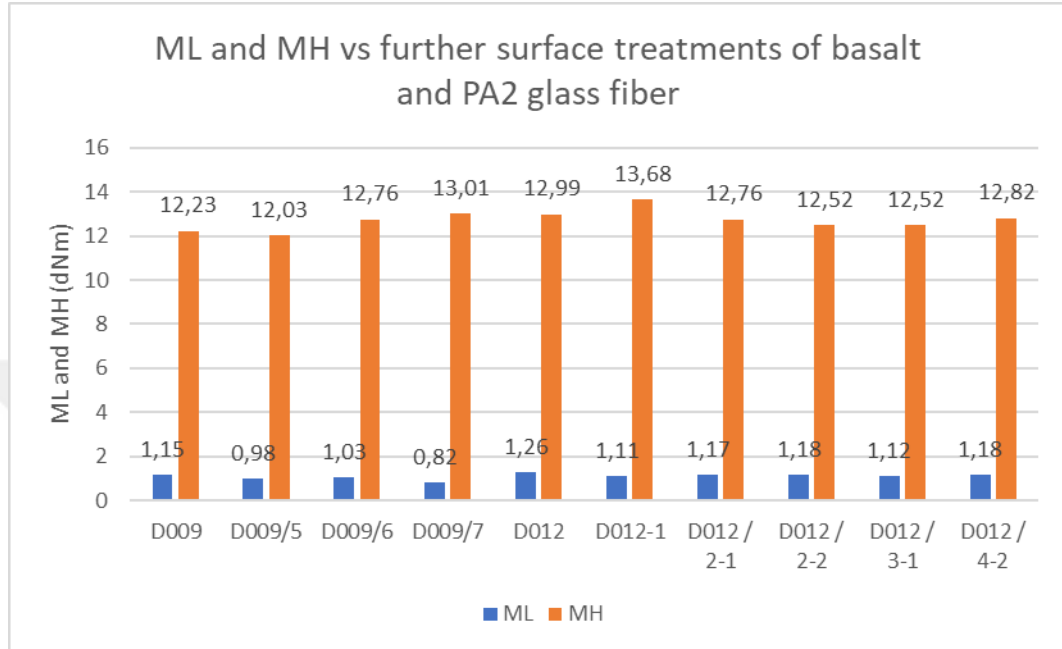


Figure 3.46: ML and MH vs further surface treatments of basalt and PA2 glass fiber

Scorch time, ts2 and t90 results due to the further treatments of basalt fiber and PA2 glass fiber in the usage ratio of 5 PHR are given in Figure 3.47. When scorch time, ts2 of basalt fiber results are observed, it is seen that all of the EPDM rubber mixtures nearly have the similar ts2 values. For ts2 values of PA2 glass fiber trials, it is observed that similar to basalt fiber finding, all of the EPDM rubber mixtures have similar ts2 results. When t90 values are investigated for basalt fiber studies, further treatment method of basalt fibers gave very close results among each other but a bit lower than the non-treated form of basalt fiber. This points out that curing time of further treated basalt fibers is faster than the non- treated basalt fiber. This shows that surface treatment of basalt fibers do not have an opposite effect on curing time. Surface treated basalt fibers form an uniform structure in the rubber mixture they are blended in by giving faster curing properties. When PA2 glass fiber studies are observed it is seen that further surface treatments increased curing time, t90 value when compared to non-treated PA2 glass fiber. The increase in curing time of further surface treated PA 2 glass fiber shows that the chemicals used to modify the fibers

shows a counter effect on the curing properties of the EPDM rubber mixture by retarding curing operation.

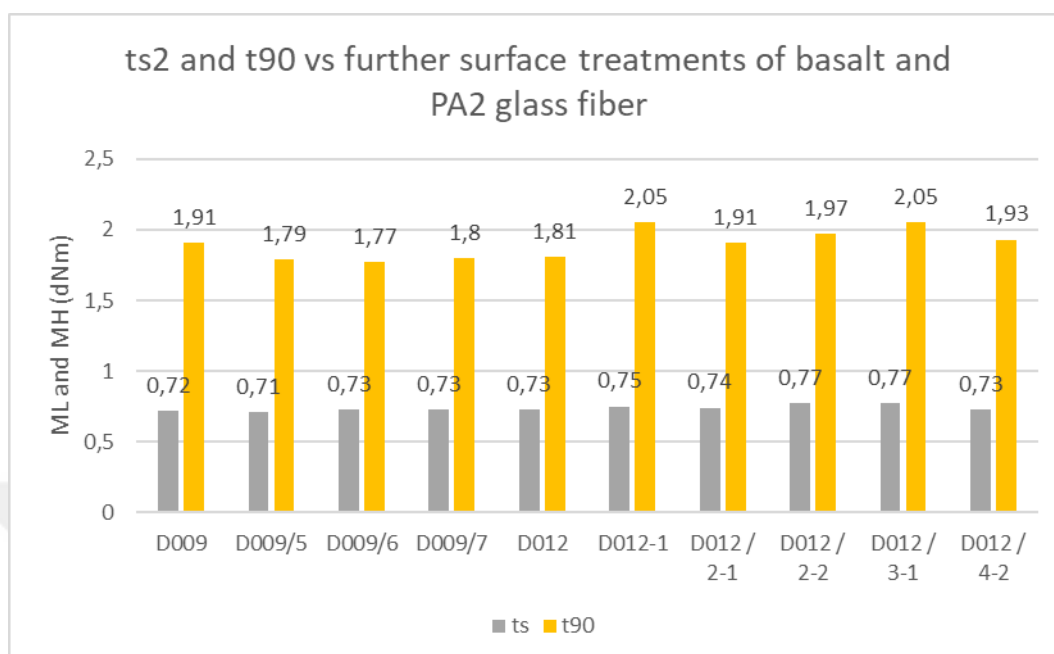


Figure 3.47: ts and t90 vs further surface treatments of basalt and PA2 glass fiber

3.3.2 Physico- mechanical and Ageing Test Results According to Further Surface Treatments of Basalt and PA2 Glass fibers

Hardness test results at initial state, after hot air ageing and coolant ageing are given in Table 3.13. Effect of further surface modification methods of basalt and PA2 glass fibers at 5 PHR usage ratio on hardness properties before and after ageing is studied.

Table 3.13: Hardness of basalt and PA2 glass fiber filled EPDM rubber mixtures

Formulation Code	Fiber/ Surface Treatment Method	Hardness Initial (ShoreA)	Hardness After Hot Air Ageing (ShoreA)	Hardness After Coolant Ageing (ShoreA)
SAE J20 E	-	65-75	+15	±10
D009	Basalt/ Non- treated	71	6	2
D009/5	Basalt/ Silane	70	10	10
D009/6	Basalt/ NaOH (%2)	70	9	9
D009/7	Basalt/ NaOH (%2)+ Silane (hybrid)	71	10	10
D0012	PA2 Glass/ Non-treated	72	7	7
D012-1	PA2 Glass/ Bare type, processed in oven	69	8	8
D012/2-1	PA2 Glass/ Bare type, alkali treated, processed in oven	66	10	10
D012/2-2	PA2 Glass/ Bare type, alkali treated, processed in hot water	68	9	9
D012/3-1	PA2 Glass/ Bare type, EPDM solution treated, processed in oven	68	9	9
D012/4-2	PA2 Glass/ Bare type, alkali+EPDM solution treated, processed in oven	68	9	9

Initial hardness results for further surface treatments of basalt and PA2 glass fibers can be seen clearly from Figure 3.48. When basalt fiber results are observed, it is understood that further surface modifications do not create difference in hardness

values. Hardness results are very similar to each other. For PA2 glass fiber study, it is observed that all further treated fibers led to hardness decrease when compared to non-treated fiber which means a better dispersion and more homogenous compound. Fiber surfaces become more suitable to be used in rubber mixture by the treatment that is applied to them.

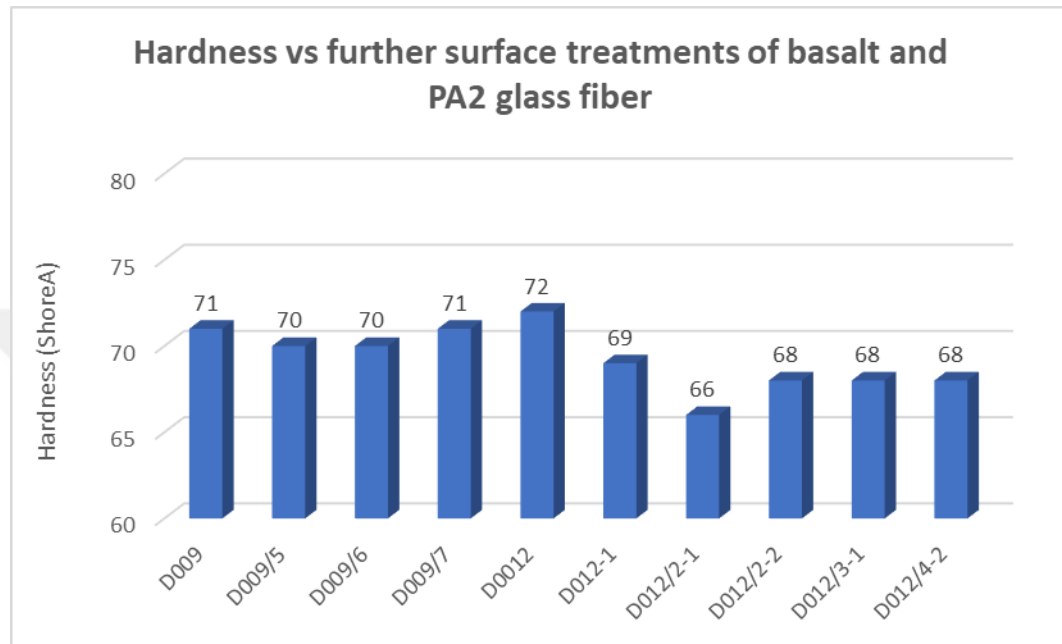


Figure 3.48: Hardness vs further surface treatments of basalt and PA2 glass fiber

Hardness change after hot air ageing and coolant ageing due to the effect of further surface modification methods of basalt and PA2 glass fibers can be seen clearly from Figure 3.49. Firstly, hardness change after hot air ageing is investigated. When basalt fiber results are examined, it is seen that hardness change is increased for all the trials. For PA2 glass fiber trials, it is observed that hardness change also increases. If the results are evaluated according to SAE J20 Class E demands, it can be said that all the mixtures can satisfy the specification in terms of hardness change after hot air ageing. Secondly, hardness change after coolant ageing is examined. When basalt and PA2 glass fiber results are observed, it is seen that hardness change after coolant ageing increases for all the further surface treatment methods of basalt and PA2 glass fiber. But the change is a slight change for PA2 glass fiber. When the results are evaluated by considering the requirements of SAE J20 Class E, it is seen that all the results are within the limits of specification.

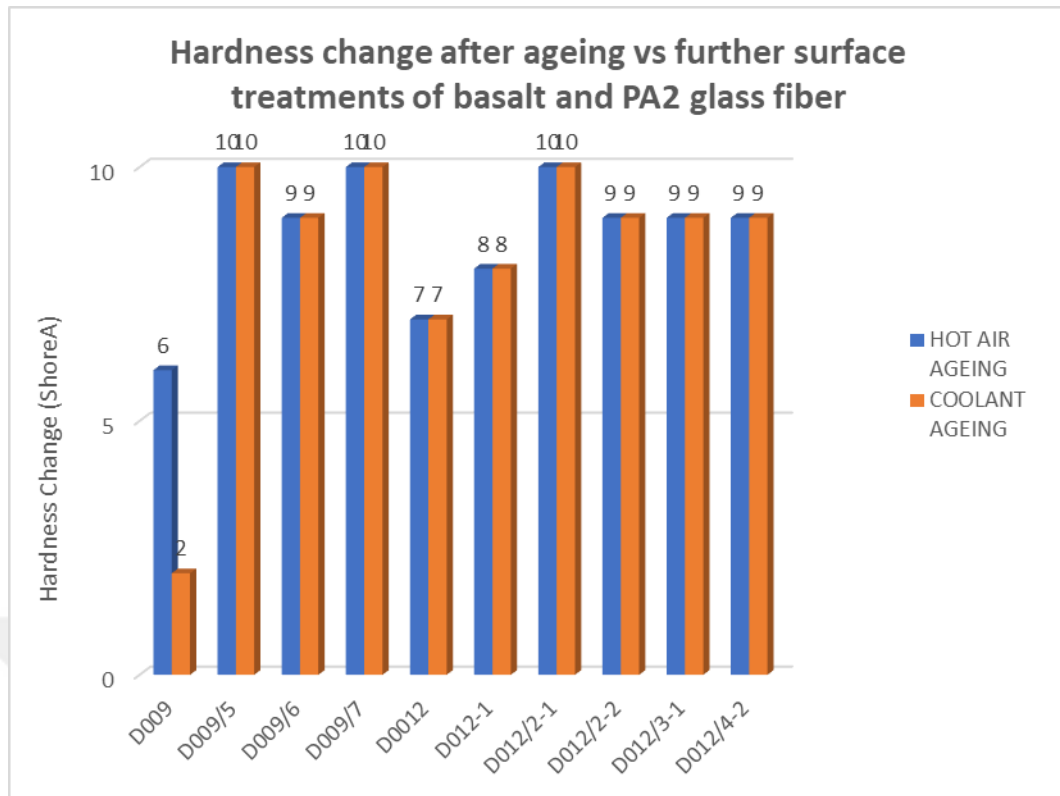


Figure 3.49: Hardness change after ageing vs further surface treatments of basalt and PA2 glass fiber

Tensile strength test results at initial state, after hot air ageing and coolant ageing are given in Table 3.14. Effect of further surface modification methods of basalt and PA2 glass fibers at 5 PHR usage ratio on tensile strength properties before and after ageing is studied.

Table 3.14: Tensile strength of basalt and PA2 glass fiber filled EPDM rubber mixtures

Formulation Code	Surface Treatment Method	Tensile Strength, Initial (Mpa)	Tensile Strength Change After Hot Air Ageing (%)	Tensile Strength Change After Coolant Ageing (%)
SAE J20 E	-	min. 5	max. -20	max. -20
D009	Basalt/ Non-treated	10,61	6,48	-0,75
D009/5	Basalt/ Silane	11,54	16,74	7,25
D009/6	Basalt/ NaOH (%2)	11,53	6,82	2,43
D009/7	Basalt/ NaOH (%2)+ Silane (hybrid)	11,59	8,44	2,54
D0012	PA2 Glass/ Non-treated	10,63	5,37	-3,20
D012-1	PA2 Glass/ Bare type, processed in oven	11,03	7,95	7,60
D012/2-1	PA2 Glass/ Bare type, alkali treated, processed in oven	11,59	-5,73	-7,64
D012/2-2	PA2 Glass/ Bare type, alkali treated, processed in hot water	11,39	-2,53	-7,07
D012/3-1	PA2 Glass/ Bare type, EPDM solution treated, processed in oven	11,11	0,68	-2,05
D012/4-2	PA2 Glass/ Bare type, alkali+EPDM solution treated, processed in oven	11,05	4,49	-2,38

Tensile strength results due to further surface treatment methods of basalt and PA2 glass fiber at 5 PHR ratio are seen from Figure 3.50. When basalt and PA2 glass fiber results are observed, it seen clearly that tensile strength at initial state increased with the effect of further surface treatments. Surface treatment led to an effect of better and more compatible surface structure of fibers by providing them to be used in EPDM rubber mixtures. The tensile strength value of basalt and PA2 glass fiber separately is higher than the tensile strength value of a rubber mixture hence the expected effect is the increase in tensile strength with the addition of fibers into the rubber mixture. When a successful bonding of fibers to the polymer structure is gained, improved tensile strength results and mechanical properties are held. When the results are considered in terms of SAE J20 Class E specification, it is seen obviously that all trials can catch the minimum tensile strength limit which is 5 MPa very easily.

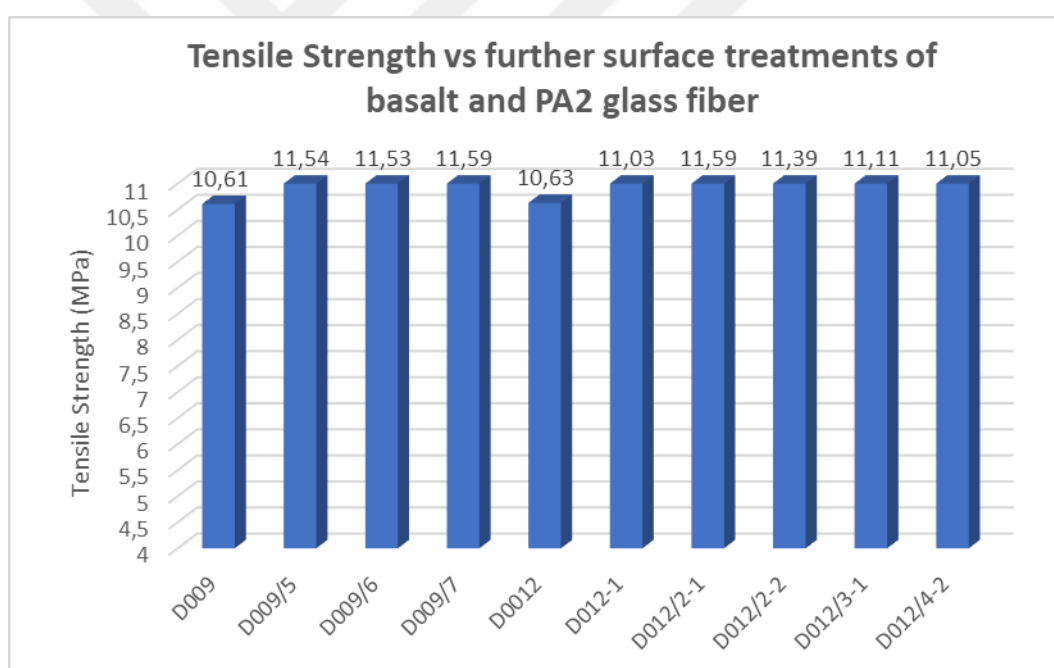


Figure 3.50: Tensile strength vs further surface treatments of basalt and PA2 glass fiber

Change in tensile strength after hot air and coolant ageing dependent on the further surface modifications of basalt and PA2 glass fiber can be evaluated from Figure 3.51. It is important to measure tensile strength after ageings because the rubber material can be deformed due to the medium its exposed to. The degree of deformation needs to be evaluated. Firstly, tensile strength change after hot air ageing is examined. When basalt fiber results are checked, it is seen that tensile

strength change remains constant for silane treated basalt fiber whereas there is an increase for NaOH (2%) treated and NaOH (2%)+ Silane (hybrid) treated basalt fibers. When the results of PA2 glass fiber are evaluated, it is understood that all the results show a decrease in tensile strength change except bare type, processed in oven. The increase shows that only processing the bare PA2 glass fiber in oven is not enough to have a fiber with good surface bonding properties to the polymer chain in the rubber matrix. For the requirements of SAE J20 Class E specification, it can be said that all the trials can meet the specification. Secondly, tensile strength change after coolant ageing is observed. When basalt fiber results are observed, it is seen that further surface treated fibers give a higher change in tensile strength when compared to non-treated fiber, however all the results can still satisfy SAE J20 Class E specification. For PA2 glass fiber trials, it is seen clearly from the Figure 3.51. That 3 mixtures have higher tensile strength change than the non-treated fiber including bare type- processed in oven, bare type- alkali treated- processed in oven, Bare type- alkali treated- processed in hot water. From these results it can be said that bare type PA2 glass fiber and alkali treatment processed both in oven and hot water do not lead the surface quality of fiber to improve. These operations do not form a better bonding property of fiber hence providing it to be well dispersed in rubber mixture. When the results are evaluated according to the requirements of SAE J20 Class E, it is seen clearly that all the trials can meet the specification.

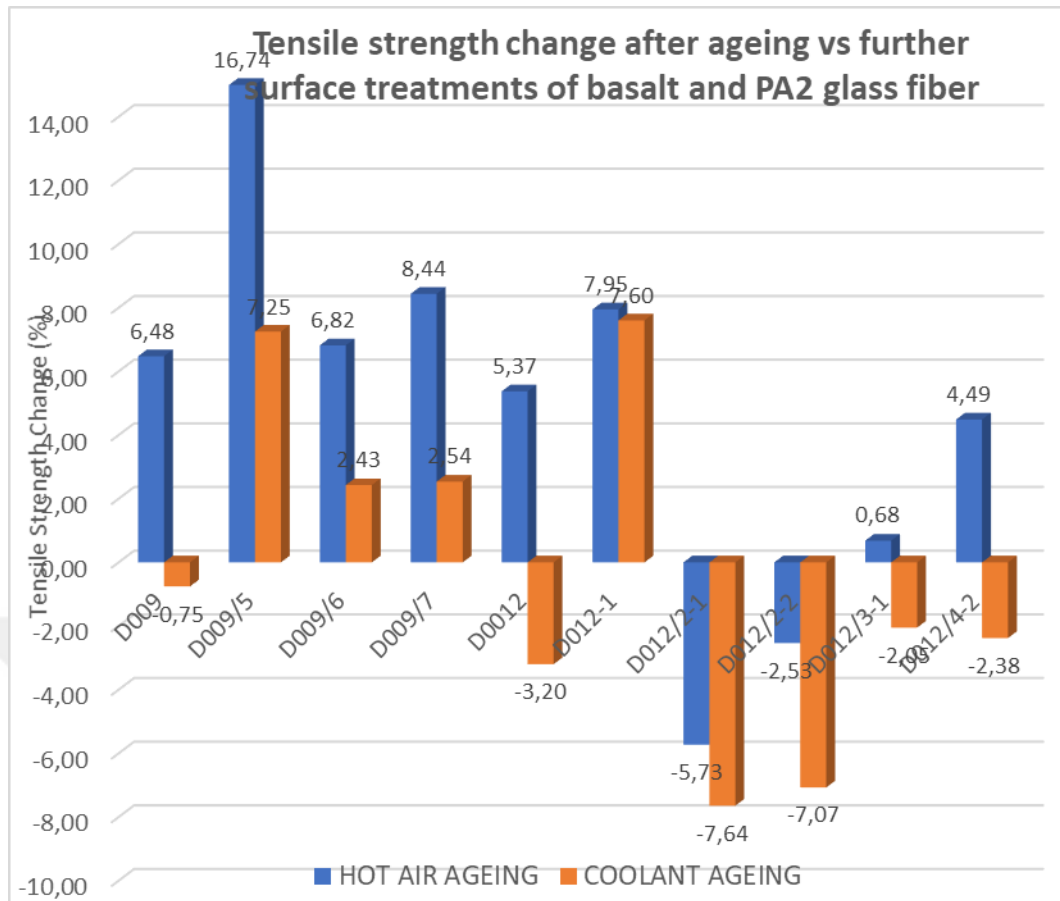


Figure 3.51: Tensile strength change after ageing vs further surface treatments of basalt and PA2 glass fiber

Elongation at break test results at initial state, after hot air ageing and coolant ageing are given in Table 3.15. Effect of further surface modification methods of basalt and PA2 glass fibers at 5 PHR fiber usage ratio on elongation at break properties before and after ageing is studied.

Table 3.15: Elongation at break of basalt and PA2 glass fiber filled EPDM rubber mixtures

Formulation Code	Surface Treatment Method	Elongation at break, Initial (Mpa)	Elongation at Break Change After Hot Air Ageing (%)	Elongation at Break Change After Coolant Ageing (%)
SAE J20 E	-	min. 100	max. -50	max. -25
D009	Basalt/ Non-treated	359,25	-46,78	-22,80
D009/5	Basalt/ Silane	324,50	-37,32	-9,78
D009/6	Basalt/ NaOH (%2)	379,86	-45,86	-21,99
D009/7	Basalt/ NaOH (%2)+ Silane (hybrid)	349,42	-43,98	-19,80
D0012	PA2 Glass/ Non-treated	353,9	-46,57	-16,8
D012-1	PA2 Glass/ Bare type, processed in oven	356,66	-39,40	-17,5
D012/2-1	PA2 Glass/ Bare type, alkali treated, processed in oven	390,49	-46,23	-26,9
D012/2-2	PA2 Glass/ Bare type, alkali treated, processed in hot water	390,49	-45,83	-24,5
D012/3-1	PA2 Glass/ Bare type, EPDM solution treated, processed in oven	386,70	-40,04	-23,8
D012/4-2	PA2 Glass/ Bare type, alkali+EPDM solution treated, processed in oven	413,62	-42,45	-32,6

Elongation at break results due to further surface treatment methods of basalt and PA2 glass fibers are seen from Figure 3.52. When basalt fiber results are examined, it is seen that there is a decrease at EAB in all trials except the EPDM rubber mixture filled with 5 PHR basalt fiber treated with NaOH (%2). For glass fiber trials, it is seen clearly that EAB increases with further surface treatments, especially there exists a significant improvement with bare type PA2 glass fiber, alkali + EPDM solution treated, processed in oven. The mixtures with higher EAB gives more elastic properties. When the results are evaluated according to SAE J20 Class E, all the trials can pass the limit of minimum %100 elongation very easily.

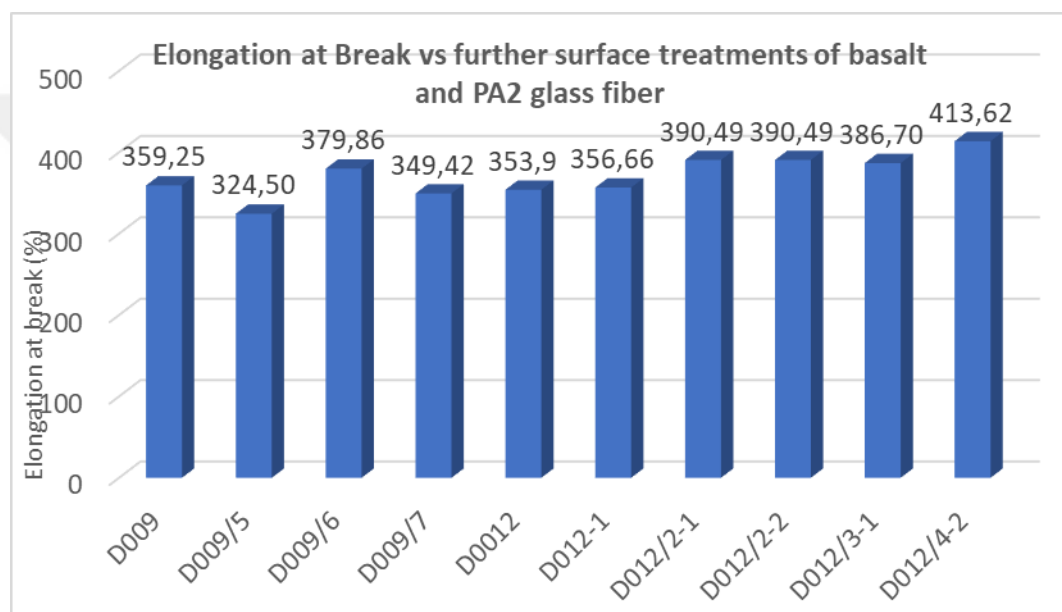


Figure 3.52: Elongation at break vs further surface treatments of basalt and PA2 glass fiber

Elongation at break change after hot air and coolant ageing due to further treatment methods of basalt and PA2 glass fiber are given in Figure 3.53. The rubber material should be still elastic after being exposed to hot air or coolant, and therefore its elasticity should be measured to see if it still will work without any problem on the medium it exists. Firstly, EAB change after hot air ageing results are evaluated. When basalt fiber trials are examined, it is seen that EAB change with further treatment methods of basalt fiber decreased. It points out a better adhesion of surface of fiber to the polymer chains. Rubber mixture remains more elastic when exposed to heat with less deformation when compared to non-treated fiber. For PA2 glass fiber trials, similar findings with basalt fiber are held. EAB change decrease for all kinds of surface treatments of PA2 glass fiber. On the other hand, according to the

requirements of SAE J20 Class E specification all the results meet the allowable limits of EAB change. Secondly EAB change after coolant ageing is investigated. When basalt fiber results are observed, EAB change tends to decrease with all further treatment methods. Most significant improvement is held by silane treatment, meaning that elastic properties are not affected by coolant exposure of rubber mixture. When PA2 glass fiber trials are examined, it is seen that EAB change increases. Elasticity is affected negatively with the effect of further surface treatment methods after coolant ageing. If the results are evaluated according to the demands of SAE J20 Class E, it is seen that even two of the trials, bare type PA2 glass fiber, alkali treated, processed in oven and bare type PA2 glass fiber, alkali+ EPDM solution treated, processed in oven can not meet the specification. The other results are suitable to the specification.

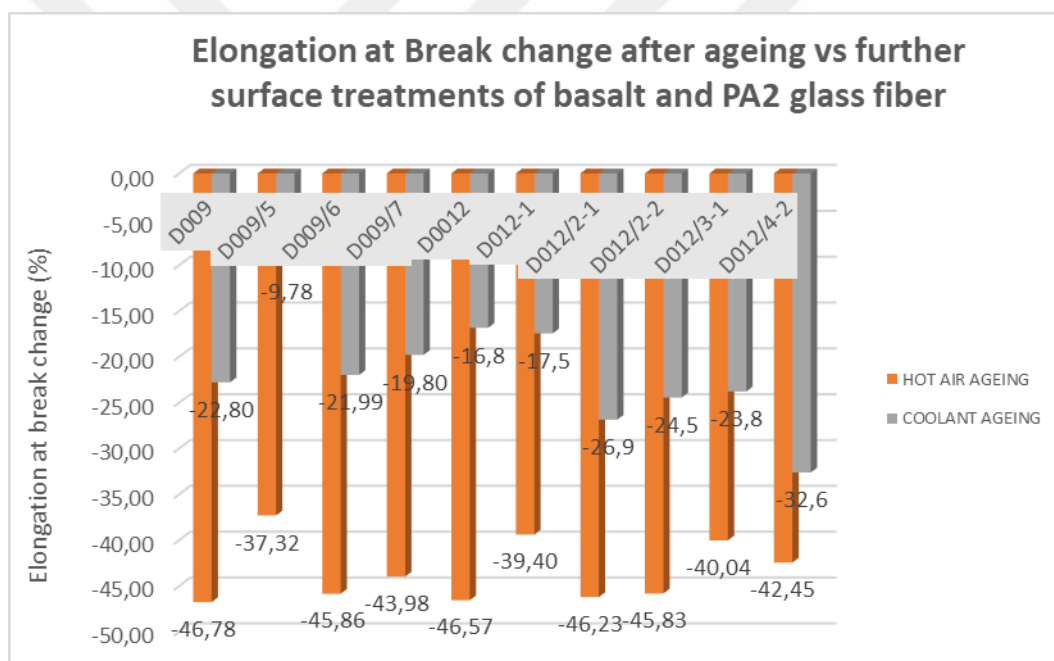


Figure 3.53: Elongation at break change after ageing vs different surface treatment methods

Volume change of EPDM rubber mixtures after coolant ageing due to the further surface treatment methods of basalt and PA2 glass fibers are listed in Table 3.16. The aim is to see the effect of further surface modification methods on the volume change results.

Table 3.16: Volume change after coolant ageing with further surface treatments of basalt and PA2 glass fiber

Formulation Code	Surface Treatment Method	Volume Change (%)
SAE J20 E	-	-5; +20
D009	Basalt/ Non- treated	0,1
D009/5	Basalt/ Silane	0,03
D009/6	Basalt/ NaOH (%2)	0,6
D009/7	Basalt/ NaOH (%2)+ Silane (hybrid)	0,13
D0012	PA2 Glass/ Non-treated	-0,4
D012-1	PA2 Glass/ Bare type, processed in oven	-0,13
D012/2-1	PA2 Glass/ Bare type, alkali treated, processed in oven	0,23
D012/2-2	PA2 Glass/ Bare type, alkali treated, processed in hot water	-0,10
D012/3-1	PA2 Glass/ Bare type, EPDM solution treated, processed in oven	-0,10
D012/4-2	PA2 Glass/ Bare type, alkali+EPDM solution treated, processed in oven	-0,23

The effect of coolant ageing on volume change of EPDM rubber mixture filled with 5 PHR basalt and PA2 glass fiber separately which have further surface treatments can be seen in Figure 3.54. When basalt fiber trials are examined, it is seen that only NaOH (%2) treated basalt fiber shows an increase in volume swell result. Silane treated basalt fiber has a significant decrease in terms of volume swell nearly to zero. It is clearly seen that surface modification of basalt fiber with silane increases resistance to coolant of EPDM rubber mixture, fibers are bonded to the polymer chains more strongly and effectively therefore it becomes difficult to break the chains with the effect of coolant. On the other hand, according to the requirements of SAE J20 Class E, all the results can meet allowable limits very easily. When results of PA2 glass fiber are checked, all further surface treatments give very good results and a decrease in volume swell is gained when compared to non- treated fiber.

Surface modifications are again successful similar to basalt trials in terms of volume swell in coolant. All the results meet the demands of SAE J20 Class E.

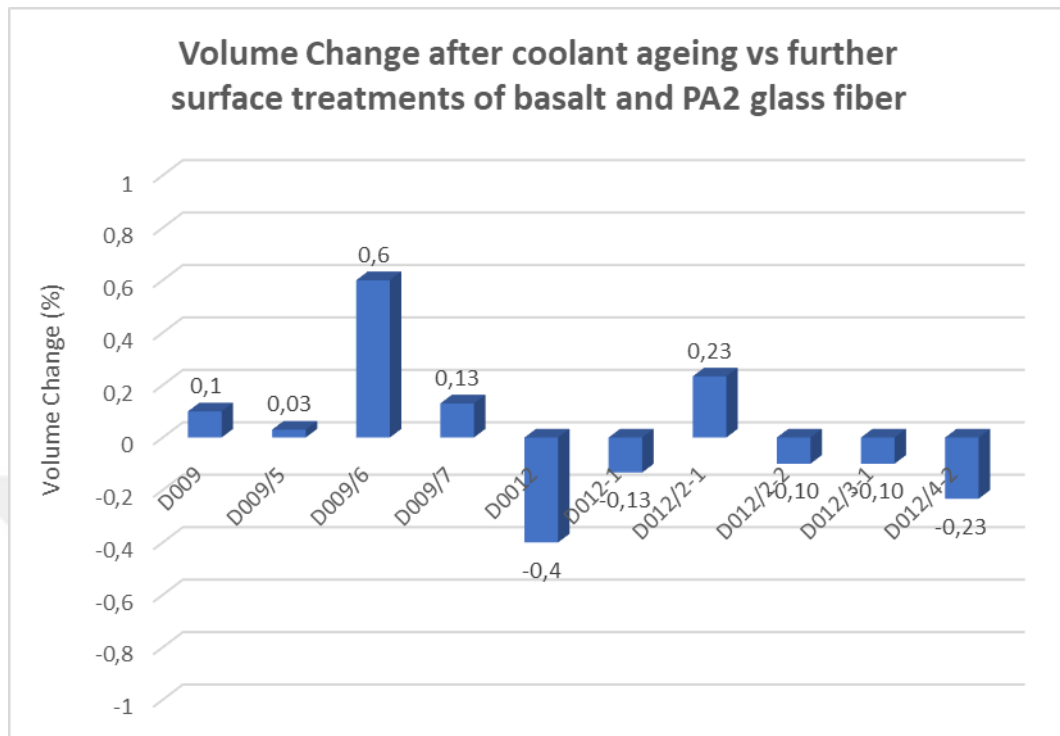


Figure 3.54: Volume change after coolant ageing vs further surface treatments of basalt and PA2 glass fiber

Tearing strength at the initial state is tested for EPDM rubber mixtures that are filled with basalt and PA2 glass fibers at 5 PHR ratio with further surface treatment methods. Results can be seen clearly from Figure 3.55. When basalt fiber trials are observed, it is understood that there is an improvement in tearing strength with further surface treatment methods except NaOH (%2)+ Silane (hybrid) trial although it is very close to the non- treated form of fiber. Increase in tear strength points out more powerful bonding of surface treated fibers to the polymer chains and more homogenous structure. When PA2 glass fiber trials are examined it is seen that further surface modifications of fibers kept tearing strength value similar to the result of non- treated fiber. It is also a good finding that tear strength is not affected negatively and remained nearly same. According to the requirements of SAE J20 Class E, all the trials can meet the specification very easily.

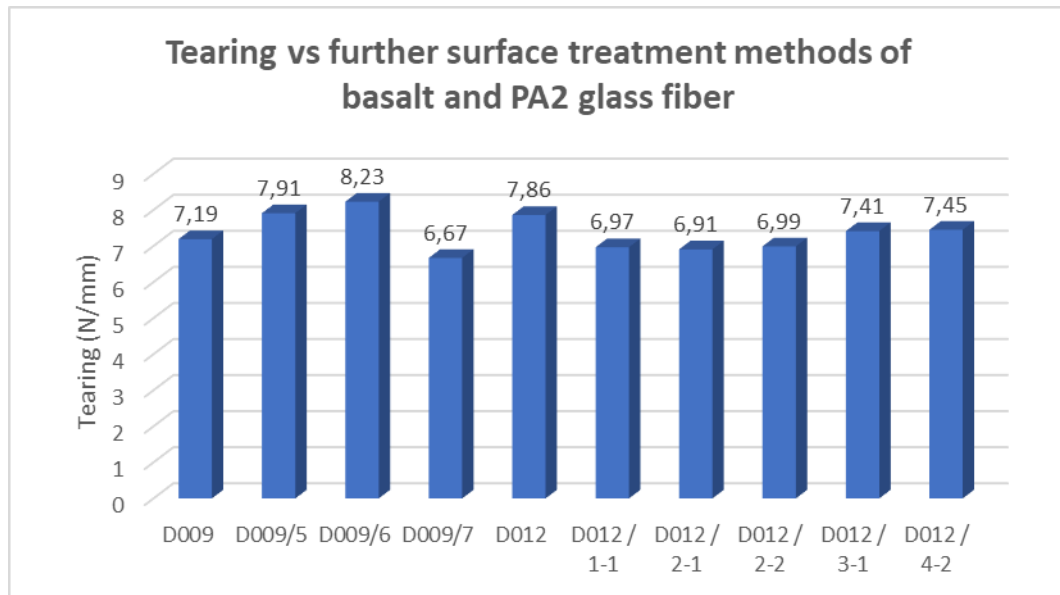


Figure 3.55: Tearing strength vs further surface treatment methods of basalt and PA2 glass fiber

Compression set test is run at the initial state from different EPDM rubber mixtures filled with basalt and PA2 glass fibers at 5 PHR ratio with further surface treatment methods. Results can be seen from Figure 3.56. Compression set test gives indication for the behaviour of rubber material when exposed to heat under a defined force and the ability of the material to recover when the force is removed. When basalt fiber trials are examined, it is seen clearly that further surface treatments of fibers improved compression set, especially eh method with NaOH (%2)+ Silane (hybrid) treatment. It gives the finding that hybrid treated fibers form a compatible structure with the rubber mixture hence improving the compression set property. When PA2 glass fiber trials are observed, a significant improvement is gained by bare type PA2 glass, alkali treated, processed in oven. The other trials also improved or kept compression set value at the same limit with the non-treated fiber except bare type PA2 glass, EPDM solution treated, processed in oven. On the other hand when all results are taken into consideration for SAE J20 Class E, it is understood that they all can meet the specification.

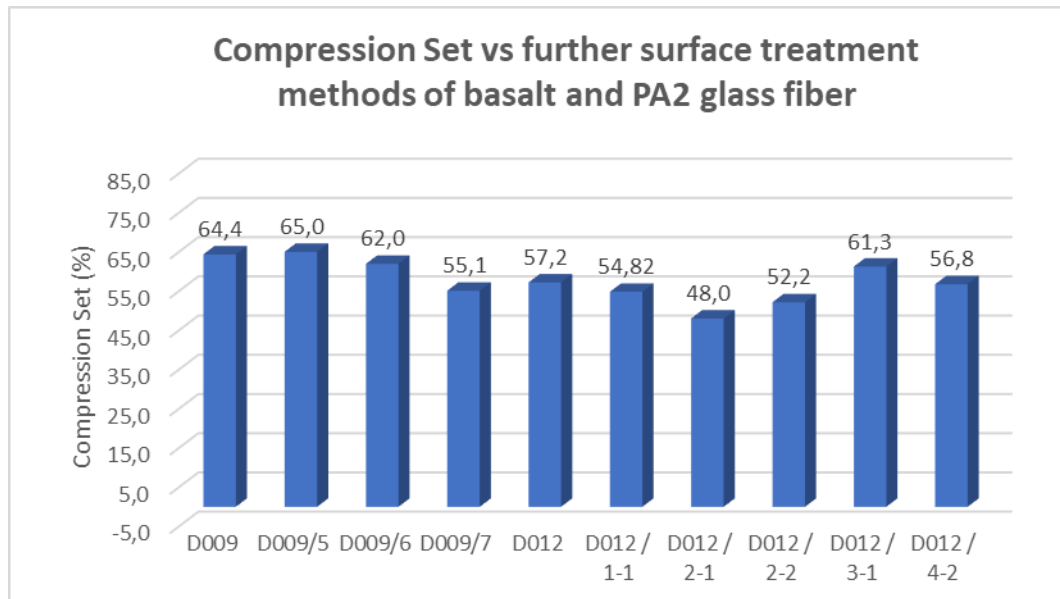


Figure 3.56: Compression set vs further surface treatment methods of basalt and PA2 glass fiber

After rheological, physico-mechanical and ageing tests are carried out from EPDM rubber mixtures filled with 5 phr basalt and PA2 glass fiber separately and treated with further surface treatment methods, some more structural tests are run. These are SEM analysis, Raman analysis and FTIR analysis. Structural tests are made from fibers, not from EPDM rubber mixtures. These tests give indication about bonding quality of fibers to the rubber mixture.

3.3.3 Surface Analysis Results According to Further Surface Treatments of Basalt and PA2 Glass fibers

SEM analysis are applied to basalt fibers and PA2 glass fibers. The type of fibers that undergo SEM analysis can be listed as follows.

Table 3.17: List of fibers that undergo SEM analysis

Formulation Code	Surface Treatment Method
D009/2	Basalt fiber NaOH (%10) treated
D009/6	Basalt fiber NaOH (%2) treated
D012	PA 2 glass fiber
D012/2	Alkali treated PA2 glass fiber
D012/3	EPDM solution treated PA2 glass fiber
D012/4	Alkali+EPDM solution treated (hybrid) glass fiber
D012-1	Bare PA2 glass fiber processed in oven
D012/ 2-1	Bare PA2 glass fiber alkali treated processed in oven
D012/ 3-1	Bare PA2 glass fiber EPDM solution treated processed in oven

When SEM images of basalt fiber are examined, it is seen that that %10 NaOH treated basalt fiber gave more damage to the fiber but %2 NaOH solution is less harmless. When SEM images of bare PA2 glass fiber and PA2 glass fiber under 1000X are examined, it is seen that NaOH and EPDM coating on silane PA2 glass fiber have more homogenous surface structure and better adhesion property when compared to bare PA2 glass fiber. Because after baring process polymer layer on the fiber was immigrated so that even NaOH and EPDM treatment did not help the fibers to adhere to the surface well and form a good structure.

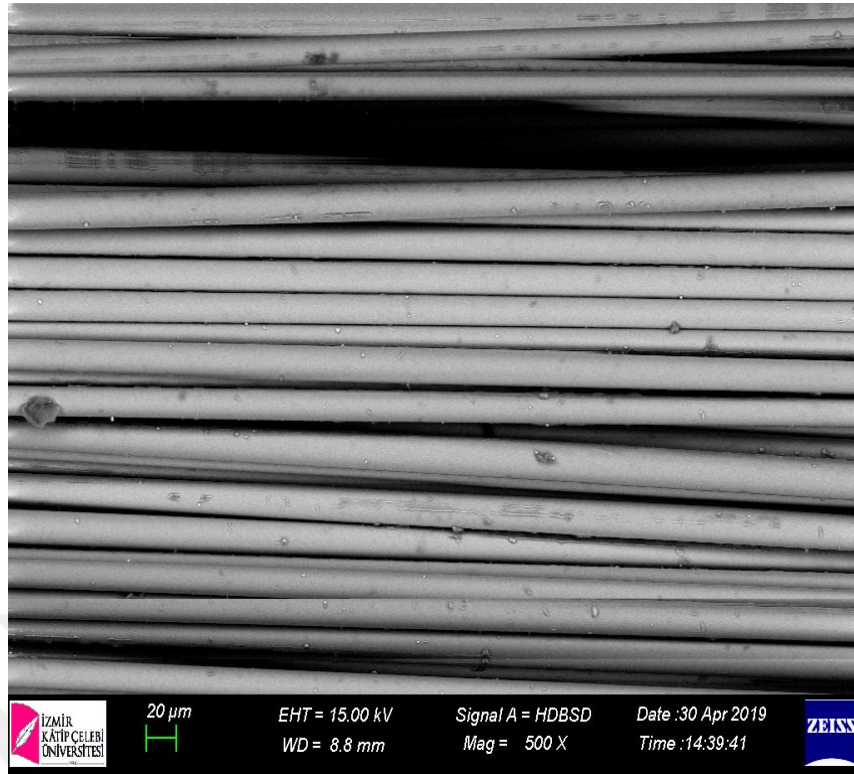


Figure 3.57: Basalt fiber NaOH (%10) treated

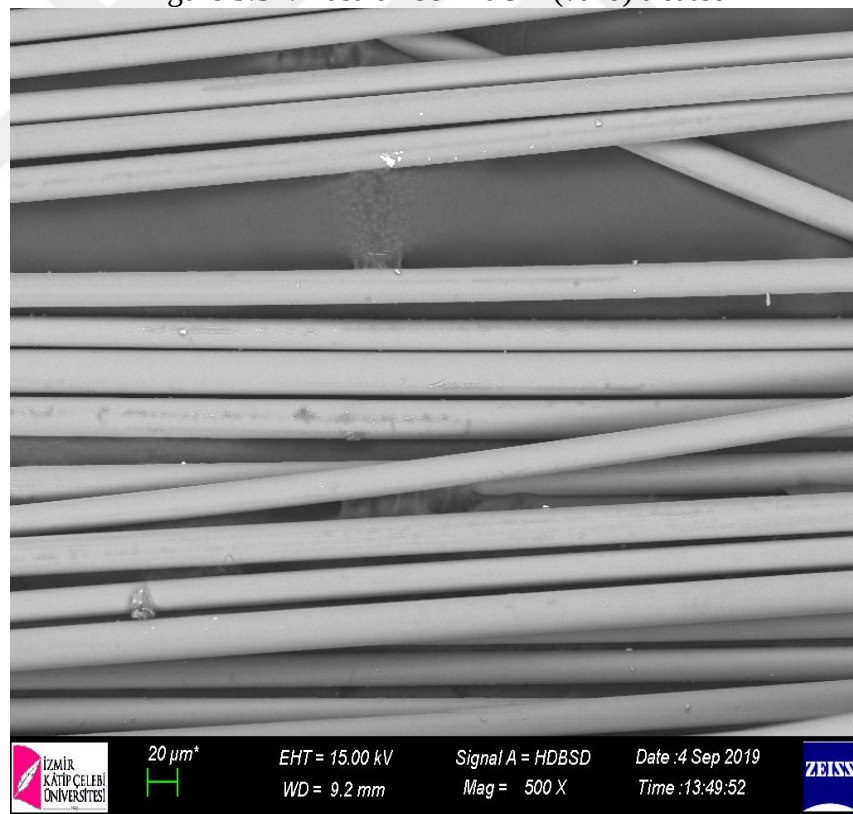


Figure 3.58: Basalt fiber NaOH (%2) treated

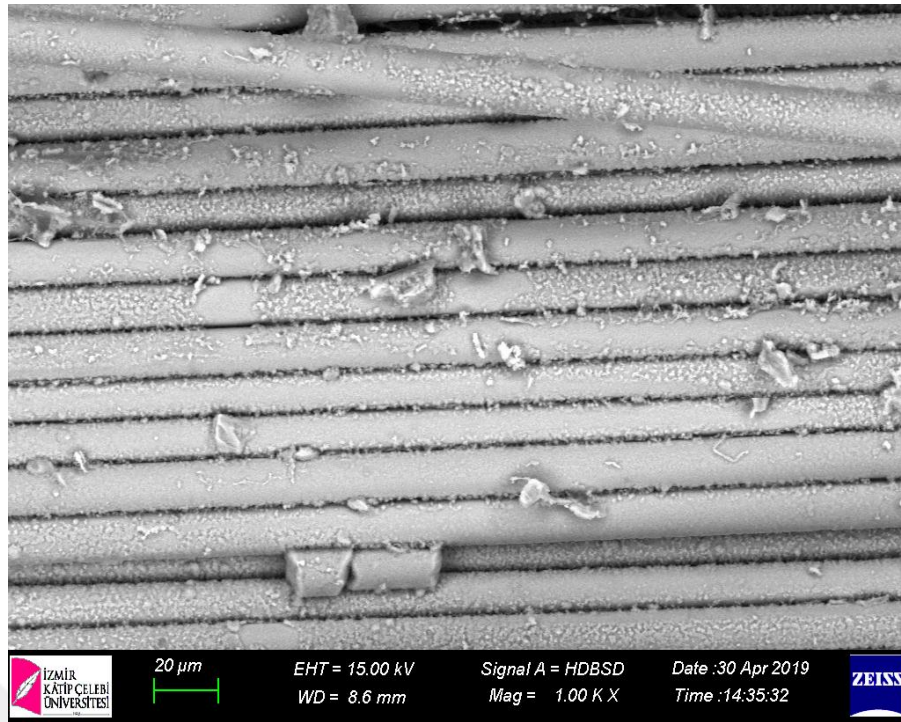


Figure 3.59: PA2 glass fiber

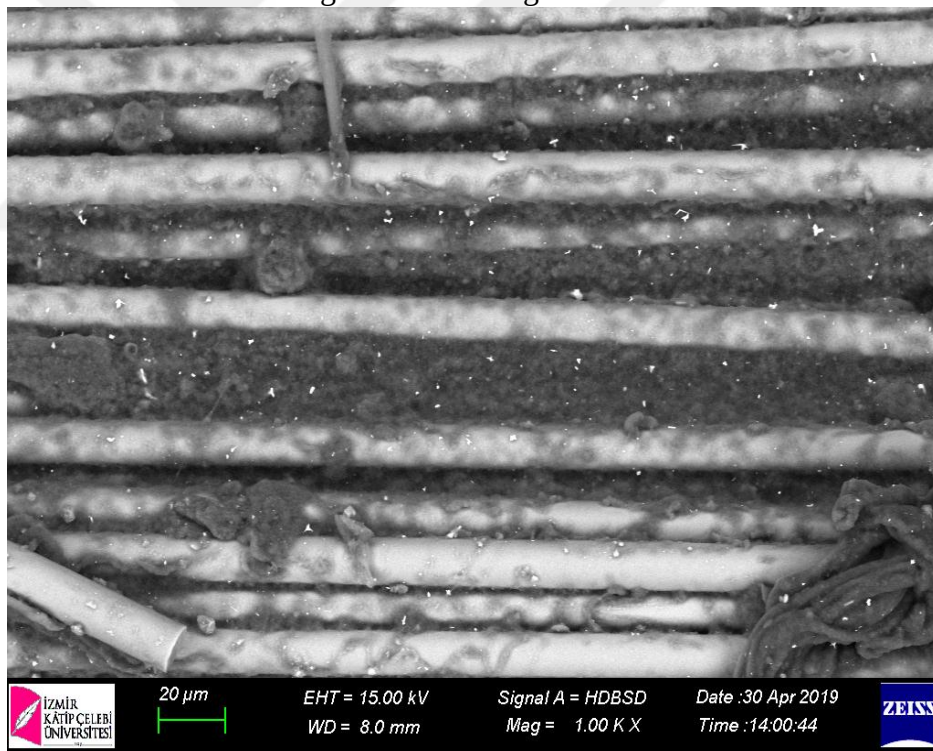


Figure 3.60: Alkali treated PA2 glass fiber

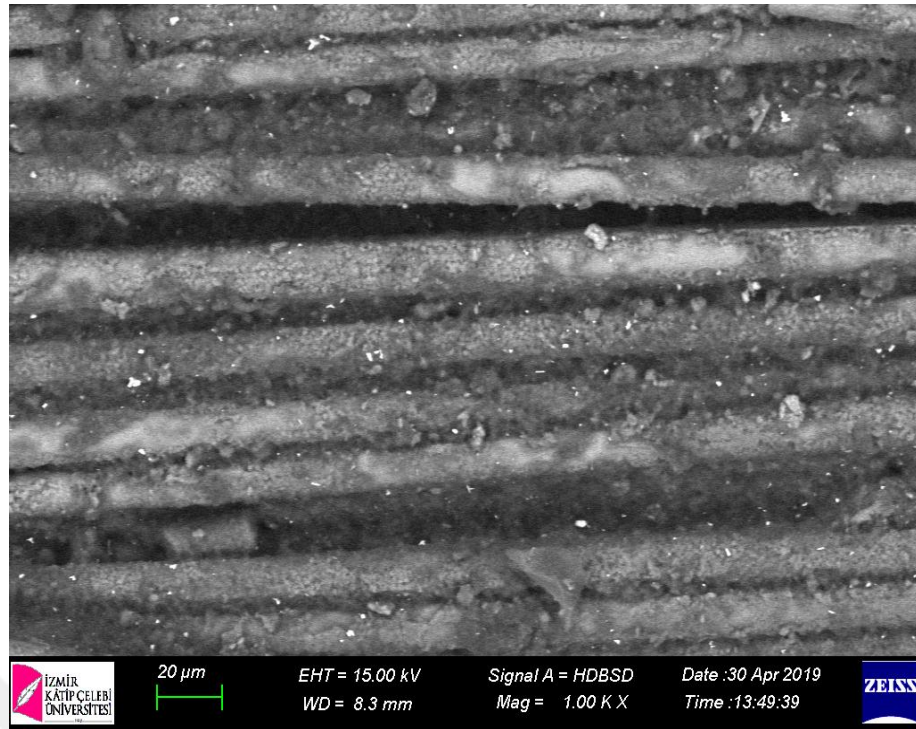


Figure 3.61: EPDM solution treated PA2 glass fiber

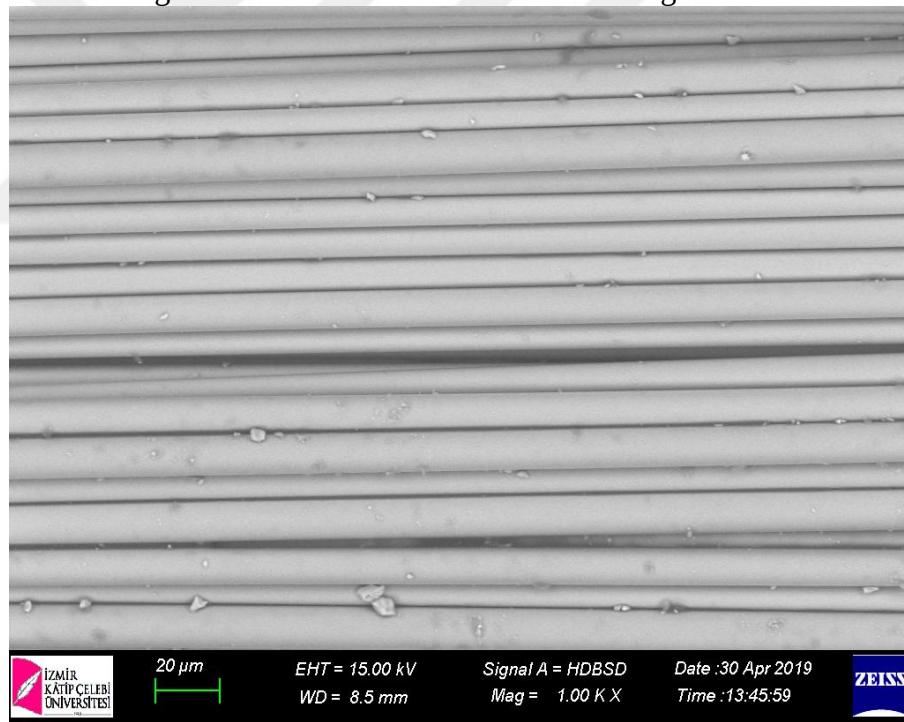


Figure 3.62: Alkali and EPDM solution (hybrid) treated PA2 glass fiber

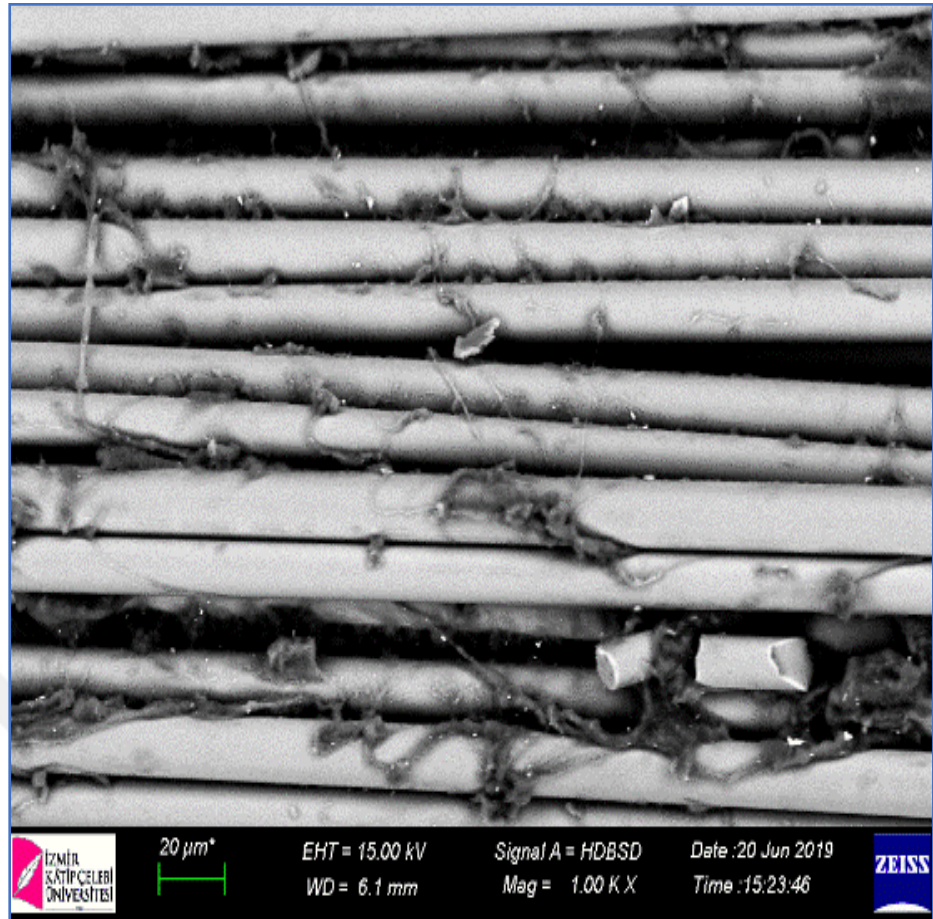


Figure 3.63: Bare PA 2 glass fiber processed in oven

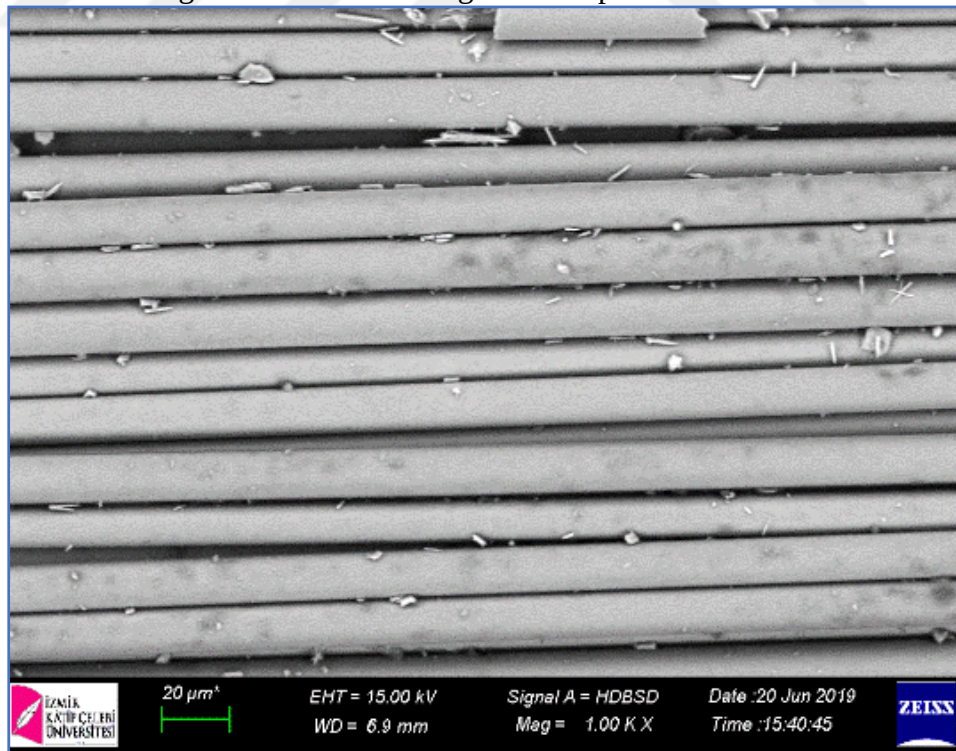


Figure 3.64: Bare PA 2 glass fiber alkali treated processed in oven

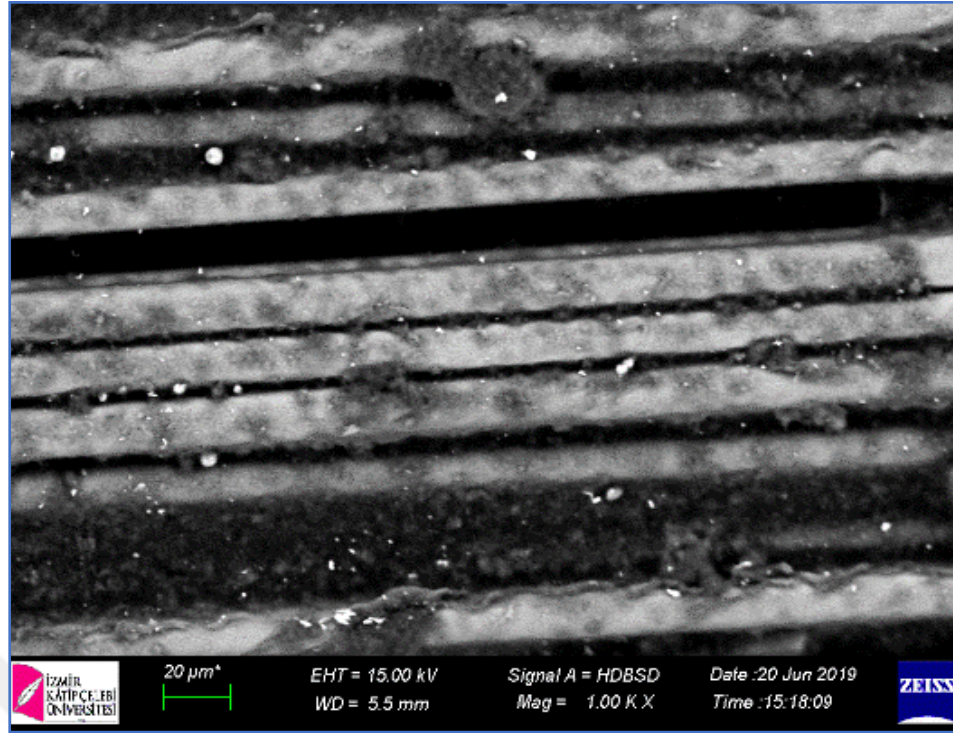


Figure 3.65: Bare PA 2 glass fiber EPDM solution treated processed in oven

Raman spectrometry analysis is carried out from PA2 glass fibers and bare PA2 glass fibers, not from EPDM rubber mixtures. The formulation codes and the surface treatment methods that Raman analysis is applied exist in the Table below. The aim is to see the effect of baring process and different surface treatment methods applied to PA2 glass fiber.

Table 3.18: Fibers that undergo Raman analysis

Formulation Code	Surface Treatment Method
D012-1	Bare PA 2 glass fiber, processed in oven
D012/ 2-1	Bare PA2 glass fiber alkali treated processed in oven
D012/ 3-1	Bare PA2 glass fiber EPDM solution treated Bare PA2 glass fiber alkali treated processed in oven processed in oven
D012/ 4-2	Bare PA2 glass fiber alkali and EPDM solution treated (hybrid) processed in oven
-	Bare PA 2 glass fiber, processed in hot water
D012/ 2-2	Bare PA2 glass fiber alkali treated processed in hot water
-	Bare PA2 glass fiber EPDM solution treated processed in hot water
-	Bare PA2 glass fiber alkali and EPDM solution treated (hybrid) processed in hot water

When images and graphs of fibers are examined after Raman Spectrometry Analyses, intensity of pgs on vertical axis are related with bond quantities and PA2 glass fibers have better interfacial quality. Intensity of pgs of bare PA2 glass fiber decreases and bond quantity decrease at a ratio of 1:3 and these show that surface quality is worse when compared to PA2 glass fiber. As a result of Raman spectrometry analyses, when new formed bonds are investigated from fibers in which interfacial quality and adhesion properties are searched, it is seen that fiber groups have better adhesion property and interfacial quality than bare fibers by checking the bond quantities.

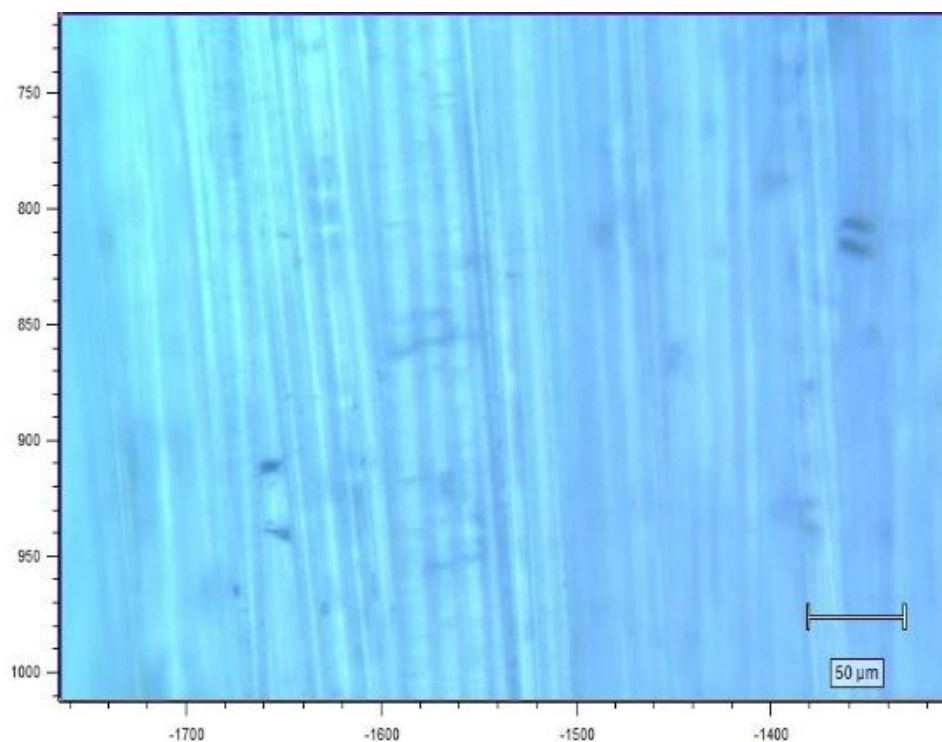


Figure 3.66: Bare PA 2 glass fiber, processed in oven

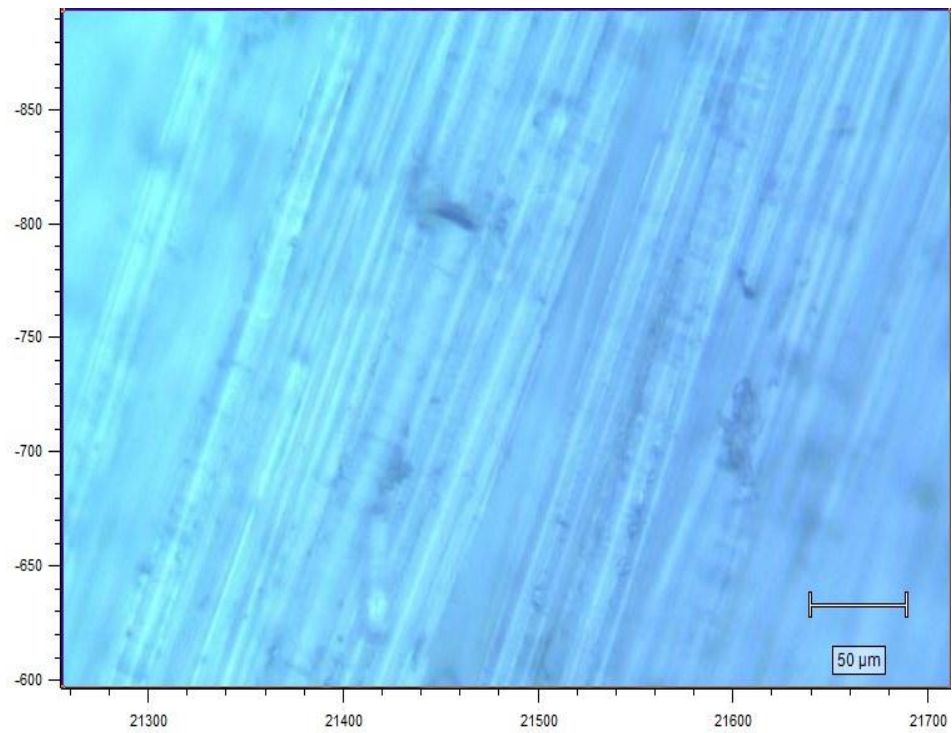


Figure 3.67: Bare PA2 glass fiber alkali treated processed in oven

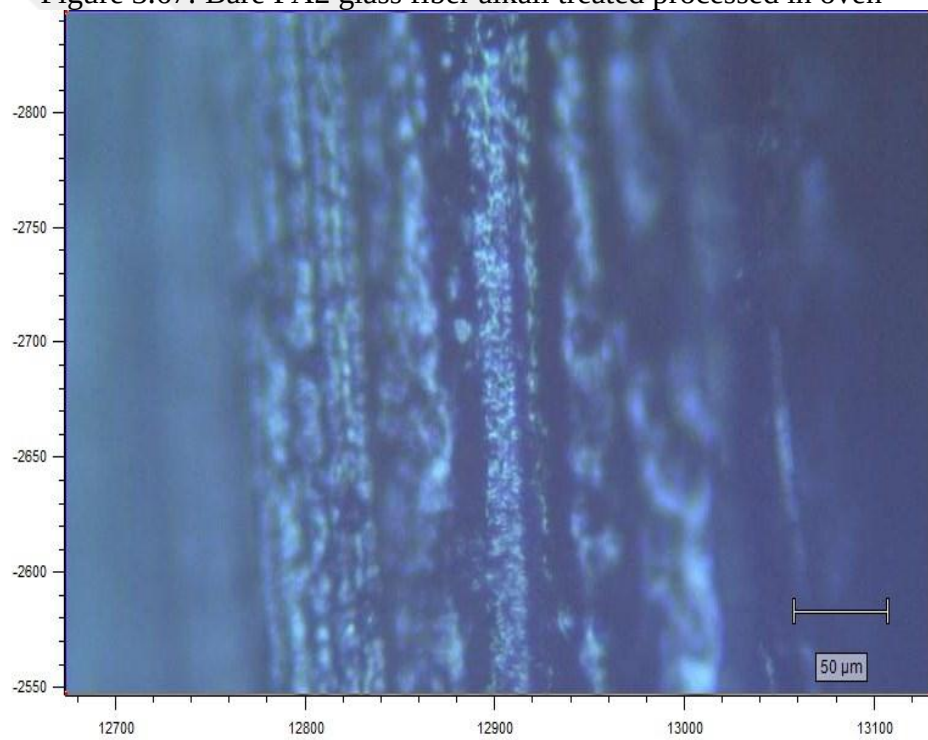


Figure 3.68: Bare PA2 glass fiber EPDM solution treated processed in oven

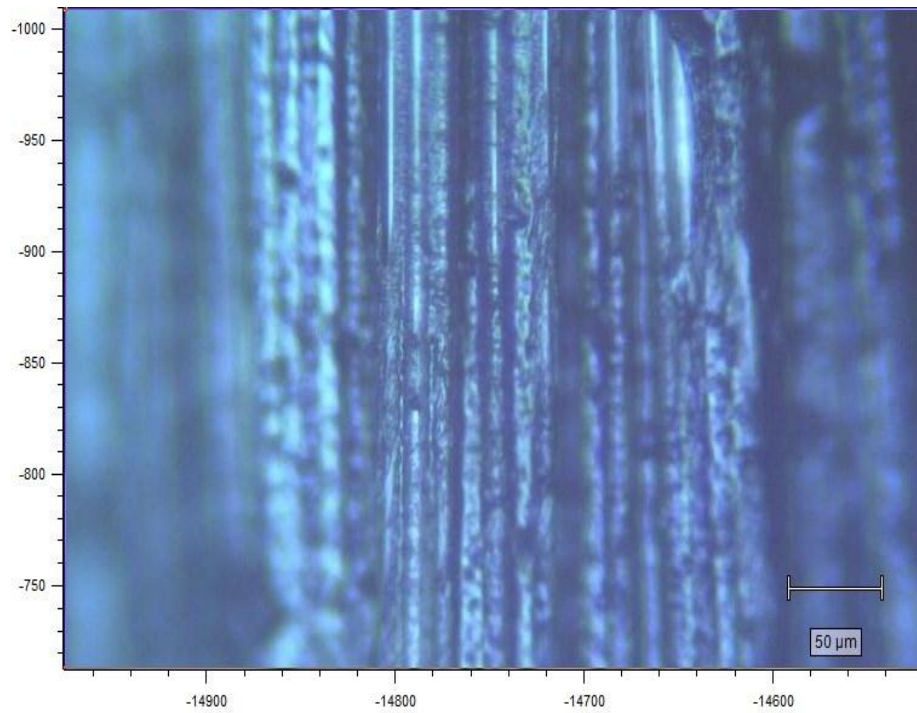


Figure 3.69: Bare PA2 glass fiber alkali and EPDM solution (hybrid) treated processed in oven

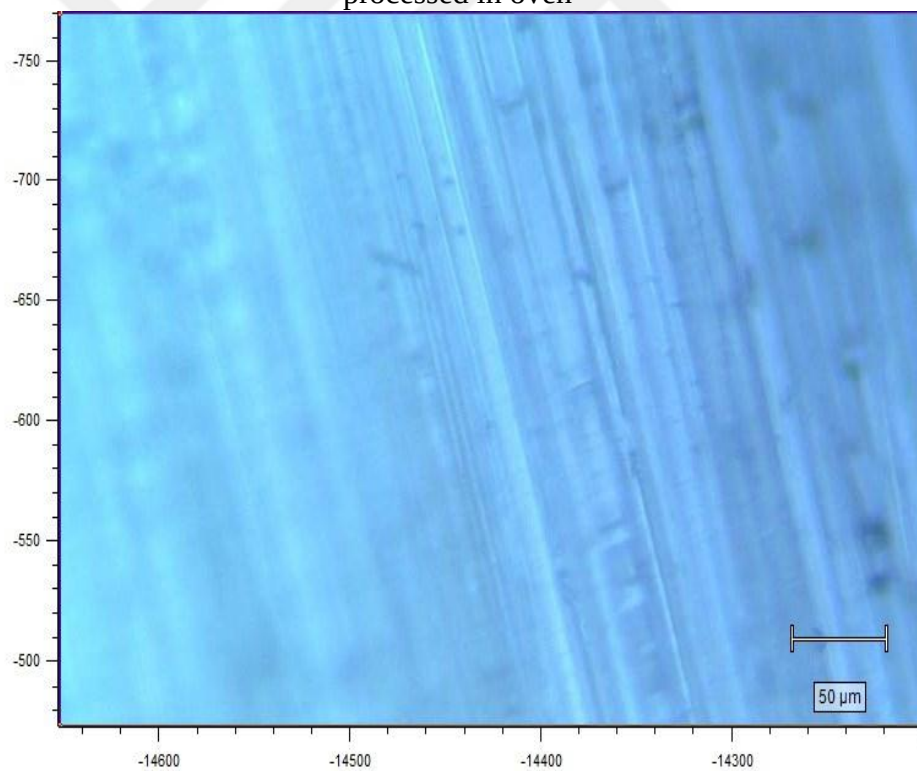


Figure 3.70: Bare PA2 glass fiber processed in hot water

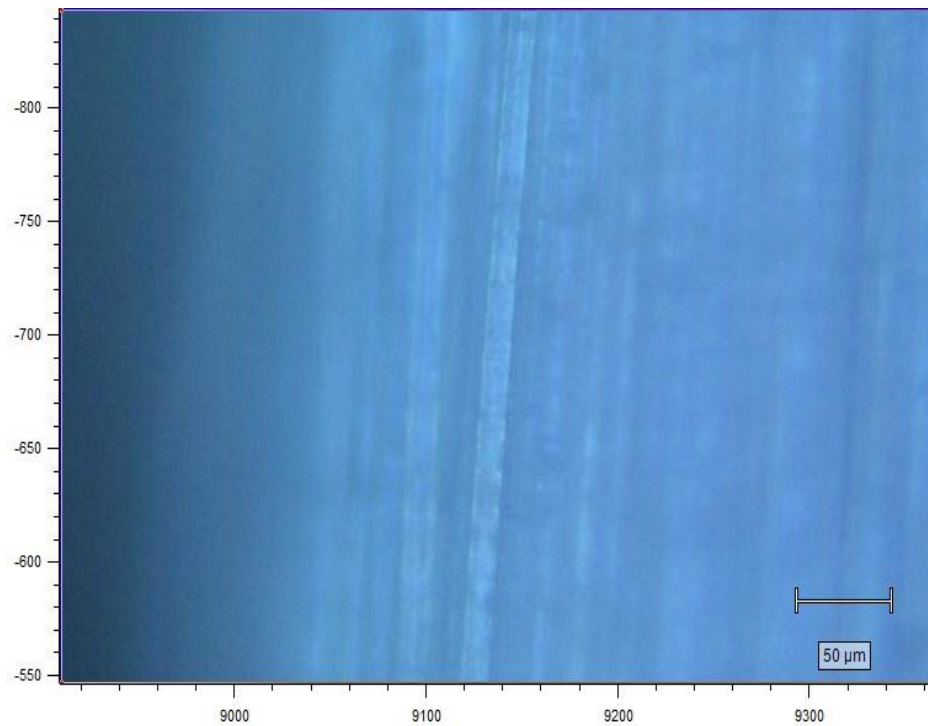


Figure 3.71: Bare PA2 glass fiber alkali treated processed in hot water

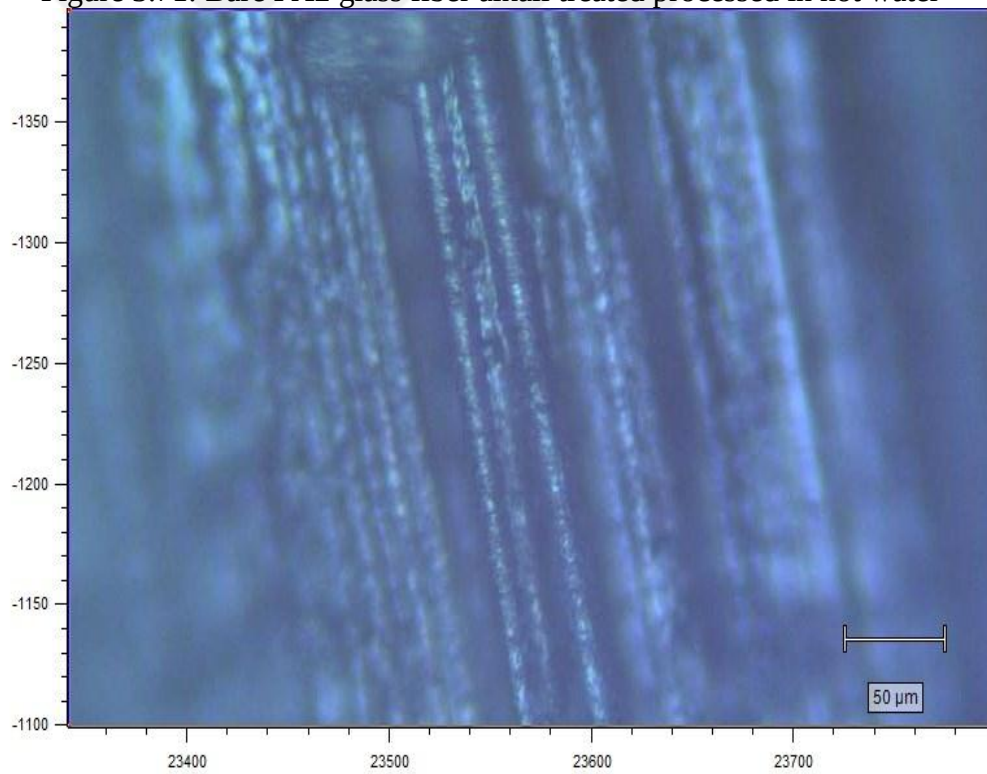


Figure 3.72: Bare PA2 glass fiber EPDM solution treated processed in hot water

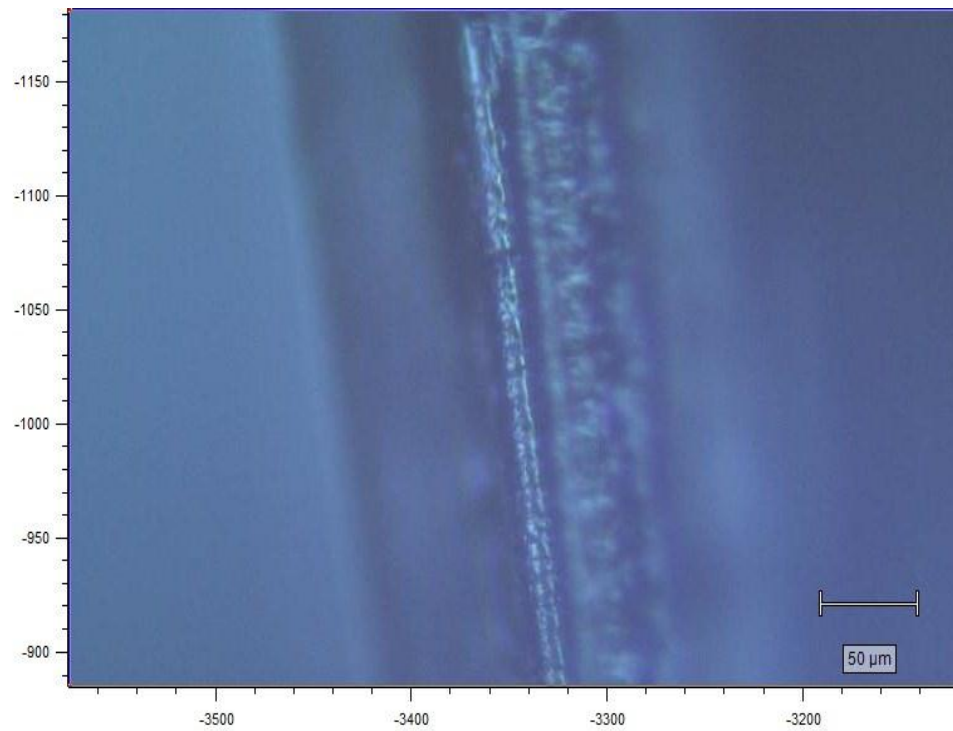


Figure 3.73: Bare PA2 glass fiber alkali and EPDM solution treated (hybrid) processed in hot water

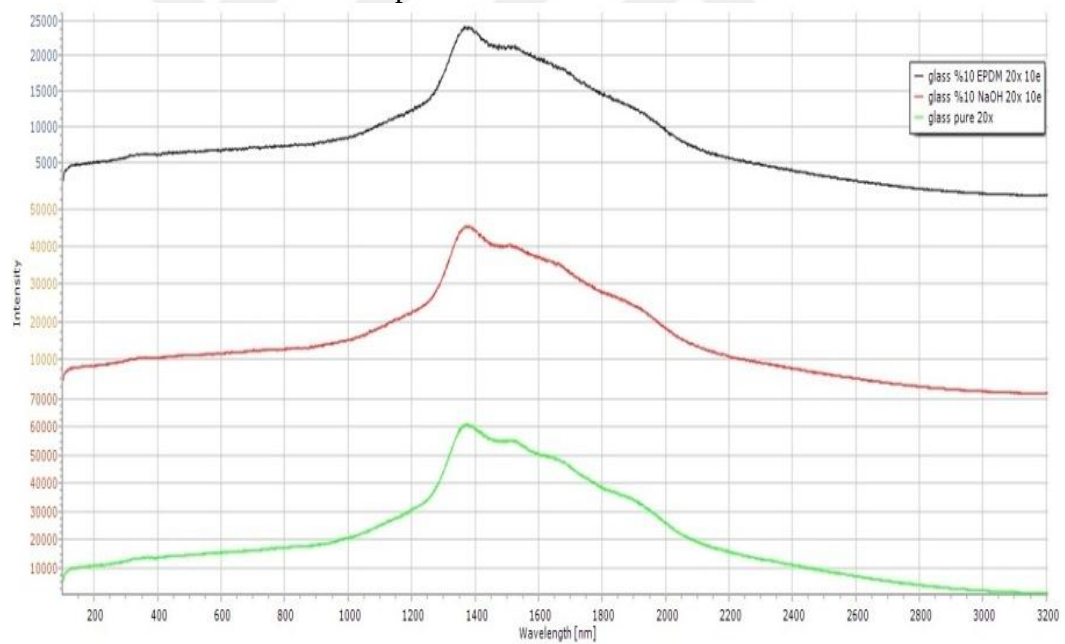


Figure 3.74: PA2 glass fiber, PA2 glass fiber alkali treated, PA2 glass fiber alkali and EPDM solution treated

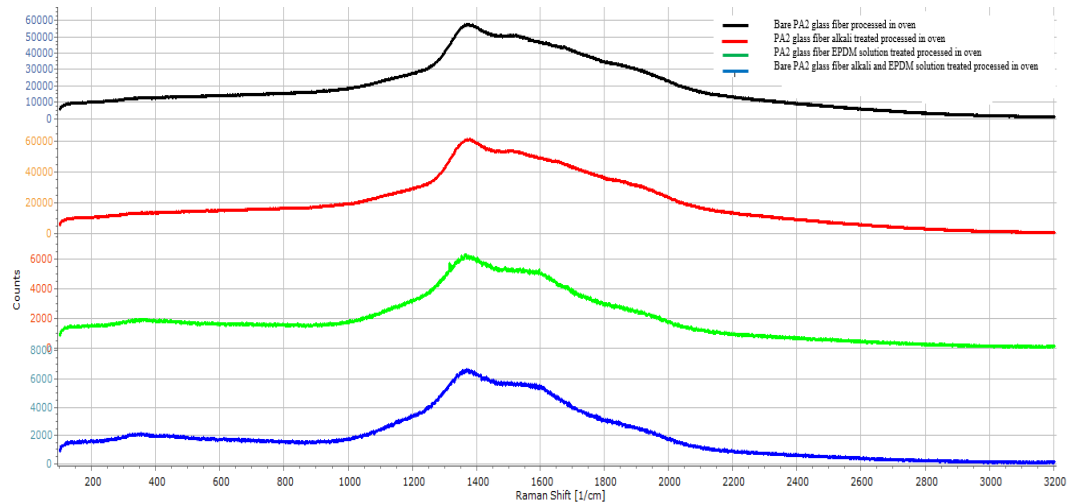


Figure 3.75: Bare PA2 glass fiber processed in oven, PA2 glass fiber alkali treated processed in oven, PA2 glass fiber EPDM solution treated processed in oven, Bare PA2 glass fiber alkali and EPDM solution treated processed in oven

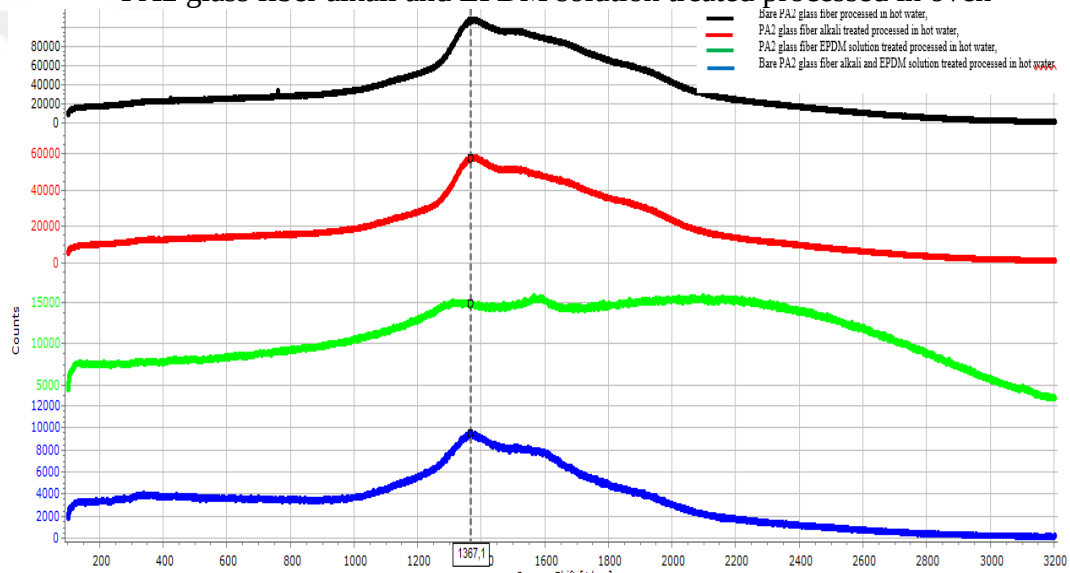


Figure 3.76: Bare PA2 glass fiber processed in hot water, PA2 glass fiber alkali treated processed in hot water, PA2 glass fiber EPDM solution treated processed in hot water, Bare PA2 glass fiber alkali and EPDM solution treated processed in hot water

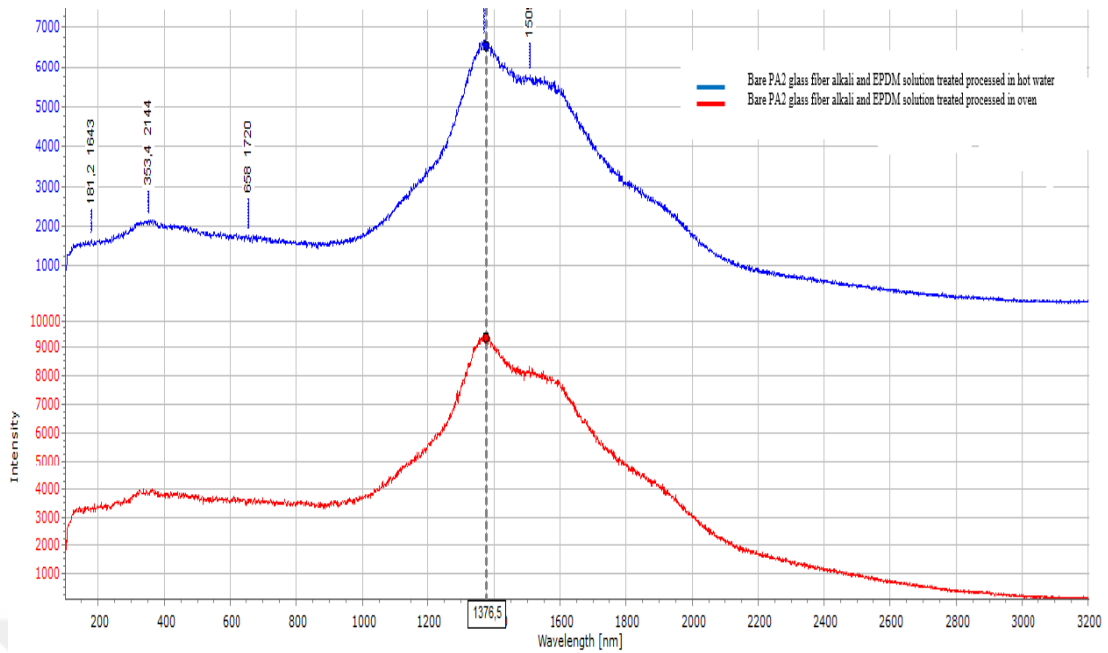


Figure 3.77: Bare PA2 glass fiber alkali and EPDM solution treated processed in hot water, Bare PA2 glass fiber alkali and EPDM solution treated processed in oven

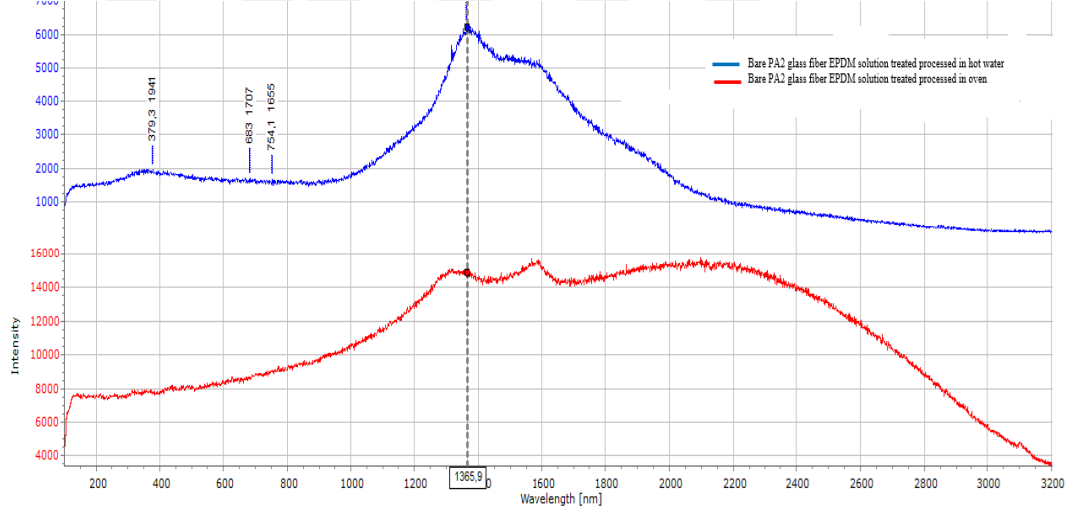


Figure 3.78: Bare PA2 glass fiber EPDM solution treated processed in hot water, Bare PA2 glass fiber EPDM solution treated processed in oven

FTIR test is applied to PA2 glass fibers, including non-treated form, alkali treated form, EPDM solution treated form and alkali+ EPDM solution treated form (hybrid). The Figure 3.78 shows the FTIR analysis of the fibers. Analysis in FTIR gives that after NaOH process on fibers number of C-O bonds increase. In EPDM coating while carbon is increasing oxygen decreases and while carbon is decreasing oxygen and Si increase. In PA2 glass fiber it is seen that CH_2 , CH_3 bonds realize the distribution on the areas where pig points are marked. These pigs show C=C bonds. Newly formed bonds show that processes that are applied on fibers effect surface

quality. As number of bonds on silane coated fibers are much more it is understood that surface quality is better.

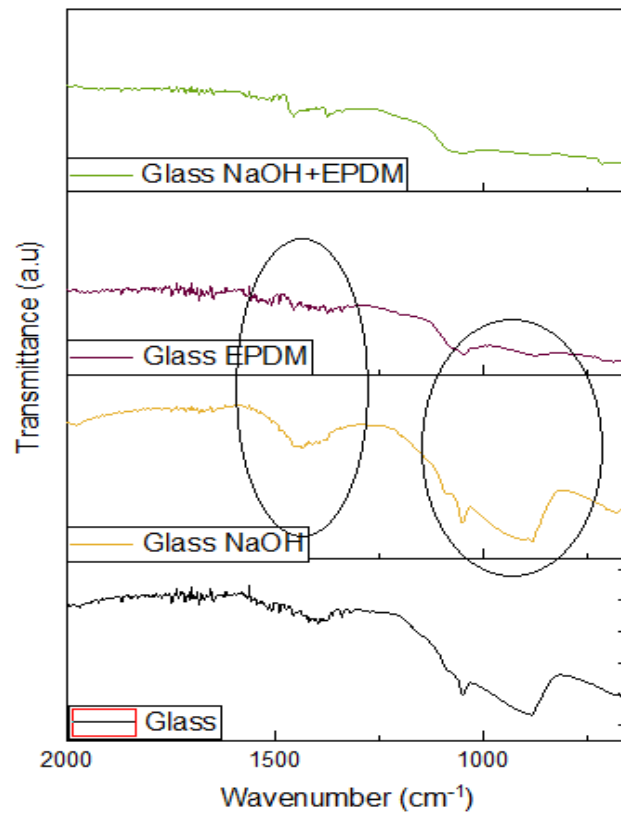


Figure 3.79: FTIR analysis of PA2 glass fibers.

After investigating all the results gained by rheological, physico- mechanical, ageing, SEM, Raman and FTIR tests some evaluations are done. When rheological values are taken into consideration silane+NaOH coated hybrid basalt fiber have the min. torque (M_L) value. Silane coating creates a more homogenous surface structure on the fibers and therefore silane coated fibers are evaluated to have better adhesion properties inside the rubber compound matrix. Additionally, lower ML values are desired especially to have easy processing characteristics in various rubber production machines. When physico-mechanical properties are examined, the same trial defined above has the best tensile and compression set properties. Both these characteristics are related to cross linking density and vulcanization properties. These succesful findings held us to think that better surface quality fibers can disperse inside rubber matrix well and have a positive effect on curing and curing related properties. When ageing properties are checked, again same silane coated basalt fiber trial is seen to give the best properties in case of volume swell after coolant ageing.

We can relate this situation better adhesion properties of silane coated basalt fiber and better surface quality. As explained above for SEM, Raman and FTIR analysis surface treatment of fibers has positive effect for them to be bonded well inside the EPDM rubber mixture. Some further studies are decided to be applied to basalt fiber trials for the successful findings gained from them like RPA (Rubber process analyzer) tests. RPA tests are run to check their processability properties and have a pre-assumption about their process characteristics before realizing the production. This study gives us very helpful outputs by comparing different fiber filled compounds.

3.4 RPA (Rubber Process Analyser) Studies

After having all the results collected from fiber filled EPDM rubber mixtures, lastly process characteristics of these mixtures are studied in RPA test machine. RPA tests are applied to basalt fiber filled EPDM rubber mixture (D009), NaOH (%10)+ EPDM solution treated basalt fiber filled EPDM rubber mixture (D009/4) and aramid fiber filled EPDM rubber mixture (D018) as a reference. The trials and the test type in RPA test machine is listed in the Table 3.19 as follows.

Table 3.19: Formulations of RPA studies

Formulation Code	Fiber Type	Treatment Method	Test Type
D009	Basalt	Non-treated	Cure Test (180C, 30 min.)
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	Cure Test (180C, 30 min.)
D018	Aramid	Non-treated	Cure Test (180C, 30 min.)
D009	Basalt	Non-treated	Frequency Sweep
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	Frequency Sweep
D018	Aramid	Non-treated	Frequency Sweep
D009	Basalt	Non-treated	Strain Sweep-1
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	Strain Sweep-1
D018	Aramid	Non-treated	Strain Sweep-1
D009	Basalt	Non-treated	Strain Sweep-2
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	Strain Sweep-2
D018	Aramid	Non-treated	Strain Sweep-2

Cure test (180°C, 30 min.) is applied at isothermal conditions to determine torque, scorch and curing properties of compounds. Comparison is also possible. Frequency sweep test is applied at 80°C, with a %1 Strain value where frequency varies between 1 cpm to 100 cpm. $\tan\delta$ vs S' graph is held as an output of the test. The aim is to check how the compound behaviour is in extrusion process in terms of good surface quality, easy flow and easy processing. Strain Sweep-1 test is applied at 100°C with a frequency of 0,1 Hz. and a strain value between 0,07° and 70,310°. $\tan\delta$ vs Strain graph is gained from the test. It evaluates extrusion die swell of the compounds. Strain Sweep-2 test is carried out at 80°C with a frequency of 0,1 Hz. and a strain changing from 0,035° to 0,1°. G' at %1 strain gives a correlation for the evaluation of hardness.

RPA cure test results are given in Table 3.20 at 180°C for 30 minutes for D009, D009/4 and D018.

Table 3.20: RPA Cure test results

Formulation Code	Fiber Type	Treatment Method	ML (dNm)	MH (dNm)	ts2 (min.)	t90 (min.)
D009	Basalt	Non-treated	1,31	12,41	0,44	3,31
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	0,95	11,54	0,6	3,58
D018	Aramid	Non-treated	1,12	13,69	0,55	3,81

All the outputs of RPA cure test can be seen clearly from Figure 3.79. NaOH surface treated basalt fiber has the lowest ML value among all trials meaning a faster and easier flow characteristics in process conditions hence providing less energy consumption. Aramid fiber filled EPDM rubber mixture has the highest ML value which means higher cross linking density, more stiff compound and higher mechanical properties like hardness. NaOH surface treated basalt fiber has the lowest scorch time which points out safer processing conditions in mixing, extrusion or molding without any pre-curing problems. Aramid fiber filled EPDM rubber mixture has the highest t90 value. It is the mixture which needs to be cured more than the other trials to have its curing completed whereas the basalt fiber filled EPDM rubber mixture has the lowest t90 hence shortest curing time.

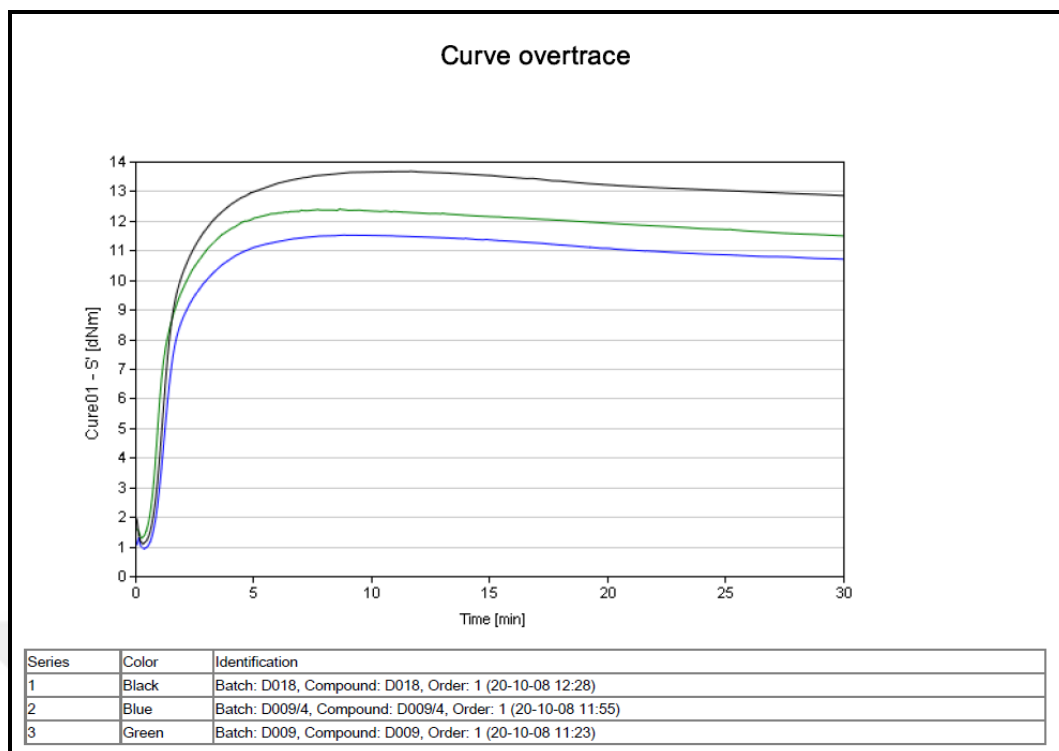


Figure 3.80: RPA cure test graph

RPA frequency sweep test result can be seen from Figure 3.80. As explained before test is run at 80°C, at %1 strain, in a frequency range between 1 cpm to 100 cpm. $\tan\delta$ vs S' graph is plotted to check how the compound behaviour will be in extrusion process in terms of good surface quality, easy flow and easy processing. The mixture with a lower $\tan\delta$ has worse processing conditions than the other. When $\tan\delta$ values are checked it is seen that aramid fiber filled EPDM rubber mixture has the highest value hence it has the best processing conditions, surface quality and easy flow characteristics in extrusion. After aramid fiber, NaOH (%10) + EPDM solution (hybrid) treated basalt fiber gives the highest $\tan\delta$ value meaning that it is the second-best option to be used when process conditions are considered.

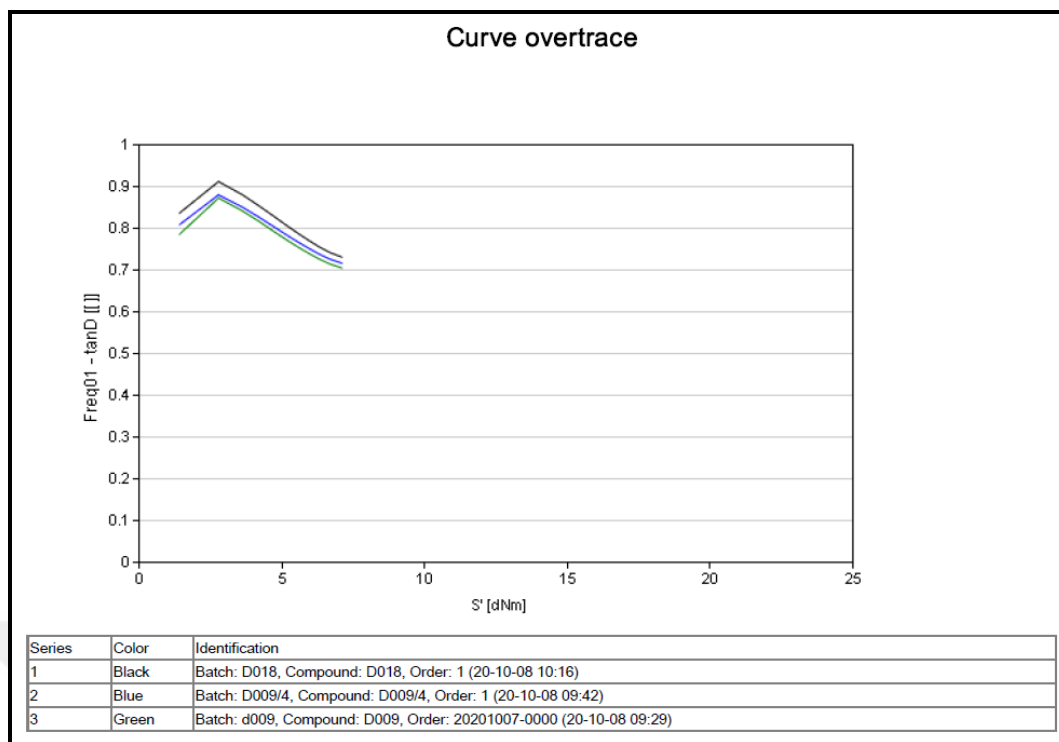


Figure 3.81: RPA frequency sweep test graph

RPA strain sweep-1 test graph can be seen clearly from Figure 3.81. As mentioned before, strain sweep-1 test is run at 100°C, at 0,1 Hz frequency, at a strain between 0,07° and 70,31°. Tan δ vs strain graph is plotted. Result and graph help to foresee the extrusion die swell of the mixture in extrusion process. The higher strain value gives lower extrusion die swell. When the results are checked it is seen that aramid fiber filled EPDM rubber mixture gives the highest strain value, whereas the NaOH (%10) + EPDM solution treated basalt fiber gives the second highest value and the basalt fiber filled EPDM rubber mixture gives the lowest strain result. If aramid fiber trial is considered as a reference trial it can be said that hybrid treatment of basalt fiber worked well to have lower die swell in extrusion. Low die swell property is important for a rubber mixture to have stable process conditions in extrusion which can be managed and adjusted easily. When die swell is high, desired dimensional properties can not be reached, an adjustment on the mold at the extrusion head should be done. This brings the disadvantage of scrap material, energy and labor lost.

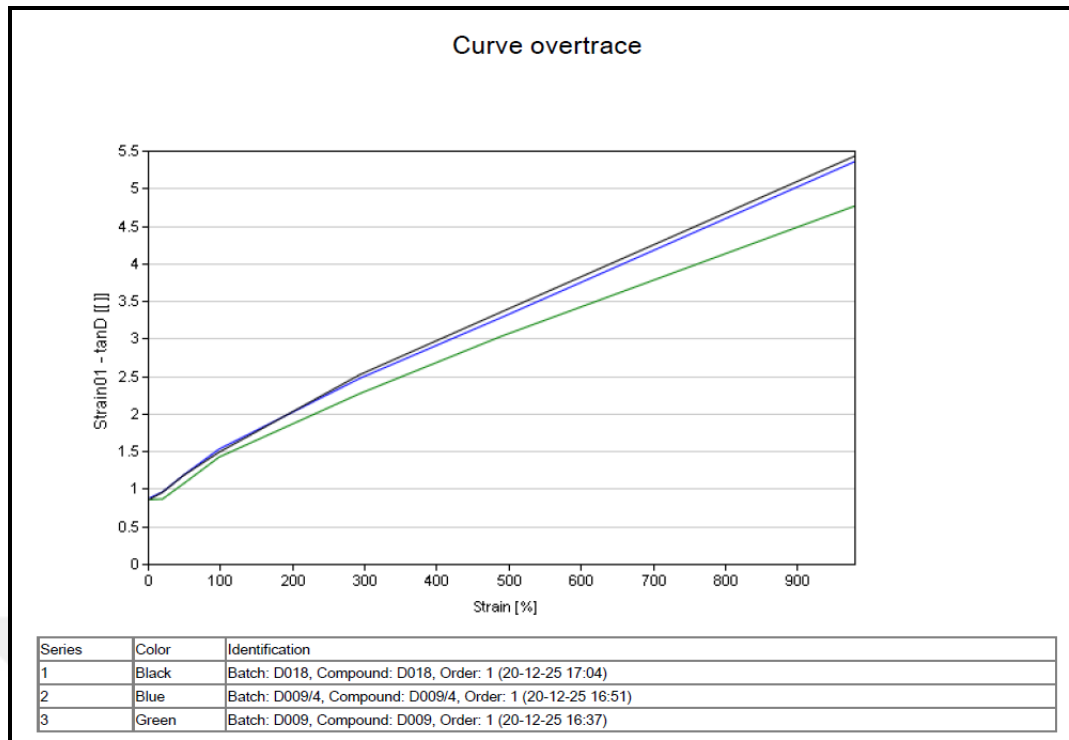


Figure 3.82: RPA strain sweep-1 test graph

RPA strain sweep-2 test result can be seen clearly from Table 3.21. As mentioned before test is carried out at 80°C, with a frequency of 0,1 Hz, and a strain value between 0,035° to 0,1°.

Table 3.21: RPA strain sweep-2 test

Formulation Code	Fiber Type	Treatment Method	G' at %1 strain (Mpa)	Hardness (ShoreA)
D009	Basalt	Non-treated	0,19	67
D009/4	Basalt	NaOH (%10)+ EPDM solution treated	0,19	68
D018	Aramid	Non-treated	0,25	71

From RPA tests, finished part properties also can be evaluated. This is a big advantage because normally to measure finished part properties, a piece of rubber mixture should be cured in a mold and after curing the compound needs to rest for a defined period. Procedure is too long and lots of labor and hand work exist. This situation also brings some risks like wrong measurement coming from the nature of the human. But in RPA an uncured piece from a rubber mixture is taken and put into the RPA test machine which conditions are adjusted just before the test. There is less human work and risk. G' at %1 (0,07°) strain gives a correlation for the evaluation of

hardness. The higher G' at %1 strain gives a higher hardness result. From Table 3.21, it is seen clearly that G' at %1 strain of basalt fiber filled EPDM rubber mixture is nearly same with NaOH(%10) + EPDM solution treated basalt fiber filled EPDM mixture and aramid fiber filled EPDM rubber mixture gives a higher hardness result. In reality the results of hardness are well known from the previous tests, and they are in the same rating with the RPA outputs which are listed in Table 3.21.

RPA testing gives chance to see the behaviour of compounds in processes without producing them. It gives results about the phases like before cure, during cure and after cure. Material and time consumption is prevented by evaluating RPA results. Aramide is a fiber which is well known in rubber industry. Mostly it is blended with rubber compounds to form a fiber reinforced composite. Therefore, basalt and NaOH (%10) + EPDM solution treated basalt fiber (hybrid basalt fiber) reinforced rubber compound results are compared both in between and with aramid reinforced rubber compound. Hybrid basalt fiber reinforced rubber compound is evaluated to give more succesful results in terms of processing behaviours than basalt fiber reinforced rubber compound by using the advantages of RPA tests. As an after-cure property of RPA, hardness of the compounds are compared by using the strain sweep results of RPA.

Chapter 4

Conclusions and Suggestions

At the beginning of the study, different fibers at different ratios are mixed into the EPDM rubber compound. The fiber types are carbon, basalt, PA2 glass, PP4 glass and aramid fibers. The ratios are 2 PHR, 5 PHR and 10 phr for all the fiber types. The EPDM mixtures are prepared in laboratory scale mixer, cured in laboratory press according to the outputs of the rheometer test. Physico- mechanical tests at the initial state are applied and similar tests run at the initial state are also applied after hot air and coolant ageing tests to see the effect of hot air and coolant on the fiber filled rubber compounds. When all rheometer tests, physico-mechanical tests and ageing test results are checked, it is seen that fiber ratio 5 PHR gives the optimum results. When the ratio is increased to 10 PHR some properties are lost. If it remained at 2 PHR some properties are not improved as desired. Also there are some fluctuating results with increasing fiber ratio to 10 PHR. This is related to the poor surface bonding of fibers to the polymer matrix. Therefore surface structure of fibers is decided to be improved with different surface modification methods.

Second step of the study is to apply fibers surface modification for better bonding and interfacial area. NaOH (alkali) treatment, EPDM solution treatment and NaOH + EPDM solution (hybrid) treatment is applied to fibers. The fibers that are used in this part of the study are carbon, basalt, PA2 glass and aramid fibers. The fibers with surface treatment are added to EPDM rubber mixture at 5 PHR ratio. The mixtures are blended in laboratory scale mixer, cured in laboratory press by considering the rheometer test results. Rheometer tests, physico- mechanical tests at initial state and similar tests with the initial state tests after hot air and coolant ageing are made. Also SEM analysis, Raman analysis and contact angle tests are run to see the effect of surface treatment. These tests are carried out from EPDM rubber mixtures with

EPDM solution treatment method. When all the results including rheological tests, initial physico-mechanical tests, ageing tests, SEM analysis, contact angle measurements, Raman analysis are taken into consideration for different kind of treated fiber filled EPDM rubber mixtures, it is seen obviously that treatment of fibers improved properties of blends. Especially treatment brought a better surface bonding of fibers inside the rubber matrix, more homogenous and well dispersed mixture as well improved interface. In studies of basalt and PA2 glass fiber, fluctuations in the results are seen. They are selected to be studied in more details in the next section. Further surface treatments will be carried out with these fiber types.

In the third section of the study, basalt and PA2 glass fibers are focused. Further surface treatment methods are applied to them. Basalt fibers are treated with silane, NaOH (%2), and NaOH (%2) + silane (hybrid). For PA2 glass fibers, baring operation is applied. Different treatment methods like NaOH treatment, EPDM solution treatment, NaOH + EPDM solution treatment (hybrid) are used processed both in oven and hot water. Then these various type of fibers are mixed with EPDM rubber compounds in laboratory mixer. They are cured in laboratory press to have samples according to t90 held from rheometer test. Rheometer tests, initial physico-mechanical tests and similar tests after hot air and coolant ageing are made. Also from fibers SEM analysis, Raman analysis and FTIR analysis are carried out to see the effect of surface treatment structurally. After investigating all the results gained by rheological, physico- mechanical, ageing, SEM, Raman and FTIR tests some evaluations are done. When rheological values are taken into consideration silane+NaOH coated hybrid basalt fiber have the min. torque (ML) value. Silane coating creates a more homogenous surface structure on the fibers and therefore silane coated fibers are evaluated to have better adhesion properties inside the rubber compound matrix. Additionally, lower ML values are desired especially to have easy processing characteristics in various rubber production machines. When physico-mechanical properties are examined, the same trial defined above has the best tensile and compression set properties. Both these characteristics are related to cross linking density and vulcanization properties. These successful findings held us to think that better surface quality fibers can disperse inside rubber matrix well and have a positive effect on curing and curing related properties. When ageing properties are checked, again same silane coated basalt fiber trial is seen to give the best properties

in case of volume swell after coolant ageing. We can relate this situation better adhesion properties of silane coated basalt fiber and better surface quality. As explained above for SEM, Raman and FTIR analysis surface treatment of fibers has positive effect for them to be bonded well inside the EPDM rubber mixture. Some further studies are decided to be applied to basalt fiber trials for the successful findings gained from them like RPA (Rubber process analyzer) tests. RPA tests are run to check their processability properties and have a pre-assumption about their process characteristics before realizing the production.

In the fourth section of the study, RPA tests are done. RPA tests are applied to basalt fiber filled EPDM rubber mixture, NaOH (%10) + EPDM solution (hybrid) filled EPDM rubber mixture and aramid filled EPDM rubber mixture. RPA testing gives chance to see the behaviour of compounds in processes without producing them. It gives results about the phases like before cure, during cure and after cure. Material and time consumption is prevented by evaluating RPA results. Aramide is a fiber which is well known in rubber industry. Mostly it is blended with rubber compounds to form a fiber reinforced composite. Therefore, basalt and NaOH (%10) + EPDM solution treated basalt fiber (hybride basalt fiber) reinforced rubber compound results are compared both in between and with aramide reinforced rubber compound. Hybride basalt fiber reinforced rubber compound is evaluated to give more successful results in terms of processing behaviours than basalt fiber reinforced rubber compound by using the advantages of RPA tests. As an after-cure property of RPA, hardness of the compounds are compared by using the strain sweep results of RPA.

As a conclusion among 40 different EPDM rubber mixtures that are blended NaOH (%2) + silane (hybrid) treated basalt fiber filled EPDM rubber mixtures seem to be more advantageous by considering its test results including SEM analysis and RPA tests. It is also an advantage to meet an international specification requirement called SAE J20 Class E with this formulation. Findings from this thesis for this formulation gives benefit of adding valuable results to the publish

as well as providing a useful formulation for the automotive industry. The studies applied in this thesis combines the academical research perspective with the demands of the automotive industry.

As a suggestion, the outputs of this thesis would be the starting point of a new study. The most optimum formulation defined above can be tried in extrusion conditions with specially designed extrusion heads to orient the fibers in the same direction for having necessary functional demands. The hoses produced with the optimum formulation in extrusion should be cured and tested on engine conditions to see the functionality of the product.



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