Relations between Outside Conditions and Wax Desorption/Sorption in the Rubber

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Master Thesis

2014

Univerzita Tomáše Bati ve Zlíně
Fakulta technologická

Tomas Bata University in Zlín
Faculty of Technology
Department of Polymer Engineering
Academic Year: 2013/2014

MASTER'S THESIS ASSIGNMENT

(PROJECT, ARTWORK, ARTISTIC PERFORMANCE)

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Degree Course:	**Polymer Engineering**
Thesis Topic:	**Relations between Outside Conditions and Wax Desorption/Sorption in the Rubber**

Thesis Guidelines:

The theoretical part of the Diploma Thesis will deal with the effect of wax during the caoutchouc processing and on the resulting rubber properties. Suitable substitution of the wax in order to eliminate the flowering problem while the positive properties for the final use as a silentblock in automotive industry are maintained will be discussed as well. The influence of real storage conditions on the wax or its appropriate substitution sorption and desorption from different rubber samples using suitable methods will be investigated in the practical part of the Diploma Thesis.

1. Make a literature review on the given topic
2. Prepare rubber samples differing in their composition
2. Measure wax desorption/sorption characteristics of prepared samples
3. Evaluate and interpret obtained results

Thesis Extent:

Appendices:

Form of Thesis Elaboration: **printed/electronic**

Bibliography:

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3. Online databases accessible from TBU in Zlín.

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ABSTRACT

The theoretical part of the Master Thesis deals with the effect of wax during the caoutchouc processing and on the resulting rubber properties. Suitable substitution of the wax in order to eliminate the flowering problem while the positive properties for the final use as a silent block in automotive industry are maintained will be discussed as well. The influence of real storage conditions on the wax or its appropriate substitution sorption and desorption from different rubber samples using suitable methods is investigated in the practical part of the Master Thesis.

Keywords: Rubber, Wax, Flowering, Caoutchoc, Sorption, Desorption.

ABSTRAKT

Teoretická část diplomové práce se zabývá vlivem vosků při zpracování kaučukových směsí a na vlastnosti hotových pryžových výrobků. Je popsána možná náhrada běžných vosků za účelem snížení jejich vykvétání při zachování optimálních vlastností výrobků pro použití v podobě silentbloku v automobilovém průmyslu. V praktické části je zkoumána a pomocí vhodných metod následně vyhodnocována desorpce a sorpce vosku z pryžových výrobků o různém složení za reálných skladovacích podmínek.

Klíčová slova: Pryž, Vosk, Vykvétání, Kaučuk, Sorpce, Desorpce

ACKNOWLEDGEMENT

I would firstly like to thank my supervisor, Mr. Michal Sedlacik, for the patient guidance, encouragement and advice which he has provided throughout my time as his student. I have been extremely lucky to have a supervisor who cared so much about my work, and who responded to my questions and queries so promptly. I would also like to thank Mr. Dvorak and all the members of staff at Tomas Bata University.

I would like to express my special appreciation and thanks to Mr. Lukas Richter, you have been a tremendous mentor for me. I would like to thank you for encouraging me always.

A special thanks to my father Mr. Modnath Jha, my mother Mrs. Manju Jha and my sister Miss Swarna Jha. Your prayer for me was what sustained me this far. I would also like to thank all of my friends who supported me in writing, and motivated me to strive towards my goal.

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INTRODUCTION

Rubbers are viscoelastic polymeric materials having high elasticity, resilience, toughness, electrical insulation, moisture resistance, shock absorbance etc. Due to these properties, rubbers are used in every possible field, for example in cars, mechanical components, textiles etc. But rubber when exposed to air/sunlight produces cracks and hence deteriorates its properties. In order to avoid such problems antioxidants and anti ozonants are used. Wax is most widely used as antioxidant and antiozonant for rubbers as it plays an important role to protect rubber by migrating on the surface of rubber and thus forming a thin film which prevents contact of rubber from ozone and sunlight.

However sometimes excess of wax tends to migrate on the surface of the rubber and leads to deteriorated physical properties, surface interfacial properties and poor adhesion with itself or any other substrate.

This study is important on several grounds. The reason for discussing effect of outside condition on wax desorption and sorption is that these samples are to be used in stabilizer bars, and are expected to adhere on the surface of metal bars where wax is one of the main reason for bad bonding between rubber and metal.

The broad objective of this study is to analyse the phenomena of sorption and desorption in various rubber mixtures and to compare the results on basis of storage condition, time, wax type, concentration, and type of rubber etc. Only very few studies have been carried on wax migration till now. An adequate knowledge of the factors is important to achieve optimum adhesion.

I. THEORY

1 RUBBER

Rubber is an elastomeric polymer which is characterized by the presence of a network structure that when subjected to external forces may temporarily be deformed. In simple words they are the materials which show elastic properties. Products made from rubber are able to withstand under force large deformations due to a flexible and stable 3-Dimentional (3-D) chemical structures. For example rubber material can be stretched repeatedly to at least twice its original length and, it will return with force to approximately its original length, upon immediate release of the stress. Under certain load the product should not show creep or relaxation. The modulus of rubber is about 100 – 10,000 times lower when compared to other solid materials like steel, plastics and ceramics. The combination of these unique properties gives rubber its specific applications like in seals, shock absorbers and tires.

Rubber materials used these days consists of approximately 60 % of synthetic polymers followed by other additives which will be discussed in later sections. The additives are very important to achieve the desired properties of the final product. Few of its unique properties include high extensibility, high strength, high-energy absorption, and high resistance to fatigue followed by good environmental resistance and high resilience which are responsible for its versatile use. Natural rubber (NR) and synthetic rubber are both commercially used in the manufacturing of different types of products. Various types of synthetic rubbers are commercially used namely styrene-butadiene rubber (SBR), butadiene rubber (BR), ethylene-propylene diene monomer rubber (EPDM), butyl rubber (IIR), etc. One of the most important is SBR, which is primarily used as a major component of all passenger tires and also in significant amounts in most tire products. Rubbers usually undergo vulcanization or curing process in order to improve their properties. It is carried out mostly by reaction with sulphur, leading to the formation of a 3-D structure due to the formation of sulphur bridges between the polymer chains. Other vulcanizing agents are for example peroxides, metal oxides, amines, etc. The following sections deals with history of vulcanization, rubber production, its elasticity, curing, types and also the compounding ingredients. [1, 2]

1.1 History of vulcanization

Centuries after the initial discovery quite few products were made up of rubber usually it was limited to water proof coating or perhaps an eraser. Unvulcanized rubber cannot have a stable dimension and when wear it turn out to be very sticky. Vulcanization was discovered by Charles Goodyear in 1939. He discovered that when sulphur was added to raw rubber and then heated, the substance similar to putty, it lost its stickiness and was found to be elastic, i.e. it would come back to its original shape following any deformation. After this discovery rubber started being used in variety of consumer products until now.

A century after the discovery of vulcanization, most of the rubber goods were made from NR vulcanized with sulphur. But in the 20th century, synthetic rubbers were developed and were available for commercial uses. They were prepared by reaction of some low-molecular weight monomers to form polymers with long chain. Figure 1 explains the history of sulphur vulcanization. [3]

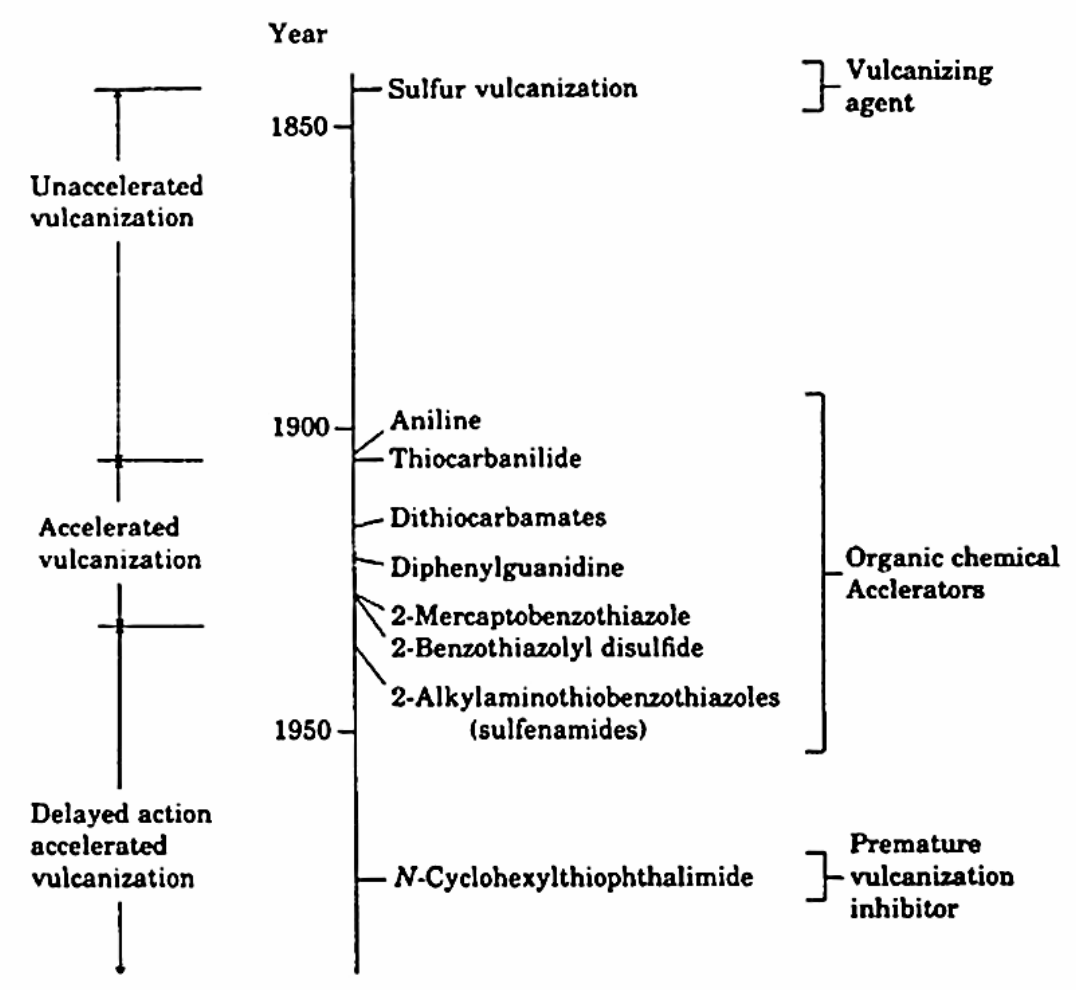

Figure 1: History of rubber vulcanization by sulphur [4]

1.2 Crosslinking and curing

On applying heat to the rubber mixture, a chemical reaction, namely vulcanization or cure, takes place. The process in which chains are chemically bonded to one another and forms a network, and hence transforms the elastomeric liquid into an elastic solid is known as curing. The chemical bonds and those atoms forming them are called crosslinks. In this process, the chain molecules are overlapped or better say tied together at various locations along their lengths by these crosslinks. Even though the crosslinks are far apart, still the effect on material properties is dramatic. The crosslinking is responsible for giving rubber its elastic properties. With higher crosslink the density, modulus, and strength increases while hysteresis and set decrease. During curing, sulphur atom bonds both chains at the points where double carbon-to-carbon bonds exist. Generally, the sulphur atoms form chains between them; for example, three sulphur atoms may exist between the two polymers chains linked together. The type and the level of crosslinking are both important. During sulphur curing (Figure 2), the type of crosslinks depends on of course sulphur level and accelerator type, accelerator/sulphur ratio, and cure time. Generally, high accelerator/sulphur ratio and large cure time will gradually increase the number of mono-sulphide linkages than that of polysulphide ones. On the other hand, compounds containing a large proportion of polysulphide crosslinks possess higher fatigue cracking resistance and tensile strength compared to compositions with mono-sulphide links [5].

The curing process is generally carried at a temperature of at least 140 °C, under pressure in metal molds and takes from a few minutes to several hours depending on the type of vulcanizing system being used. Peroxides are yet another type of curing agent for elastomers. Double bonds are not required for peroxide vulcanization unlike sulphur curing, and thus, they may be used to crosslink saturated rubbers. It occurs by a free radical mechanism leading to carbon-carbon crosslinks, which result in good aging, compression set resistance and are quite stable [3,5].

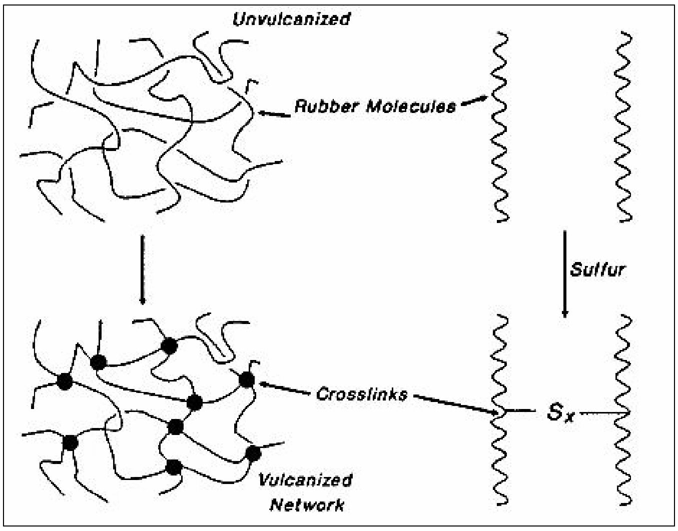

Figure 2: Crosslinking of rubber molecules by sulphur.

1.3 Elasticity of rubber

Rubber elasticity explains the behaviour of polymeric solids which are made up of flexible chains which are joined together to form a 3-D structure referred to as a network. Due to chain flexibility and connectivity, the network exhibits high elasticity and may be deformed reversely to several times of its original length. The state of deformation may be shear, extension, compression, or any combination of these. The volume of network may increase by several folds due to swelling in suitable diluents. Volume changes of such networks may be observed and managed precisely by modifying environmental variables, hence making networks suitable for controlled drug delivery, etc. Also, fillers can be used as reinforcement in a network to increase the ultimate properties, such as the ductility and strength, to levels needed in technological applications. The reversible large deformability and good swelling ability make elastomeric networks indispensable in technological applications [6].

As an engineering material, rubber is unique in its physical behaviour that is in between a solid and liquid giving the appearance of solidity, while possessing the ability to deform substantially. Many solid materials have an extensibility of only a few percent strains and only a small portion of that is elastic, better say Hookean in character, i.e. a linear stress-strain relationship. Rubbers may be extensible up to over 1000 % strain, almost all of which is elastic and non-Hookean. In the unvulcanized state rubber shows substantial flow apart from elasticity and should be regarded as a high-viscosity fluid, a factor which is crucial for manufacturing operations. Hence rubber is a viscoelastic material having complex flow behaviour [7].

Rubbers exhibit properties due to the fact that unlike conventional solids, in which atoms occupy fixed positions relative to each other, rubbers are formed from molecules that are arranged in order to form a flexible, polymer or long-chain macromolecule. Not all polymers are rubber-like, all rubbers are polymeric. The property that makes a polymer rubber-like is its ability to undergo rapid molecular movement, allowing it to deform readily, and its ability to return to its original configuration after the removal of deforming forces. A number of properties are required to attain rubber-like properties. Polymers may exhibit many different properties, which are dependent on temperature. Heat is a major source of the energy required for molecular mobility as shown in Figure 3. At lower temperatures, the polymer behaves as a rigid solid as the molecular rotation is slow. As temperature increases, the polymer become leathery, followed by being rubbery, then a transition to a rubbery fluid and finally total fluidity is achieved. A rubber, therefore, is a polymer whose rubbery region coincides with ambient temperature. On cooling, the rubbery behaviour will be lost (below the glass transition temperature) and, on heating, the rubber will ultimately become more fluid and flexible [8].

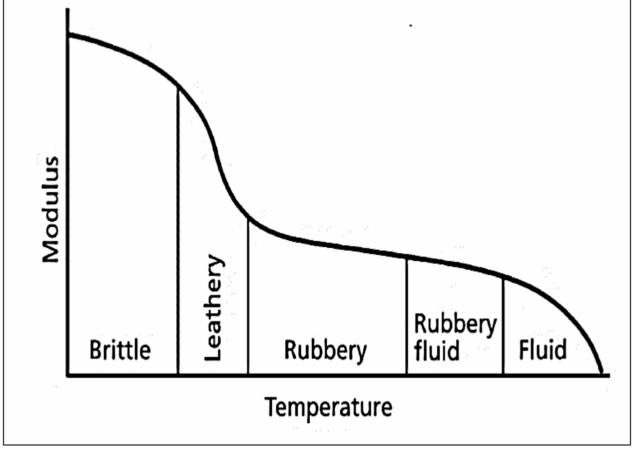

Figure 3: Variation of stiffness with temperature for polymers [8].

1.4 Types of rubber

Following are the names which refer to the raw gum elastomer and consequently are given to the name of the vulcanized compound.

1.4.1 Natural rubber

Natural rubber - Polyisoprene (IR) has the best elasticity among rubber types, very good resistance to abrasion and fatigue. The material's poor resistance to ozone (weather) and oils and fuels are its major drawbacks due to very long macromolecules in compared to synthetic rubbers. [9]

The latex of NR is gathered from the bark of the tree Hevea Brasiliensis by making cuts. Plantations are mainly done in Malaysia and other tropical countries. These trees are tapped for the latex on every second day. A milky fluid is produced out of the cuts, which is then coagulated and are sent for further processing into sheets for shipping. Even at this stage the raw rubber and has very little practical use. It tends to flows under load and remains in deformed shape after the removal of load. It crystallizes at temperatures around 0 °C and below and also becomes sticky and soft when warm. Most NR latex is produced in Southeast Asia and Thailand. [3]

Polyisoprene has the same chemical structure (Figure 4) as NR but without proteins, fatty acids and the other substances that are contained in NR and has inferior physical properties in general to NR but, in principle; the two types are very alike. Polyisoprene rubber is used in the similar products as NR [3].

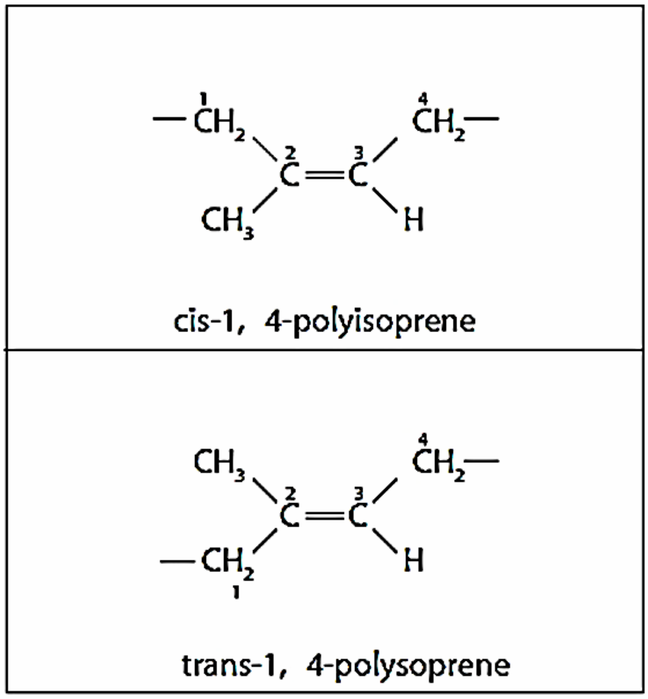

Figure 4: Chemical structure of NR geometrical pattern [3].

Main application of NR is in the production of heavy-duty tires, springs, vibration dampers, and bearings. Other special applications are in conveyor belts, coated fabrics, hoses seals etc.

1.4.2 Styrene butadiene rubber

Followed by the development of the automobile industry, demands for rubber increased rapidly. Experiments were made to synthesize a man-made rubber. At first synthetic rubber could not match NR, but after continuous research now synthetic rubber has comparable properties with NR or even better in some cases.

The most common and cheapest synthetic rubber is SBR. It is derived from petroleum (oil). Styrene and butadiene are produced by the distillation process at the oil refineries, and are then used as raw materials for the production of SBR.

The first step is the reaction of styrene and butadiene and the new material formed consists of around 25 % of styrene, and rest is butadiene. Finally SBR is formed which has a chemical structure as shown in Figure 5. It has a better heat resistance but inferior temperature flexibility and tensile strength in comparison to NR.

Styrene butadiene rubber is used in many of the same products as NR, for example to cover different types of hose and also in other products [9, 10].

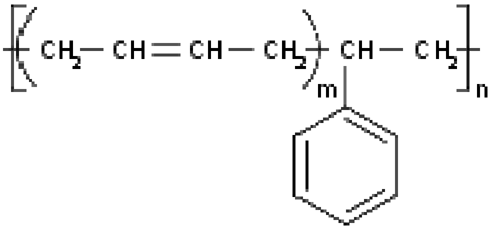

Figure 5: Chemical structure of SBR [11].

1.4.3 Butadiene rubber

Butadiene rubber is polymerized butadiene having chemical structure as shown in Figure 6. Usually it is used in blends with different rubber types to improve elasticity, wear resistance due to its superior low temperature properties. It has a typical application in truck tires in blends with NR. One of the most important applications of such rubber is in the manufacturing of high impact polystyrene [9, 12].

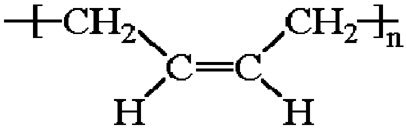

Figure 6: Chemical structure of Butadiene rubber [13].

1.5 Special types of rubber

The general purpose rubbers were discussed in the above section. Many other types are also available, each having its own special properties which are as follows.

1.5.1 Ethylene-propylene diene monomer rubber

For manufacture of the sheet used at high temperatures, EPDM rubber is used. The first two letters, E and P means that the rubber consists of ethylene and propylene, and the letter D tells us that a diene is present as well. Diene makes it possible to cure the rubber with sulphur due to double bonds into the structure, and hence change the structure to an unsaturated polymer as shown in Figure 7 [14, 9].

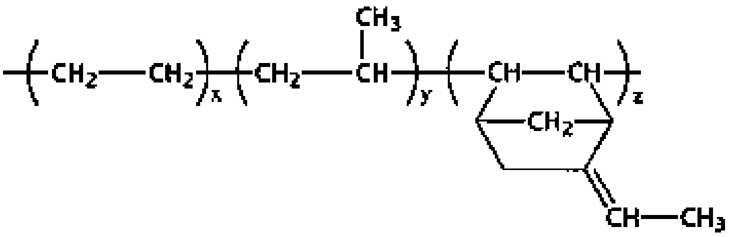

Figure 7: Chemical structure of EPDM rubber [15].

1.5.2 Butyl rubber

Products with high gas permeability resistance are based on IIR. It consists of isobutene with a minor part of isoprene which can be seen in Figure 8. It is isoprene which makes the rubber unsaturated and possible to vulcanize. Usually the gas permeability increases with increased temperature for all rubber types, but for IIR it is very low, up to 71-75 °C. Tire inner tubes are typical applications of IIR. It is an amorphous material which crystalizes on applying stress [16, 17].

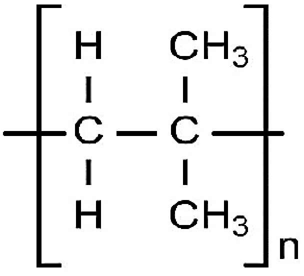

Figure 8: Chemical structure of IIR [10].

1.5.3 Chloroprene rubber

It is one of the earliest used of synthetic rubber. The Chloroprene rubber (CR) types consist mainly of polymerized CR monomers. Refer Figure 9 for chemical structure of CR. It has good weather and reasonable oil resistance. Hence it's used in products exposed to oil-based fuels and weather. Its high cost has limited its use [18].

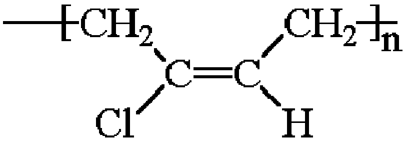

Figure 9: Chemical structure of CR [19].

1.5.4 Nitrile rubber

Nitrile rubber is a copolymer of acrylonitrile and butadiene having chemical structure as shown in Figure 10. It is the mostly used for products that are in contact with oil and fuel and is therefore used for example in inner tubes for fuel and oil hoses [9, 20].

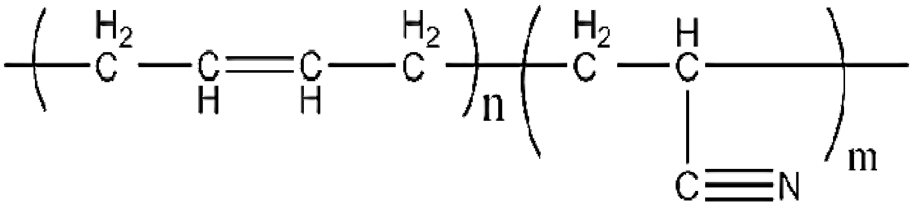

Figure 10: Structure chemical structure of NBR [21].

1.6 Properties of rubber

Some of the very important properties for rubber materials include thermal, electrical, mechanical, optical, physical, and processing properties. The most important properties are explained in more details in the following sections.

1.6.1 Specific gravity

This property is fully depends on the composition of the material. Difference in value will result in different unknown material with different composition. The specific gravity is defined as the mass per unit volume and can be measured by weighing the sample in air and in water [2].

Standards: ISO (International standard organization) 2871, ASTM D (American Society for Testing and Materials) 1817 [22].

1.6.2 Hardness

Hardness represents the elasticity of the material. This means, the hardness is inversely proportional to elasticity. The scale which is normally used is Shore-A.

Standards: ISO 48, ISO 1400, ASTM D 2240, ASTM D 1415 [23].

1.6.3 Tensile strength, elongation

Tensile strength is the maximum tensile stress required to stretch a test piece, which generally has a flat dumb-bell shape, to its breaking point. This force needed is expressed as force per unit area of the original cross section of the test length [2].

Standards: ISO 37, ASTM D 412 [24].

1.6.4 Compression set

A rubber has a tendency to deform under load and rarely return completely to their original dimensions once the load is removed. This difference between the original and final dimensions is known as compression set.

Standards: ISO 815, ASTM D 395 [25].

1.6.5 Resistance to heat aging

The properties of an elastomer can change after prolonged exposure to high temperatures. Such tests for heat aging are carried out for two main reasons. Firstly, in order to establish the changes in physical properties at elevated service temperatures. Secondly, accelerated tests at high temperatures predict the long-term life at lower temperatures. Such experiments are carried out in an air oven or an oxygen pressure chamber.

Standards: ISO 188, ASTM D 573 [26].

1.6.6 Resistance to weathering

On exposer to weather the property of rubber may deteriorate. Such deterioration can be observed as cracks, peels, chalking, colour changes and other surface defects. One of the most important causes of deterioration by weathering is the presence of ozone. Less than one ppm of ozone in the atmosphere can severely attack non-resistant rubbers if they are in a slightly strained condition. The results are cracks sheer on the direction of the strain. Other factors which affect rubbers may include sunlight, oxygen, moisture and temperature.

Standards: 1431/1, ASTM D 1149 [27].

1.6.7 Resistance to low temperatures

Even at lower temperature rubber undergoes some changes, few of them occur immediately were as some occur after prolonged time. But these changes are reversible once it comes back to room temperature. Few defects which occur at low temperature include being brittle and shatter on sudden bending or impact. Brittle point is the temperature when this takes place.

Standards: ISO R 812, ISO 2921, ASTM D 2137, ADTM D 1053, ASTM D 1329 [28]

1.6.8 Abrasion resistance

A test piece is pressed against a rotating drum which is covered with an abrasive cloth. The weight (volume) loss is measured after a certain number of revolutions and which gives an indication of the abrasion resistance.

Standards: ISO 4649, ASTM D 394 [29].

1.6.9 Resistance to liquids

On coming in contact with liquid, rubbers may absorb the liquid. This absorption is usually higher than extraction and there is a net increase in volume which is usually known as swelling.

Standards: ISO 1817, ASTM D 1817 [22].

Many other properties can be tested as well, depending on the application. The most suitable tests can be selected and performed to give the best results to predict the lifetime of a product. Properties of different types of rubbers can be found in Table 1 [9].

Table 1: Properties of different types of rubber. [9]

PROPERTY	NR/IR	SBR	BR	EPDM	IIR	CR	NBR
Max temp. of use [°C]	80	90	80	120	90	85	90
Min temp. of use [°C]	-50	-40	-75	-35	-45	-35	-30
Tear strength	4	3	3	3	3	3	3
Abrasion resistance	4-5	4-5	5	3	3	3-4	3
Oil/fuel resistance	1	1	1	1	1	2-3	3-4
Weather/ozone resistance	1-2	1-2	1-2	5	4	3	1-2
Water swelling	4	4	4	5	4	2-3	3-4
Fire resistance	1	1	1	1	1	3	1
Rebound at low temp.	5	3	5	3	1	3	3
Rebound at high temp.	5	3	5	3	3	4	3
Fatigue	4	4	4	3	3	4	2
Bonding to metal	4-5	4-5	4-5	3	2	4	4
Bonding to textile	4-5	4-5	4-5	3	2	4-5	3-4

Grading of properties: 5 excellent, 4 very good, 3 good, 2 satisfactory and 1 poor.

1.7 Additives

To produce a useful end product, rubbers are mixed with suitable ingredients better known as additives during compounding. These additives are broadly classified into fillers, accelerators, reinforcing agents, retarders, activators, antioxidants, colouring agents, rubber process oils, softeners, and vulcanizing agents. Few other classes of products which do not belong to the above classes are dusting and anti-tack. In the following sections types of additives will be discussed in detail.

1.7.1 Accelerators

Accelerators are of two types organic and inorganic. Organic accelerators are known to the rubber industry for over a century due to their use in rubber compounding which has become universal. Some of organic accelerators include hexamine, mercapto-N-cyclohexyl benzo thiazole sulphen amide, sodium diethyl dithio carbamate, tetramethyl thiuram disulphide, tetra methyl thiuram mono sulphide, etc. The above mentioned examples represent almost all the range of organic accelerators from moderate to ultra-accelerators. Inorganic accelerators used in slow curing products like rubber lining for example lime and litharge. Accelerators reduce the time required for vulcanization up to an extent it has other advantages too like of using accelerators are economy of heat, improved physical properties, greater uniformity of finished goods, improved appearance, and better resistance to deterioration.

Apart from to controlling the time and rate of vulcanization during curing process; it also controls the number and type of sulphur crosslinks which are formed [30].

1.7.2 Activators

Activators increase the vulcanization rate simply by reacting with the accelerators. Thus activators help accelerators in the vulcanization process. Zinc oxide and stearic acid are widely used as activators; Zinc oxide is also reinforcing filler [30].

1.7.3 Retarders

Retarders are used to delay the initial onset of vulcanization and also used to prevent premature vulcanization, during processing and storing called scorching of compounds. During mixing and further processing in an extruder, calendar or molding press, the rubber compound is continuously subjected to heat resulting in premature curing or pre-curing, use of retarders helps to prevent it. One of the well-known retarder is salicylic acid for NR compounds. Excessive use of retarders may lead to porosity in compounds [30].

1.7.4 Anti-oxidants

Inhibitors are used to prevent degradation of rubbers by oxidation, which is used during compounding of rubber. These inhibitors are called antioxidants. The antioxidants are grouped into amine types and phenolic types according to commercial availability. Straining peroxides are the products derived from amines, mostly aniline or di-phenyl amine, because they tend to discolour non-black vulcanizates on exposure to light, and products derived from phenol are called non-staining antioxidants.

Anti-oxidants must have the following properties, in order to fulfil their role:

- Thermal stability and non-volatile at processing temperatures
- It must be miscible in the polymer
- It shouldn’t leach out of the polymer on contact with solvents
- It shouldn’t corrode the processing equipment with acidic decomposition products
- It must be odourless, tasteless and not colour (including its degradation products)

Primary anti-oxidants are radical scavengers; it reacts with alkyl chain radicals or hydro peroxides (ROOH). Secondary anti-oxidants work in combination with primary anti-oxidants and principally act by converting peroxide radicals into non-radical stable products. Synergism often works when both classes are used together [31].

1.7.5 Process oils and plasticizers

These materials are used mainly to aid in the processing operations such as mixing, calendering, and extruding of rubbers. Usually used with fillers to reduce the cost of the compound. Paraffin waxes with a low melting point are used as plasticizers as well as antioxidant and antiozonants. They bloom to the surface and protect ozone sensitive rubbers against cracking under static stress. Different types of resins are used as plasticizers; for example, high styrene resins, phenolic resins, coumarone resins, and petroleum resins, etc. It provides very good flow characteristics to rubber compounds during extruding, and molding [30, 32].

1.7.6 Fillers

Some typical rubber fillers are namely clays, calcium carbonate, silica, etc. Carbon black is used to improve the strength of the rubber. The performance of carbon black incorporated into rubber largely depends on its oil number. Tires contain over 30 weight percentage of carbon black which is quite significant amount [2].

There are generally two categories of fillers, reinforcing and inert fillers. It has a pronounced effect on the physical properties of rubbers, such as abrasion resistance, tear resistance, tensile strength, and fatigue resistance, are called reinforcing fillers. Fillers which have no influence on the above mentioned properties are called inert fillers for example graphite and ebonite powder [30].

1.7.7 Vulcanizing agents

Vulcanization is derived from Vulcanus, the Roman god of fire and Smithery. It is the process whereby viscous and tacky raw rubber is converted into an elastic material through the incorporation of chemical crosslinks between the polymer chains. Sulphur is the most used vulcanization agent for rubbers with unsaturation such vulcanization always includes the use of accelerators, which shortens the time for curing. In Table 2 we can see that different lengths of sulphur crosslinks are obtained depending on the amount of accelerator used. Nevertheless, the final properties of the vulcanizates will differ depending on the type of vulcanization system used. A conventional system will give show mechanical properties, such as tensile strength, than an Elevated pressure (EV) system. On the other hand, the ageing properties will be vice versa since in this respect the EV system is superior to the conventional system [33].

Other types of vulcanization systems include peroxides, generally used to crosslink for example silicone, fluorocarbon, diene rubbers, metal oxides, and crosslinking with β-electron beam or γ-radiation. They involve the use of reactive chemicals, often of low molecular weight (except for the radiation-curing).

Table 2: Different systems used in sulphur vulcanization. [33]

Type of system	Sulphur/accelerator ratio	Type of crosslinks
Conventional	>2	-Sx-, cyclic sulphides
Semi EV	~1-2	C-S_2-C, C-S-C
EV	<0.3	C-S-C, C-S_2-C, C-C

The vulcanization curve represents the degree of crosslinking during vulcanization of a compound, showing some property proportional to the degree of crosslinking versus vulcanization time. It is usually done as a routine measurement (e.g. by oscillating disc or moving die rheometer) in the rubber industry and is of large importance in order to obtain products vulcanized to a certain level. Typical vulcanization curves may look as in Figure 11.

The upper curve (A) shows a marching behaviour that can be seen in CR and SBR-based compounds. (B) Is the ideal behaviours where the cure level reaches a plateau level, typical for NBR, and (C) shows reversion.

Scorch time is the time from the start of the measurement to the onset of the crosslinking process (i.e. when the increase in the curve starts) [33].

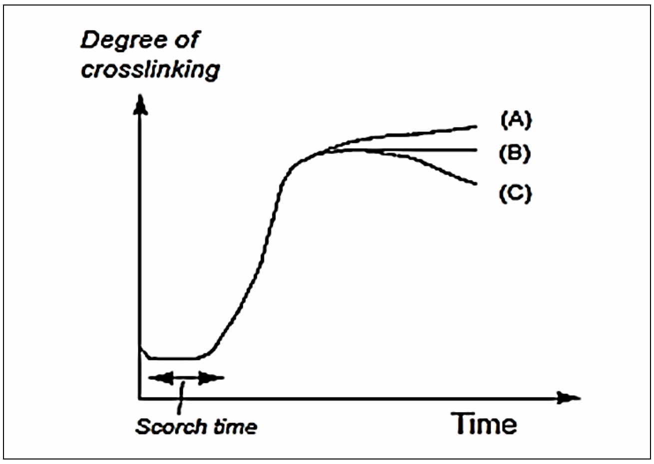

Figure 11: Vulcanization curves showing (A) marching behavior, (B) plateau level, and (C) Reversion [33].

1.7.8 Pigments in light-coloured compounds

Pigments are the virtually insoluble, finely dispersed colorant in binders, solid, solvents or binder dispersants, which gives a coloured appearance when finely distributed. It can be used in the form of inorganic or organic pigment is during textile printing, in pigment dyeing, for paints, etc. Plastics can be dyed using soluble or insoluble, inorganic or organic dyes. The one which is insoluble are called pigments. Dyes and pigments are generally added to plastics in quantities of 0.001–5 %. [34]

1.7.9 Antistatic lubricants

Materials such as plastics, rubber and synthetic fibres show the ability to generate strong electrostatic charges on being rubbed (tribocharging) or by induction (transfer from other charged materials). Nasty or sometimes even dangerous effects may result. Soil may be attracted to plastic articles making them look unattractive, textile fabrics may stick to each other, and uncomfortable electric shocks may be experienced by people walking on a synthetic fibre carpet and may even have dangerous effects like explosions at sudden discharging. It is therefore highly desirable to control this static electricity by use of antistatic lubricants. This can be done either by addition of conductive substances (metal, car-bon black, graphite) to the polymer mass or by addition of polar organic substances (surfactants) to the batch prior to compounding. Antistatic agents can also be on to the surface by padding or spraying. So, generally antistatic agent acts by creating a film of higher humidity on the surface [35].

1.7.10 Blowing agents for sponge rubber

Blowing agent is a substance responsible to incorporated into a mixture in order to produce foam. One of its type decomposes when heated to processing temperature and evolve a gas, usually carbon dioxide, which is suspended in small globules in the mixture for example sodium bicarbonate or ammonium carbonate (cellular or sponge rubber), halocarbons and methylene chloride in urethane, baking powder (bread and cake), pentane in expanded polystyrene, and hydrazine and related compounds in various types of foamed plastics. Other type is when air used at room temperature as a blowing agent for rubber latex. It can be introduced mechanically by whipping, after which the latex is coagulated with acid [36].

1.7.11 Flame retarders to improve non-inflammability

Flame retardants are the additives which suppress or delay the production of flames to prevent the spread of fire it can be added to materials, such as plastics and textiles, and surface finishes and coatings. Flame retarders can be mixed with the base material (additive flame retardants) or chemically bonded to it (reactive flame retardants). Mineral flame retardants are used just as an additive while organo-halogen and organo-phosphorus compounds can be either reactive or additive. [37]

1.7.12 Reinforcement

In order to increase the mechanical strength, many rubber products are reinforced. It can be in the form of fibre, granules etc. Now day's reinforcements are used widely in hoses, in protective clothing etc. [9]

2 WAX EFFECTS IN RUBBER

Waxes are used in the rubber industry for the production of rubber hoses, conveyor belts, rubber toys, fitting gloves, tires, gaskets and many other similar rubber applications.
Waxes have the following applications in rubber industry [38]:

- It acts as antiozonant, by migrating on to the surface a thin protective layer is formed insuring protection against ozone attack and brittleness. Paraffin Wax gives rapid protection for newly produced goods but in case of microcrystalline Wax, it provides durable protection and slow release. The just right composition of paraffin waxes and microcrystalline waxes guarantees the control of migration insuring the quick acting and long lasting.
- Wax is used as a carrier for protective chemicals.
- Wax is used as mold release agent, anti-aging agent, plasticizer and lubricant in the rubber and tire industry.

Rubber on exposure to air or sun light produces cracks, and if any tensile stress is applied the cracks appears clearly. To avoid these cracks so far it has been known to use the antioxidants from amines and those from wax. Usually amines are subjected to a chemical reaction selectively with ozone and consumes the ozone in the surface layer of rubber to prevent the rubber from aging under static or dynamic conditions, whereas wax incorporated in a rubber exudes to the surface to form a thin film, which prevents the rubber from contacting with ozone to produce an antioxidizing effect, particularly under static conditions. Moreover, generally the above two kinds of agents are used together at the same time. The antioxidant wax for rubber relates to the latter, namely, the static antioxidant.

Since old times various antioxidant wax for rubber have been available commercially. For such antioxidant mainly used for rubber, however, properties often vary according to temperature. This means that due to their unsuitable carbon to carbon bonding mode and carbon number distribution, those agents (wax in this case) have made excessive wax bloom exuded on the rubber surface at a specified temperature and the appearance of rubber surface significantly worse and lead to deterioration of physical properties, and therefore was not economical. [39]

For protection against ozone manufacturers add waxes to their compounds at common dose rates between 1 and 3 parts per hundred parts of rubber (phr). During operation the rubber parts bends and flexes, leading to the migration of the antiozonant wax to the surface of the rubber part forming a thin, protective wax film. This migration increases with increasing temperature. Ozone attack on rubber compounds can take place in a temperature range between 0-55°C. Below this temperature range the ozone does not have activation energy high enough to react with the rubber and above this temperature range ozone levels in the atmosphere decrease to minimal levels. The solubility of antiozonant waxes in rubber is increased with decreasing molecular weight (carbon atom number). Wax migrates from the bulk of a rubber article to its surface to form a physical barrier to ozone attack. The extent of migration depends upon the solubility/mobility or sorption/desorption characteristics of the specific wax under a given set of environmental conditions. [40]

Following are the factors which influence migration include:

- Time
- Temperature of storage after cure
- Wax concentration
- Wax composition
- Amount and type of filler
- Extender oil present.

These factors make it difficult to choose a wax which performs effectively over a broad temperature range. Paraffin waxes usually protect better at low exposure temperatures, whereas microcrystalline waxes are more effective at elevated temperatures. In this case wax blends offer a wider temperature range of protection. An optimum migration temperature exists for each wax, and dynamic thermal analysis (DTA) can predict this optimum. Best ozone resistance is also attained at the temperature corresponding to optimum wax migration [40]. Despite of having poor mechanical properties, use of additives can make it suitable for different applications. The type and quantity of additives in the mixture depends on the chemical nature of the base rubber as well as the properties expected in the finished products [41]. Once these properties are attained now it becomes necessary to prevent it from changing during service, one of the main problems occurs due to oxidation and ozone attack. In order to prevent this antioxidants and antiozonant are added in the rubber mixture. As we already discussed various additives which are added into rubber mixture include filler, antioxidants, vulcanizing agents and activators, but the problem arises when during vulcanization stearic acid is added which react with zinc oxide forming zinc stearate combined with hexamethylene tetra mine to form an highly unstable complex followed by its migration onto the rubber surface which results in anti-adhesion properties [42].

Whereas some additives such as wax are responsible for desorption on the surface i.e. migration of wax to the surface forming a thin film [43], which acts as a physical barrier against ozone attack [44,45].

This phenomenon occurs continuously until as equilibrium is reached, and depends on rubber composition, the specific wax nature and exposure to ozone condition which includes temperature and time [46]. Also this migration depends upon adhesion and density of the rubber [44].

Two types of waxes are used commonly these days to protect rubber against ozone namely paraffin wax and microcrystalline wax which would be discussed in further sections [47].

Although this migration or better say blooming protects the rubber from ozone etc. but at the same time it affects the surface interfacial and adhesion properties. It reduces the surface free energy resulting in poor adhesion to itself and to other materials such as stabilizer bar in our case. This weak layer of wax on the surface has been recognized as the main reason of poor adhesion [48].

Among the first study on the Migration or blooming of antiozonant wax to the rubber surface was carried out by carbon-14 tracing in synthetic and natural rubber containing an oil extender [49]. Lederer and Fath [50] confirmed migration of wax on rubber surface by scanning electron microscopy (SEM). One of the reported studies on migration of wax on rubber surface was carried by Choi [51-53]. Among his findings one was that the amount of wax inversely proportional to the length of carbon chain i.e. amount of wax migrated to the surface increased when the carbon chains were shorter [51]. It was also studied that the amount of wax or the thickness of wax on the surface has very little effect on the migration of wax [52-53]. In

Figure 12 the amount of wax blooming with respect to temp can be seen. Also in Figure 13 the effects of wax and PPD (p- Phenylenediamine) on ozone protection under static, dynamic and intermittent conditions.

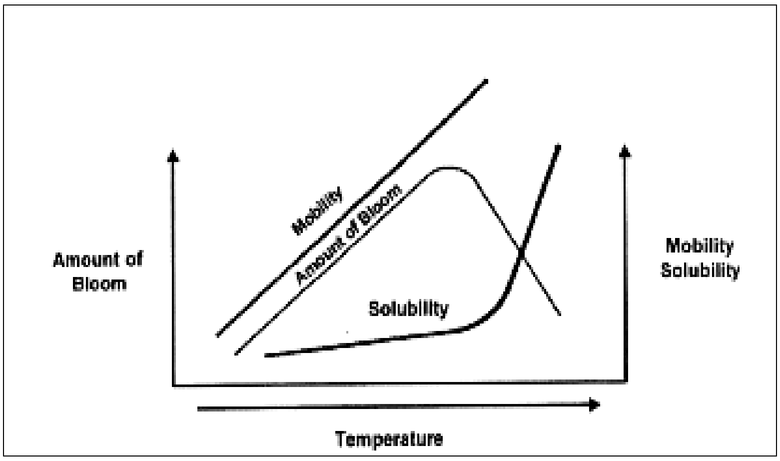

Figure 12: Effect of solubility and mobility on wax bloom. [54]

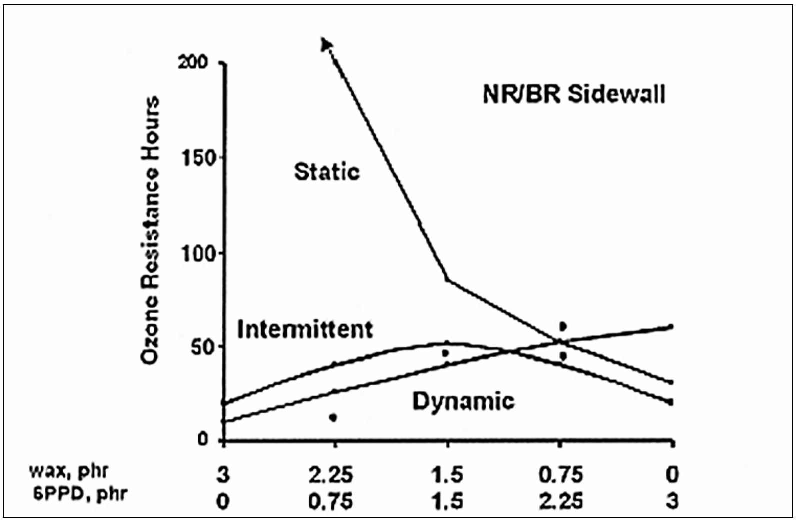

Figure 13: Effects of wax and PPD on ozone protection under static, dynamic and intermittent conditions. [54]

2.1 Waxes

Waxes are also a class of materials used to enhance rubber ozone protection primarily under static conditions.

Waxes used in elastomeric formulations are of two categories:

- Microcrystalline
- Paraffin.

Microcrystalline wax's melting point lies in the order of 55 -100 °C and it is ultimately a product derived from petroleum. Paraffin wax's melting point falls in the range of 35–75 °C and is extracted from the light lube distillate of crude oil. The properties of waxes are listed in Table 3 below. As discussed earlier these waxes safeguards rubber against static ozonolysis by forming a barrier on the rubber surface. Migration of the wax is a continuous process in case of rubbers from the bulk to maintain an equilibrium concentration on the surface of the rubber. On the other hand microcrystalline waxes also do migrate on the surface of the rubber but at a slower rate than the paraffin wax because of the higher molecular weight and branching. Furthermore, microcrystalline waxes outclass paraffin waxes to perform best at high service temperatures, whereas paraffin waxes show best ability at low temperatures. This is associated to the rate of migration of the wax to the product surface. [55]

Table 3: Comparison of microcrystalline and paraffin waxes. [7]

Property	Microcrystalline	Paraffins
Molecular Weight	500-800	340-430
Melting Point (°C)	55-100	35-75
Mean Carbon chain length	C-25	C-60
Features	Branched molecule	Linear Molecule
Physical property	Malleable	Brittle
Crystallinity	Amorphous	Crystalline
Colour	White- Coloured	White
Hardness	Soft	Hard
Transparency	Opaque	Translucent

It should be noted that dynamic conditions leads to the breakdown of the protective wax film, after which the anti-ozonants system in the rubber formulation will serve as the primary stabilizer. Protection against ozone for products in storage, such as tires in a ware house is the prime motive for using waxes in rubber.

In summary, a number of methods can be employed to develop an anti-degradant system for a rubber formulation [7]:

- Short-term static protection is attained by use of paraffin waxes
- Microcrystalline waxes impart or deliver long lasting ozone protection while the finished product is in storage
- Static-ozone protection can only occurs if there is critical wax bloom on the surface of the rubber
- Optimized blends of waxes and polymer photo-detectors provide long-term product protection under both static and dynamic applications and over a range of temperatures
- Excess levels of wax bloom can have a pernicious effect on fatigue resistance, because the thick layer of wax can undergo crack under strain and the crack can start propagating into the product

Although few things about both microcrystalline wax and paraffin wax have been already discussed, it would be better to discuss it separately in the next section.

2.1.1 Microcrystalline wax

Microcrystalline wax is a mixture of solid, saturated aliphatic hydrocarbons, made by de-oiling certain fractions from the petroleum refining process. Microcrystalline waxes are different from paraffin wax due to its molecular structure which is more branched and contains hydrocarbon chains which are longer resulting in higher molecular weight. Due to this the crystal structure of microcrystalline wax is much finer than paraffin wax, and this directly influences many of the physical properties. Microcrystalline waxes are having superior qualities that includes tougher, more flexible and generally higher in melting point than paraffin wax. The fine crystal structure also helps microcrystalline wax to bind solvents or oil, and thus saves the sweating-out of compositions.

In disparity to the more familiar paraffin wax which contains alkanes mostly unbranched, microcrystalline wax contains iso-paraffinic (branched) hydrocarbons and naphthenic hydrocarbons. It has smaller crystal size as compared to paraffin wax. It comprises of high molecular weight saturated aliphatic hydrocarbons. It is basically darker, denser, more elastic, viscous and tackier than paraffin waxes, and has a higher melting point and molecular weight. The adhesive and elastic properties of microcrystalline waxes are because of the non-straight chain components which they contain. Generally microcrystalline wax crystal structure is small and thin, making them more flexible as compared to paraffin wax. It is extensively used in cosmetic formulations [56].

Because the matrix consists of extremely small crystals, they are sometimes also referred as amorphous wax. In the case of molecular structure of both the waxes a complex mixture of hydrocarbons including polycyclic compounds, normal paraffin, monocyclic compounds and branched paraffin [55].

Microcrystalline wax has broad use in industries such as the tire and rubber, castings, candles, corrugated board, adhesives, and cosmetics. Microcrystalline waxes have exceptionally great demand regarding small sculptures and custom made jewellery. Different formulations give waxes ranging from soft enough to be molded by hand to those hard enough to be carved with rotary tools respectively. The melted wax can be casted to make multiple copies that are further carved with details. Wax molded into the basic forms of rings as well as details that can be welded together by heating and sheets and tubes for cutting and building the models made of wax. Microcrystalline waxes are extensively used to modify the crystalline properties of paraffin wax. The microcrystalline wax affects the branching of the carbon chains in the backbone of paraffin wax. This is vital when some desired changes are needed in the paraffin wax, such as flexibility, higher melt point, flexibility and increased opacity. They also have their application as a slip agent in printing ink. Microcrystalline wax is also used in sports application, specifically in snowboarding and ice hockey. It is applied to the friction tape of an ice hockey stick to prevent degradation of the tape due to water destroying the glue on the tape and also to increase control of the hockey puck due to the waxes adhesive quality. It is also used in snowboards' underside to reduce friction and increase the gliding ability of the board, making it easier to control and reducing the lethargy of the rider. [56]

2.1.2 Paraffin Wax

Paraffin wax is a white or colour less soft solid derived from petroleum. It consists of a mixture of hydrocarbon molecules containing between 20-40 carbon atoms, typical component of paraffin wax is a hydrocarbon $C_{31}H_{64}$. It is solid at room temperature and has a melting point approximately 35-75 °C; its boiling point is greater than 370 °C. Paraffin wax is mostly odourless, tasteless, and waxy with density of around 900 kg/m^3. It is insoluble in water, but soluble in benzene, ether and certain esters.

Paraffin Wax is a natural product derived from the molecular components of decayed vegetable and material derived from animals. Paraffin wax consists of a complex mixture of hydrocarbons with the following general properties.

- Non-reactive
- Non-toxic
- Good water barrier
- Clean-burning fuel
- Colourless

Paraffin waxes are characterized by a clearly defined crystal structure and have the tendency to be hard and brittle. [56]

2.2 Substitutes for wax

Wax has good anti-ozone and anti-stress properties but regardless of this fact it is also true that it is one of the main causes responsible for poor adhesion between rubber and stabilizer bars. There are few other ways to protect rubber from ozone, i.e. by addition of ozone-resistant polymers such as halobutyl, polyethylene, polyvinyl acetate etc. to the rubber mixture. According to microscopic studies these mixtures show that these added polymer acts as a separate and dispersed phase. [57] These anti-ozone polymers also reduces the stress at the crack tip, which leads to increase of critical stress for cracking to take place resulting in cease of crack grow. In dynamic conditions where very less or no stress is required, such polymers helps to prevent cracking by reducing segmental motion of rubber chains. But the disadvantage of this method is that it is only effective when the polymer level lies between 20–50 %. Higher level leads to depletion in ozone protection. [58] Whereas at lower levels the propagation cracks obstacle the reduction of segmental motion sufficiently. This method of using ozone resistant polymers is used on limited basis, since the final product exhibit poorer properties. But it is the only effective way of protecting rubber in dynamic conditions without discolouring it. [59]

Apart from this different surface treatments such as solvent wiping [59,60], halogenation [61], corona discharge [62,63], low pressure and atmospheric plasma [63-66] or ultraviolet radiation [67-69] have been proposed to improve adhesion property by removing weak boundary layer. In the first stage the effectiveness can be noticed but in later stages it fails and the wax starts to migrate on the surface hampering the adhesion.

Although some research has been carried out [70] but the wax sorption and desorption phenomena has not been properly studied. In the next part this phenomena will be studied in detail.

II. ANALYSIS

3 AIM OF WORK

The aim of this Master Thesis is to study the wax sorption and desorption phenomena in rubber mixture in different storage conditions in order to eliminate the flowering problem which affects the adhesion of rubber to metal which would be used in stabilizer bar in an automobile industry.

Individual objective of the thesis can be summarized in the following points:

- To prepare samples with two different types of rubber mixtures with two different types of waxes and with 3 different concentrations.
- To determine the vulcanization time of these mixture by moving disc rheometer.
- To prepare rubber samples by compression moulding process.
- To determine melting point of both types of waxes by Thermogravimetric Analysis (TGA) and prepare samples of both the waxes.
- To measure Attenuated Total multiple Reflection – Infra-Red Spectroscopy (FTIR-ATR) of all the samples both in summer and winter condition.
- To measure contact angles of all the samples both in summer and winter condition.
- To take photographs of all the samples in both the conditions every day at same time in both the summer and winter condition.
- To do SEM of the samples.

4 PREPARING RUBBER MIXTURES

This section deals mainly with preparation of rubber samples. Two types of rubber mixtures were used for this purpose, i.e. one containing NR and the other containing mixture of NR, Buna Rubber and SBR, and at this point the samples are also assigned names, A and B, respectively. The formulation of first mixing step of rubber mixtures under investigation are given in Tables 4 and 5.

Table 4: First step of mixing- formulation of NR mixture (A).

Mixture Name	**A**
Ingredient	phr
Natural rubber	85
Carbon black	5
Zinc oxide	3
Total	**93**

Table 5: First step of mixing- formulation of NR, Buna rubber and SRB mixture (B).

Mixture Name	**B**
Ingredient	phr
Natural rubber	50
Buna rubber	25
Styrene butadiene rubber	25
Carbon black	44
Active silica	10
Plasticizer	12
Zinc oxide	3
Silanes	2.5
Total	**171.5**

Density of sample A after the first step of mixing was 0.972 g/cm^3 and that for B was 1.119 g/cm^3.

Carbon black, three types of anti-oxidants and two types of waxes, i.e. paraffin and microcrystalline wax, of three different concentrations were added in rubber mixtures A and B in the second mixing step (Tables 6 and 7). It must be noted that there were only two concentrations for microcrystalline wax for sample B due to lack of material. The densities of sample A and B after second mixing were 1.112 g/cm^3 and 1.136 g/cm^3, respectively.

Table 6: Second step mixing- formulation of rubber mixture A with two types of wax in 3 different concentrations.

Compound name	**A1**	**A2**	**A3**		**A4**	**A5**	**A6**
Ingredients		phr				phr	
Sample A	93	93	93		93	93	93
Buna rubber	15	15	15		15	15	15
Carbon black	40.5	40.5	40.5		40.5	40.5	40.5
Active silica	4.5	4.5	4.5		4.5	4.5	4.5
Antioxidant(1)	1	1	1		1	1	1
Antioxidant(2)	1.5	1.5	1.5		1.5	1.5	1.5
Antioxidant(3)	0.75	0.75	0.75		0.75	0.75	0.75
Paraffin Wax	1	1.5	2	Microcrystalline wax	1	1.5	2
Stearic acid	1	1	1		1	1	1
Processing Additive	3	3	3		3	3	3
Total	**161.25**	**161.75**	**162.25**		**161.25**	**167.35**	**162.25**

Table 7: Second step mixing- formulation of rubber mixture B with two types of wax, followed by 3 different concentrations of paraffin wax and 2 different concentration of microcrystalline wax.

Compound Name	B1	B2	B3		B4	B6
Ingredients	phr				phr	
Sample B	171.5	171.5	171.5		171.5	171.5
Carbon black	10	10	10		10	10
Antioxidant(1)	1	1	1		1	1
Antioxidant(2)	1.5	1.5	1.5		1.5	1.5
Antioxidant(3)	1	1	1		1	1
Paraffin Wax	1	1.5	2	**Microcrystalline wax**	1	2
Stearic acid	1	1	1		1	1
Processing Additive	2	2	2		2	2
Total	**189**	**189.5**	**190**		**189**	**190**

In the final step of the mixing, vulcanizing agents, inhibitors and accelerators were added (Tables 8 and 9).

Table 8: Final step of mixing for sample A.

Sample	A1	A2	A3	A4	A5	A6
Ingredients	phr					
Second step of mixing	161.25	161.75	162.25	161.25	161.75	162.25
Accelerator	1	1	1	1	1	1
Soluble Sulphur	1.4	1.4	1.4	1.4	1.4	1.4
Pre-Vulcanization Inhibitor	0.1	0.1	0.1	0.1	0.1	0.1
Total	**163.85**	**164.35**	**164.75**	**163.85**	**164.35**	**164.75**

Table 9: Final step of mixing for sample B.

Sample	**B1**	**B2**	**B3**	**B4**	**B6**
			phr		
Second step of mixing	191	191	191	191	191
Accelerator	1.4	1.4	1.4	1.4	1.4
Soluble Sulphur	1.4	1.4	1.4	1.4	1.4
Pre-Vulcanization Inhibitor	0.15	0.15	0.15	0.15	0.15
Total	**193.95**	**193.95**	**193.95**	**193.95**	**193.95**

The total number of samples are 11 namely A1, A2, A3, A4, A5, A6, B1, B2, B3, B4 and B6. The hardness of sample A was measured 62 Sh and that of sample B was 63 Sh.

After the final step these mixtures were masticated in two roll mill at 30 °C for about 5 min until the samples attained a thickness of 0.2 cm. In order to calculate the vulcanization time of the samples Moving disc rheometer (ISO 3417) was used. This test was performed in Mitas a.s. Refer Table 10, Figure 14 and Figure 15 for details of vulcanization time and safety time.

Table 10: Representing vulcanization time for sample A as well as sample B.

Variable	Value		Unit
	A	**B**	
Test Temperature	160	160	^{o}C
Test Time	20	20	min
Least Torque	9.35	2.77	dNm
Maximum Torque	33.68	17.79	dNm
t_{10}	2.06	3.37	min
t_{40}	3.08	4.86	min
t_{90}	9	8.02	min

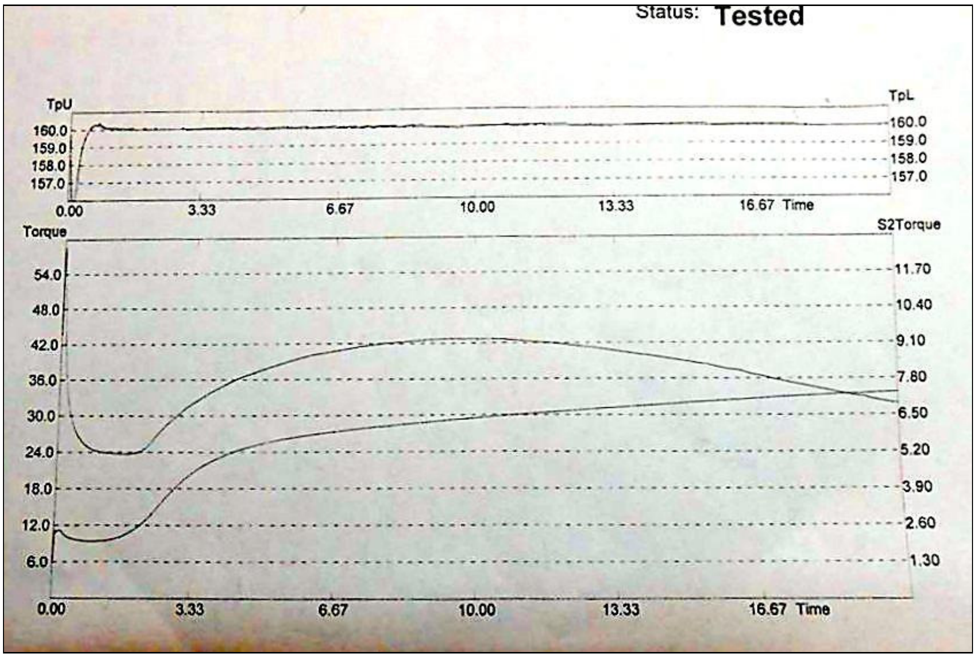

Figure 14: Vulcanization curve for sample A.

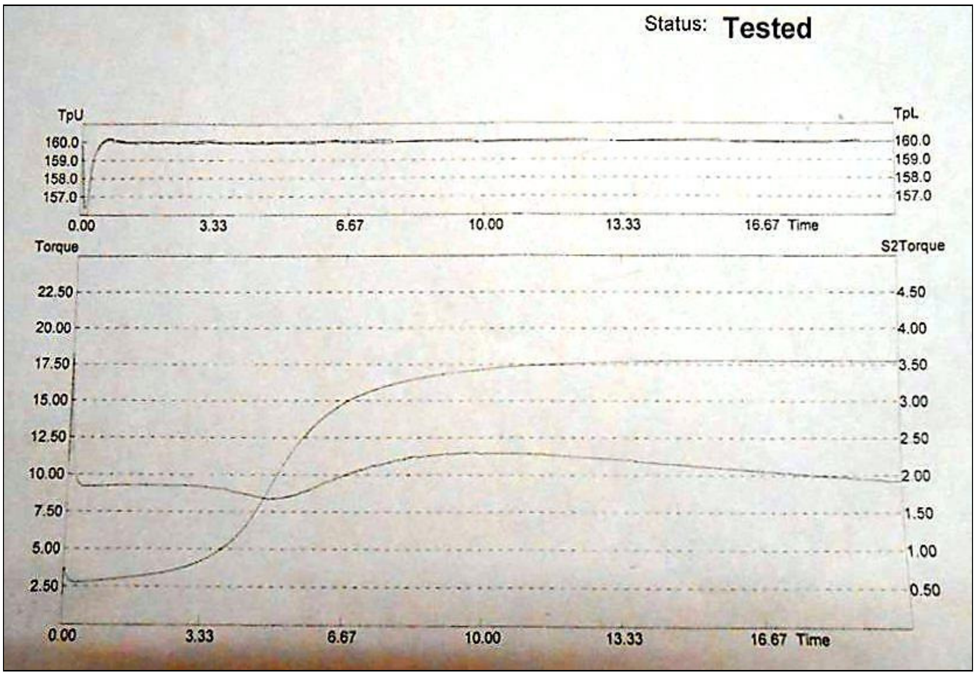

Figure 15: Vulcanization curve for sample B.

After calculating the vulcanization time for both types of rubber mixtures, samples were ready for compression moulding. All the samples were compressed at 160 °C and time varied according to the sample. For sample A it was 9 min and that for sample B was 8.02 min. The compressed sheets had a dimension of 15 cm × 15 cm× 0.2 cm. After the compression moulding the samples were kept in summer (35 °C) and winter (4 °C) condition for further analysis which is discussed in the further parts of the Master Thesis.

5 EXPERIMENTAL METHODS

This section will deal with brief study of various experimental techniques used during thesis which include ATR-IR, contact angle measurement, TGA, SEM and photography.

5.1 Attenuated total multiple reflection – Infra-Red Spectroscopy

For measuring the chemical changes occurring in the rubber samples these were monitored via IR Spectroscopy in Thermo Scientific Nicolet iS5 FT-IR Spectrometer (Figure 16) in the range of 680-4000 cm^{-1} at 64 scans per spectrum at 2 cm^{-1} resolution attenuated total reflectance technique with Germanium crystal. To avoid deep penetration of the IR radiation into the sample, ATR-IR method was used.

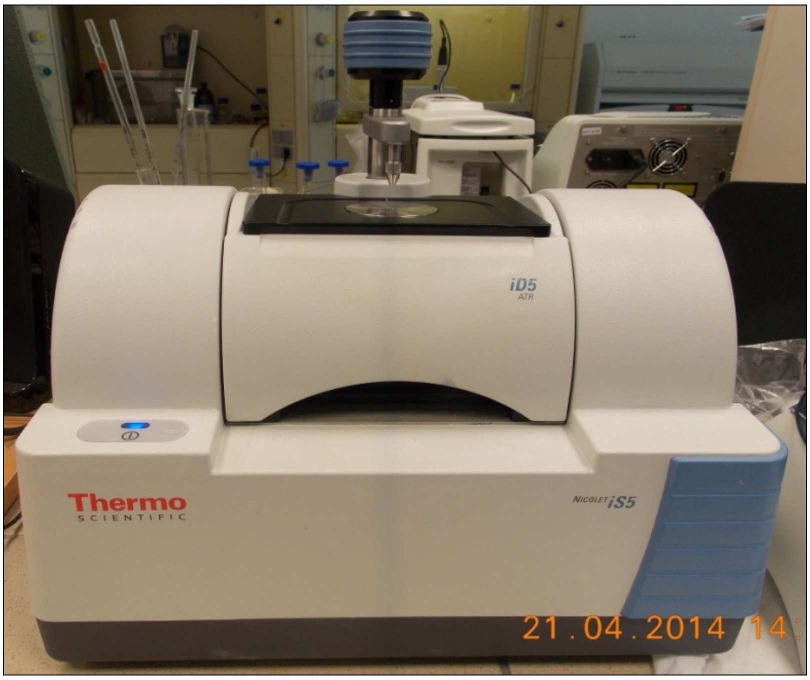

Figure 16: Thermo Scientific Nicolet iS5 FT-IR Spectrometer.

ATR significantly enhances surface sensitivity and is a technique which enables samples to be analyses directly without any preparation. An ATR instrument operates by measuring changes in the totally reflected IR beam after the beam comes in contact with the sample (Figure 17).

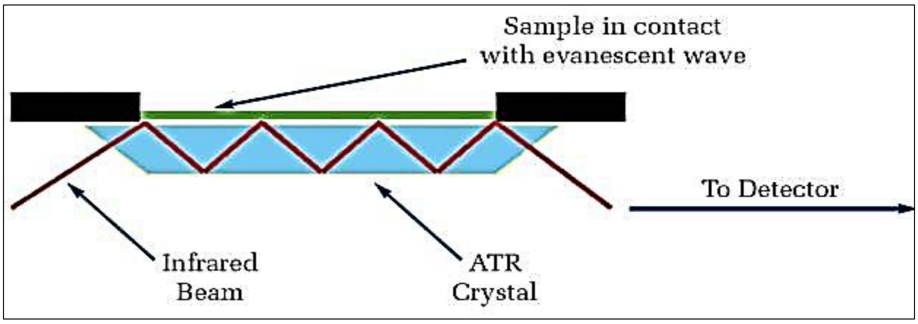

Figure 17: ATR working.. [71]

The ATR-IR measurements were taken thrice for every 11 samples both in winter and summer condition for ten days for analysing the chemical changes taking place on the surface of the samples during desorption phenomena and for sorption it was measured at time interval of 0 min, 30 min, 60 min, 90 min and 120 min. It was also performed on both types of wax. The data was interpreted using ORIGIN LAB software.

5.2 Contact angle measurement

The contact angle measurement was done using the Sessile drop technique and See system E software of Advex Instruments (Figure 18). Water was used as a test liquid. It is a portable computer based technique for measurement of contact angle and surface energy determination. It is a device for relatively quick measurements of static contact angle method, sessile drop are captured by a camera for computer evaluation of the actual values of contact angle. Profiles drops can be exported as images as a proof material which can be seen in result and discussion part of this Thesis. Figure 19 describes the effect of contact angle on various property of the surface.

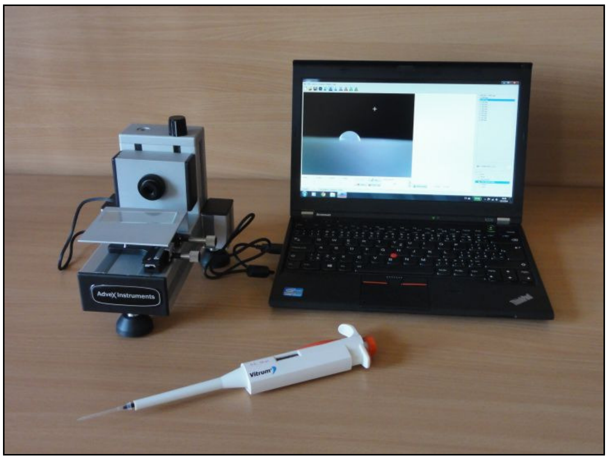

Figure 18: See System Instrument for analysing contact angle. [72.

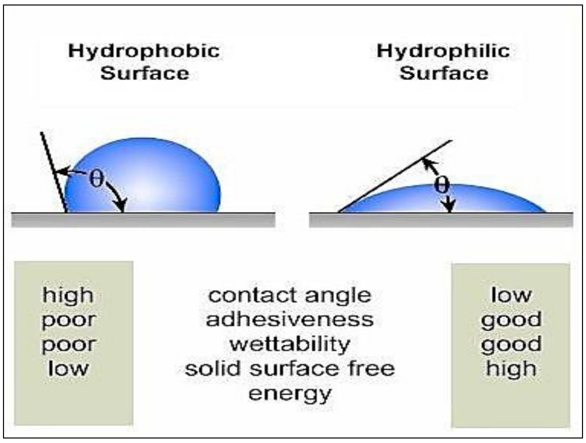

Figure 19: Effect of contact angle on surface properties. [73]

Three points across the circumference should characterize the drop shape and also the boundary between liquid and solid were marked (Figure 20). It is possible to assign more points as to fit the shape of drops. The contact angle is then evaluated as a tangent to circumference.

The contact angle of all the 11 samples both at winter and summer condition were measured daily at nearly same time (± 1hour) for ten days for desorption and for sorption it was measured at time interval of 0 min, 30 min, 60 min, 90 min and 120 min. The experimental error was ± 3^{o}

as the wax distribution on the surface was uneven. Also contact angle of both the wax was measured.

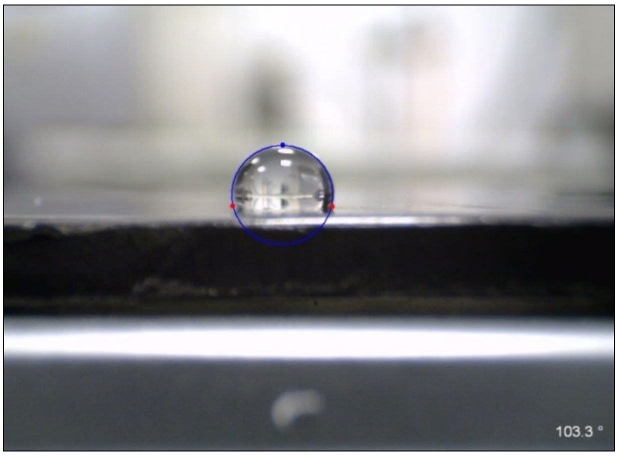

Figure 20: There points characterizing the shape of the drop.

5.3 Thermogravimetric Analysis

To find the melting point of both paraffin and microcrystalline waxes TGA was performed with TGA Q500 V20.13 Build 39 under normal atmospheric conditions at a heating rate of 10 °C/min. In a thermo-balance the mass of a sample is recorded and determined continuously while the sample is being slowly heated. This technique is used to measure the change in mass of a sample as a function of time or temperature and sometimes both. Changes of mass occur due to sublimation, evaporation, decomposition, and chemical reaction, magnetic or electrical transformations. [74]

5.4 Scanning electron microscope

In order to observe the topography of the surface before and after migration, SEM (VEGA II LMU, Tescan Ltd., Czech Republic) was used, with an operating voltage of 5 kV and magnification of 100 x, 1000 x and 7000 x (Figure 21).

SEM is a suitable method for the observation of morphology and topography. High-energy beam of electron is used to scan the surface. The electrons interact with the sample atoms and produce signals with information about the topography, composition and other properties of the surface. Electron beam produces more types of signals like secondary electrons, back-scattered electrons

(BSE), or characteristic X-rays. Signals for secondary electron detectors set in the interaction of the electron beam with atom on or nearby the surface. Obtained images have high-resolution and because of narrow electron beam also a large depth to the field. BSE signal is obtained by the electrons that are reflected from the surface.

Figure 21: SEM, VEGA II LMU, Tescan Ltd., Czech Republic.

5.5 Photography

In order to see visible changes in appearance of the surface of the samples pictures were taken every day at nearly same time (± 1 hour) for all the samples in both the conditions. The photographs were taken by Nikon COOLPIX L810 camera.

6 RESULTS AND DISCUSSION

In order to analyse the effect of outside condition on wax desorption all the 11 samples were kept in both summer (35 °C) and in winter (4 °C) condition for 10 days, after an interval of 24 hours (± 1) they were taken out and their contact angle, ATR-IR and photographs were taken for studying the wax desorption.

For sorption the samples were heated at 80 °C and were taken out at the interval of 0 min, 30 min, 60 min, 90 min and 120 min and the measurements were carried in the same way as desorption.

Throughout this section the following points would be discussed:

- Confirm the chemical presence of wax
- Study the increase in amount of wax on the surface against time
- Compare samples kept in summer and winter storage conditions
- Compare samples on the basis of other factors as well for example type of wax, its concentration and type of rubber used

It must be noted that the wax desorption and sorption on the surface was uneven which could be the reason for some minute error in results, and it must be neglected.

6.1 Thermogravimetric analysis

Thermogravimetric analysis was done to find out melting temperature of both the waxes and also the safety temperature, so that a sample could be prepared for both paraffin and microcrystalline wax on which experiments like contact angle and ATR-IR would be performed.

It was found that the melting point of both the waxes were about 100 °C (Figure 22). From Figure 23 and Figure 24 it is clear that there is no degradation before 200 °C but after this temperature weight loss is observed.

Both the waxes were then melted at 90 °C for 10 min in vacuum so that no air bubbles are formed in the sample and after subsequent cooling, the samples were taken for other measurements which are discussed in following parts.

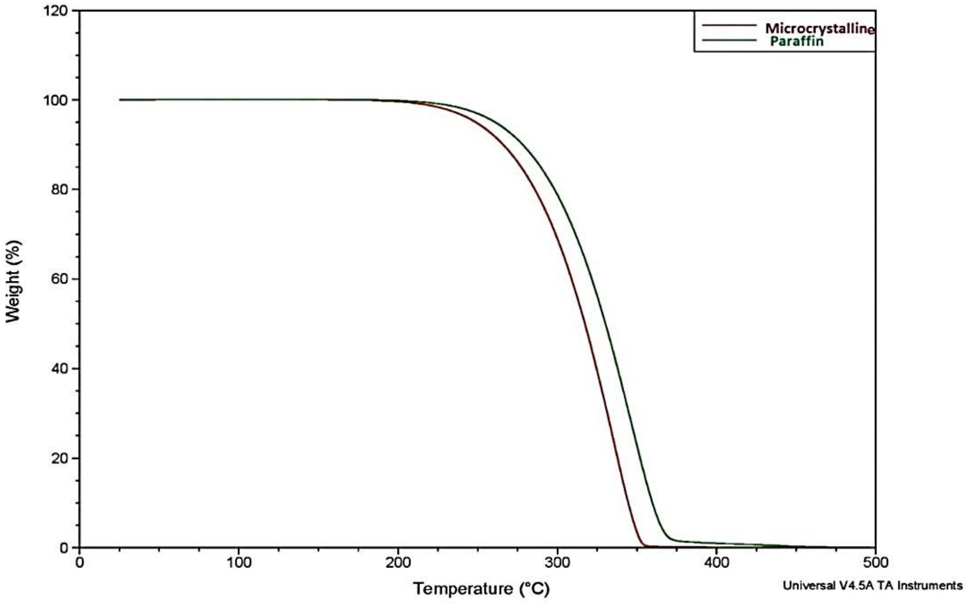

Figure 22: Graph comparing weight percentage vs. temperature for both types of waxes.

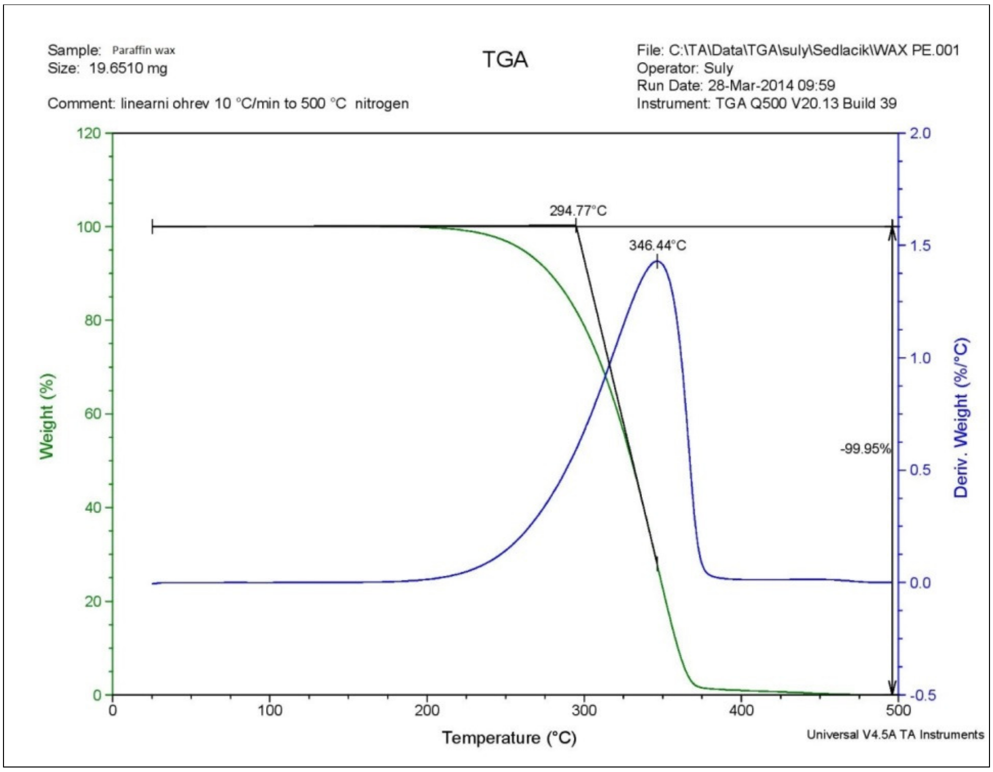

Figure 23: TGA graph for paraffin wax.

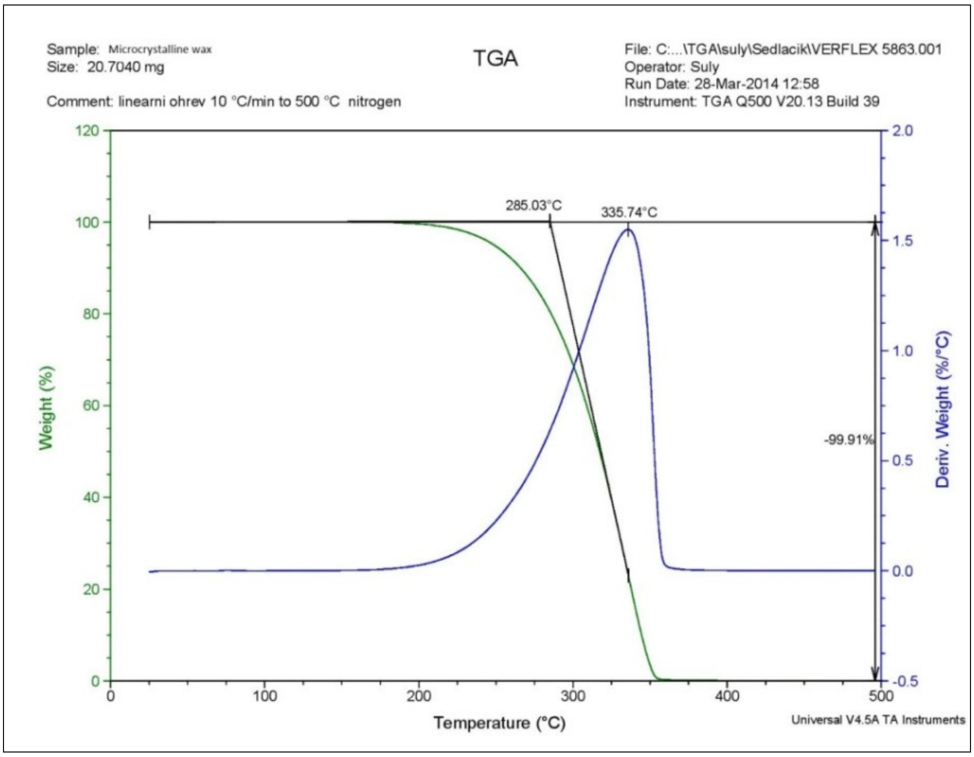

Figure 24: TGA graph for microcrystalline wax.

6.2 Attenuated total multiple reflection – infra-red spectroscopy

In order confirm the chemical presence of wax on the surface of rubber samples and to analyse the effect of storage condition, ATR-IR was performed.

This section is divided into 3 parts, the first one deals with ATR-IR of wax in which the peaks of wax would be identified, followed by ATR-IR for desorption in which all the samples would be analysed each day in both summer and winter condition, the final section deals with sorption in which all the samples heated at 80 °C and taken out at time interval of 0 min, 30 min, 60 min, 90 min and 120 min respectively.

6.2.1 Wax

In order to observe changes on the surface of the rubber samples due to deposition of wax, it is first necessary to study the ATR-IR spectra of both the waxes and identify its peaks. Wax samples were prepared by melting it on a petri dish followed by its cooling. Figure 25 represents IR spectra of both paraffin and microcrystalline waxes.

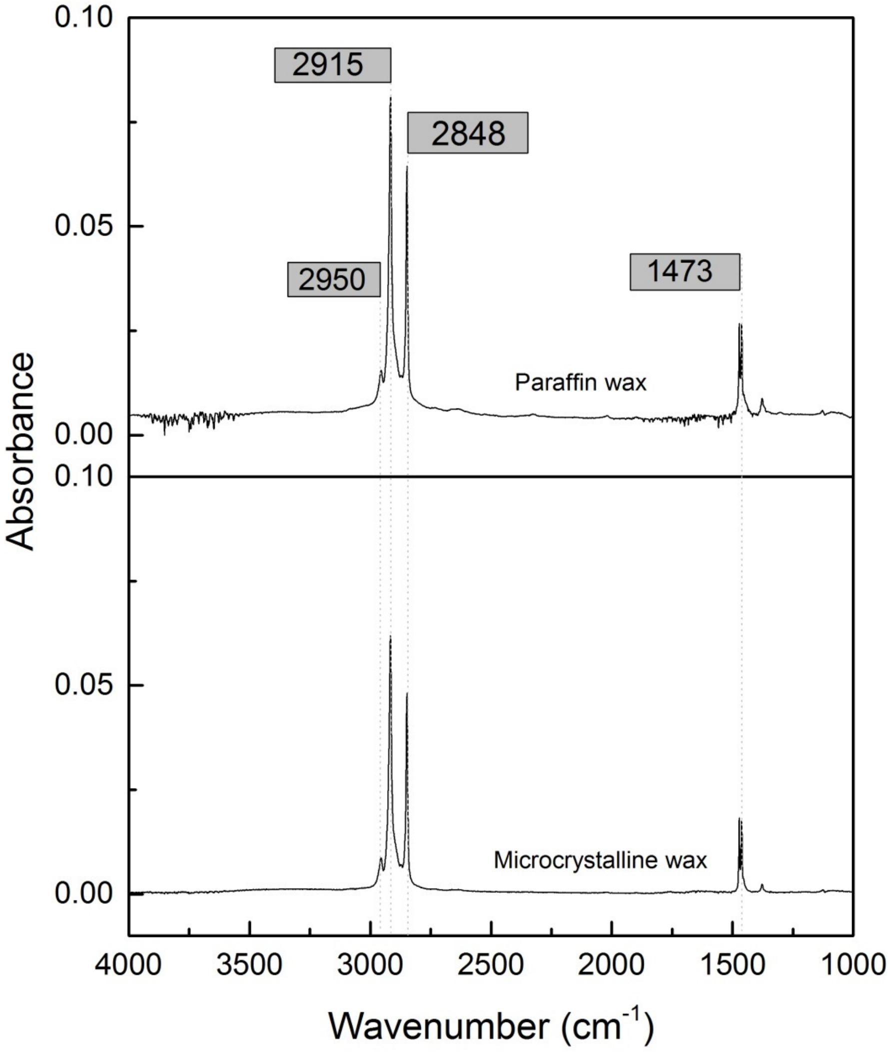

Figure 25: IR spectra of paraffin and microcrystalline wax.

Intense absorbance bands in the IR spectra (2915, 2848 and 1473 cm^{-1}) correspond to the presence of CH_2 rocking band. Peak at 2950 cm^{-1} corresponds to CH_3 end group. In the next two sections, focus would be mainly on these peaks. It is also observed that paraffin wax has higher peak on similar wavelengths as compared to microcrystalline wax.

6.2.2 Desorption

To confirm the presence of wax on the surface of rubber sample and to analyse the effect of outside condition on this phenomena, ATR-IR of all the samples were done for 10 days in both summer and winter condition. These samples were analysed after every 24 hours (± 1 hour). The IR was done thrice for each sample.

Even though the experiments were done every day, the difference in peak heights were not significantly visible, so it is better to compare IR spectra of day 1, day 5 and day 10 for every sample (Appendix I: Figures 53–74).

Visible peaks are observed at 2950, 2915, 2848, 1537, 1473, 1379 and 1075 cm^{-1}. Absorptions at 2950, 2915, 2848, 1473 cm^{-1} corresponding to the wax peaks indicate that wax is covering the surface of the rubber sample.

Absorption at 1379 cm^{-1} is due to rubber and absorption at 1075 cm-^{1} is related to the presence of silica filler, whereas the absorption at 1537 cm^{-1} is observed for zinc stearate. This confirms that ZnO reacts with stearic acid to form zinc stearate, which is also responsible for poor adhesive properties.

Although in all the Figures 7 absorption peaks has been marked, the main focus would be on the peak heights of the two most dominant peaks, i.e. 2915 and 2848 cm^{-1} which corresponds to the characteristic peaks of wax.

From the IR spectra it is evident that the wax desorption phenomena is taking place as the two characteristic peaks of wax (2915 and 2849 cm^{-1}) is increasing from day 1 to day 10. It is very clear from the above figures that wax desorp more in summer condition than in winter but in order to get exact estimate, a Table 11 contains peak heights of both summer and winter conditions.

Table 11: Peak heights of all samples in summer and winter conditions after 10 day of evaluation.

	Summer		**Winter**	
Absorbance at:	**2915 cm^{-1}**	**2848 cm^{-1}**	**2915 cm^{-1}**	**2848 cm^{-1}**
A1	0.08688	0.05867	0.05956	0.04293
A2	0.08352	0.06155	0.05613	0.04341
A3	0.0772	0.06012	0.05413	0.03953
A4	0.08312	0.0644	0.05123	0.03748
A5	0.09195	0.06737	0.05128	0.03747
A6	0.08895	0.06524	0.05209	0.0382
B1	0.05867	0.04483	0.04428	0.03392
B2	0.08855	0.08591	0.05071	0.03848
B3	0.0959	0.07009	0.04494	0.03414
B4	0.08145	0.06344	0.03387	0.02579
B6	0.0914	0.07234	0.04459	0.03418

On the basis of above table a bar graph has been prepared comparing desorption in summer and winter condition for peaks at 2915 cm^{-1} and 2848 cm^{-1} (Figures 26 and 27).

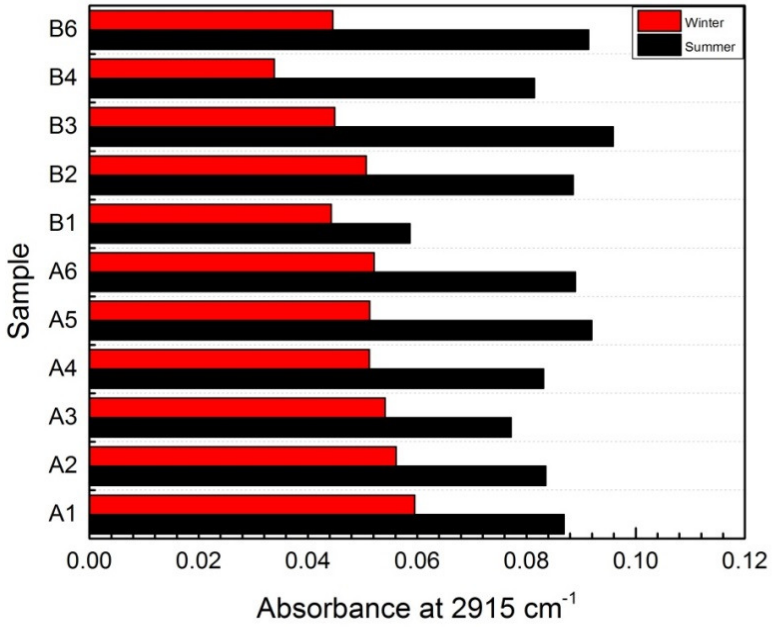

Figure 26: Bar graph comparing peak heights at 2915 cm^{-1}.

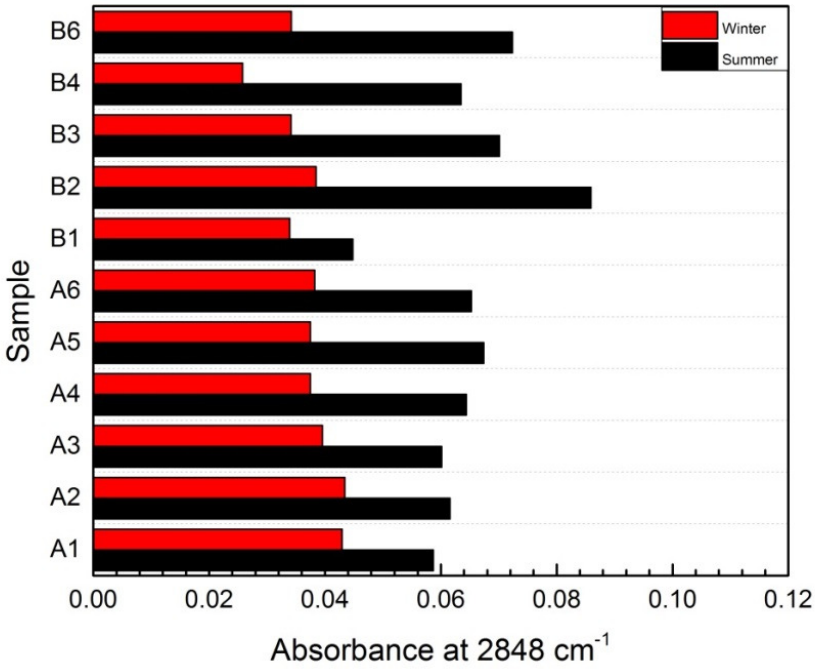

Figure 27: Bar graph comparing peak heights at 2848 cm^{-1}.

Some important notes can be concluded based on Figures 26 and 27. It worth to be mentioned that the attention should be focused on particular rubber samples, storing conditions, type of wax as well as on its concentration. As already mentioned above, the desorption phenomenon is definitely higher in summer conditions for all observed parameters in comparison with winter conditions due to higher mobility of wax macromolecules.

If the sample A in summer conditions of storing is considered, the migration of microcrystalline wax to the surface is slightly higher probably due to shorter polymer chains. Desorption of this type of wax moreover increases with its increasing concentration within the sample. Surprisingly, desorption phenomenon decreases with increasing concentration for paraffin wax which can be caused by higher steric obstruction of longer molecules. On the other hand, microcrystalline wax is better than paraffin one from suppressed desorption point of view in winter conditions. Moreover, no desorption is observed for microcrystalline wax irrespectively the concentration used within the sample. The decreased desorption for parafin wax with increasing concentration observed in summer conditions is proved also in winter conditions.

In case of sample B desorption phenomenon is following. Although desorption for microcrystalline wax increases slightly with its concentration within the sample, the resulting desorption is lower at higher concentrations comparing to the paraffin wax. The paraffin wax desorp more easily with increasing concentration. On the other hand, desorption of paraffin wax seems to be concentration independent in winter conditions, but microcrystalline wax, which desorption seems to be dependent on concentration, desorp less than paraffin one at least at lower concentrations.

6.2.3 Sorption

In order to study the sorption phenomena of wax, A samples were kept in both summer and winter condition for 10 days, after that were taken out and placed in oven at 80 °C for 0 min, 30 min, 60 min, 90 min and 120 min. The corresponding ATR-IR spectra are listed in Appendix II - Figures 75–86.

It is quite clear from Figures that with time the amount of wax on the surface of rubber is reduced. This means at time 0 min the IR peak of wax is highest and that at 120 min is the lowest. The reason for such behaviour is that wax melts at high temperature and starts to show sorption, i.e. move inside the samples. It is also observed that the phenomena of sorption are more intense in samples which were kept in summer condition (sorption was done almost to the starting position observed at the beginning of desorption test for all concentrations and both types of wax) compared to that kept in winter storage condition (additional time would be necessary to obtain the starting position observed at the beginning of desorption test for all concentrations and both types of wax).

After confirming the presence of wax on surface of rubber and confirmation of the wax desorption and sorption behaviour and role of storage condition on them, contact angle will further help to analyse dependence of other factors in details in the nest section.

6.3 Contact angle measurements

Contact angles were measured using See system software. In this section contact angle of wax, and of all the rubber samples would be analysed for studying desorption and sorption phenomena.

6.3.1 Wax

Before measuring the contact angle of various samples for sorption and desorption phenomena it is necessary to determine the contact angle of both the waxes itself. Table 12 represents contact angle of both the waxes taken three times with their mean and standard deviation and Figure 28 represents pictures of contact angle of paraffin and microcrystalline wax.

Table 12: Contact angle of paraffin and microcrystalline wax.

	Contact angle (°)	
	Praffin wax	**Microcrystalline wax**
1	110.95	111.67
2	111.02	111.19
3	113.88	110.28
STD	1.67	0.71
Mean	111.95	111.10

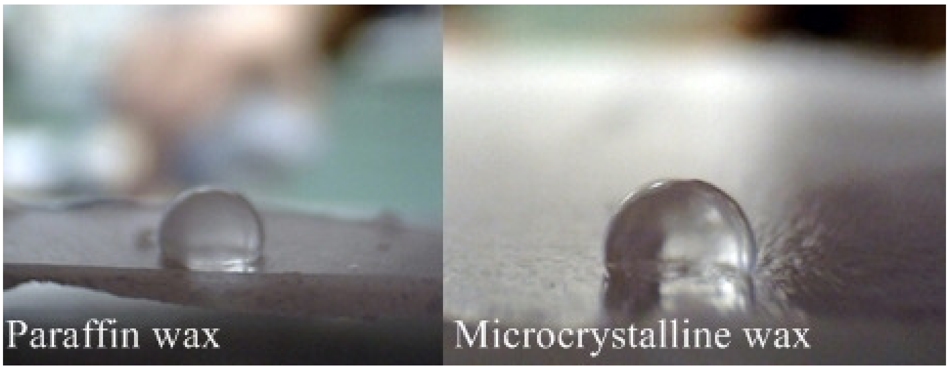

Figure 28: Droplets for measuring contact angle of both the waxes.

Although there is not much difference between the contact angle of paraffin and microcrystalline wax, paraffin wax is on a higher side.

6.3.2 Desorption phenomena

Contact angles for each sample and each day were measured 10 times since the distribution of wax was uneven on the surface. Averages and standard deviations of each sample were calculated. Values of contact angles for both rubber samples with different wax concentrations measured each day of investigation in both storing conditions are listed in Tables 13–16.

Table 13: Mean contact angle of sample A1to A6 in summer condition from day 1 to day 10.

			Contact angle(°)			
Day	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
1	95.79	97.86	98.76	102.51	99.45	103.46
2	100.32	99.39	102.63	104.01	100.90	103.52
3	101.30	100.99	103.99	104.51	101.07	104.33
4	103.64	102.45	104.09	105.07	101.25	104.54
5	104.30	104.53	109.06	105.30	102.12	105.46
6	104.90	104.92	111.85	106.06	105.10	107.14
7	105.38	105.97	113.78	107.59	106.00	108.53
8	107.03	106.67	114.07	110.65	110.74	110.55
9	109.22	109.44	116.03	113.23	113.72	111.71
10	111.99	116.92	118.72	114.60	114.84	115.50

Table 14: Mean contact angle of sample A1to A6 in winter condition from day 1 to day 10.

			Contact angle(°)			
Day	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
1	95.79	97.86	98.76	102.51	99.45	103.46
2	98.21	98.68	99.14	101.78	99.65	101.33
3	98.73	99.04	100.75	102.90	100.70	97.37
4	98.98	99.59	100.63	101.72	101.38	99.68
5	99.77	99.89	101.31	99.50	102.67	100.61
6	102.34	100.28	101.86	102.12	103.00	100.85
7	102.86	100.84	102.69	102.20	105.32	102.48
8	103.76	101.77	103.86	103.48	105.72	106.92
9	104.99	103.53	105.07	103.66	106.39	107.08
10	105.19	104.84	106.16	103.74	106.96	111.42

Table 15: Mean contact angle of sample B1to B6 in summer condition from day 1 to day 10.

			Contact angle(°)		
Day	**B1**	**B2**	**B3**	**B4**	**B6**
1	101.15	99.48	96.91	102.32	95.97
2	99.86	100.37	99.47	102.68	96.84
3	98.40	100.87	102.82	100.94	97.23
4	100.43	100.21	102.90	98.84	98.79
5	100.53	100.52	103.28	99.69	99.95
6	101.46	103.66	104.99	101.46	100.91
7	101.96	104.21	105.76	102.46	102.16
8	103.39	104.84	106.26	102.82	103.22
9	104.16	105.05	108.39	103.94	104.39
10	105.45	106.34	111.07	105.89	106.014

Table 16: Mean contact angle of sample B1to B6 in winter condition from day 1 to day 10.

			Contact angle(°)		
Day	**B1**	**B2**	**B3**	**B4**	**B6**
1	101.15	99.48	96.91	102.32	95.97
2	99.85	99.56	99.10	96.92	98.06
3	97.79	100.92	99.61	98.013	98.61
4	96.68	101.80	100.83	98.44	98.63
5	100.42	101.85	102.64	99.36	99.59
6	100.76	102.27	102.60	100.41	99.67
7	101.57	102.29	104.28	101.43	100.27
8	102.51	103.15	104.29	103.91	102.77
9	103.47	103.99	104.84	103.82	104.19
10	104.19	105.01	106.21	104.60	105.14

It can be observed in the Tables that contact angle increases as time increases. This is possibly due to migration of wax on the surface of rubber sample since the wax is evidently more hydrophobic (Table 12) than rubber alone.

In order to study the effect of storage condition raw data were analysed and desorption since day 1 to day 10 was compared for each sample in both summer and winter condition (Figure 29–38).

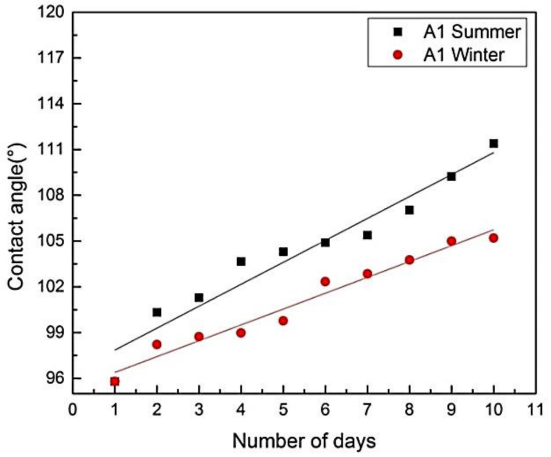

Figure 29: Graph comparing contact angles of sample A1 in both summer and winter condition from day 1 to day 10.

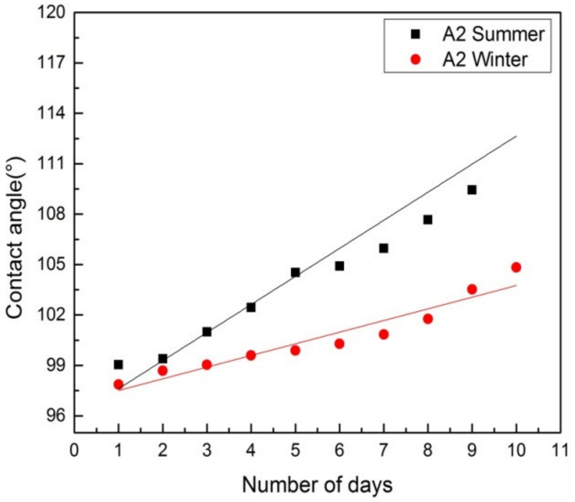

Figure 30: Graph comparing contact angles of sample A2 in both summer and winter condition from day 1 to day 10.

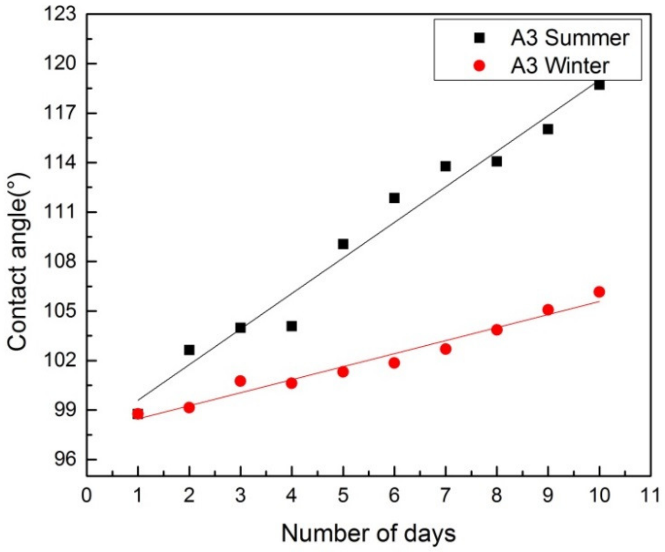

Figure 31: Graph comparing contact angles of sample A3 in both summer and winter condition from day 1 to day 10.

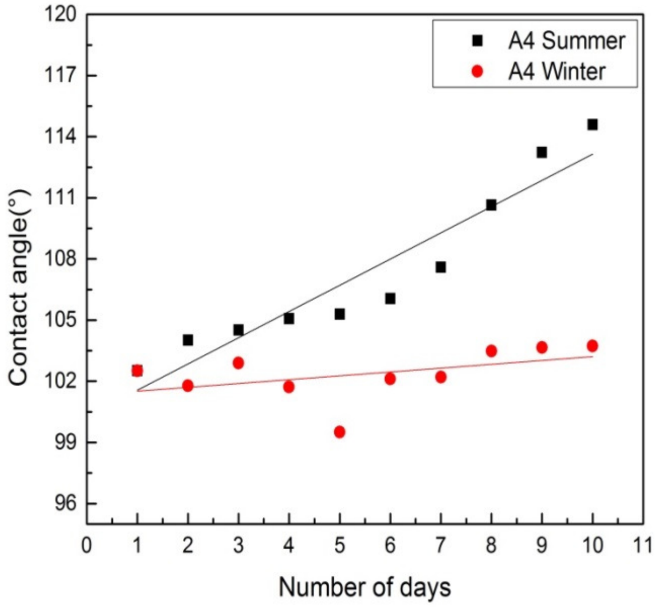

Figure 32: Graph comparing contact angles of sample A4 in both summer and winter condition from day 1 to day 10.

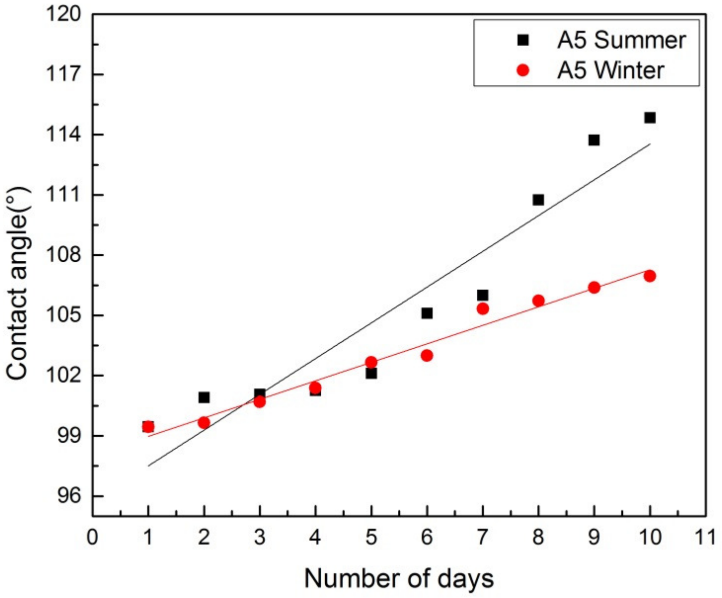

Figure 33: Graph comparing contact angles of sample A5 in both summer and winter condition from day 1 to day 10.

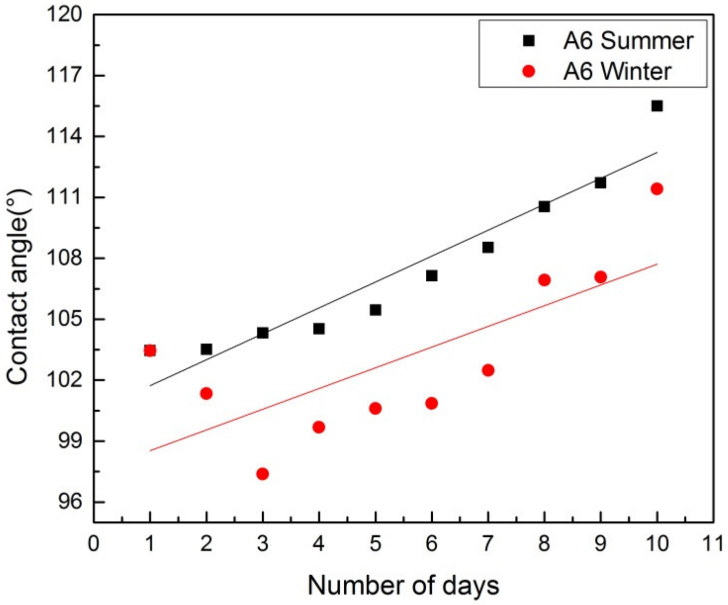

Figure 34: Graph comparing contact angles of sample A6 in both summer and winter condition from day 1 to day 10.

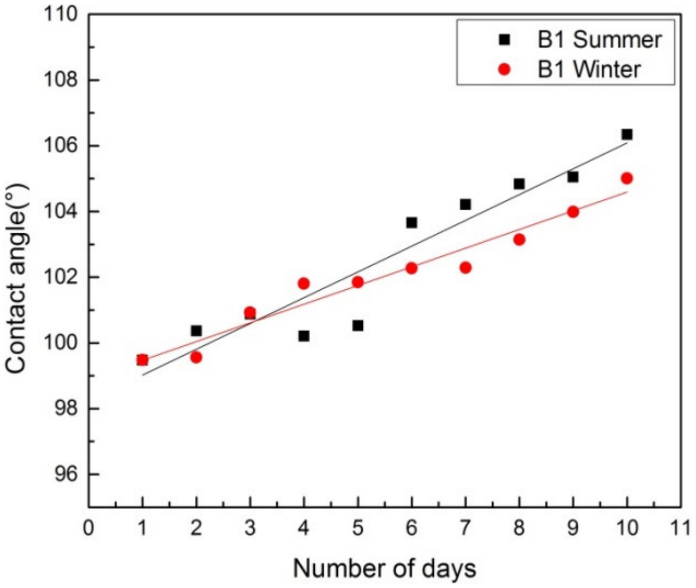

Figure 34: Graph comparing contact angles of sample B1 in both summer and winter condition from day 1 to day 10.

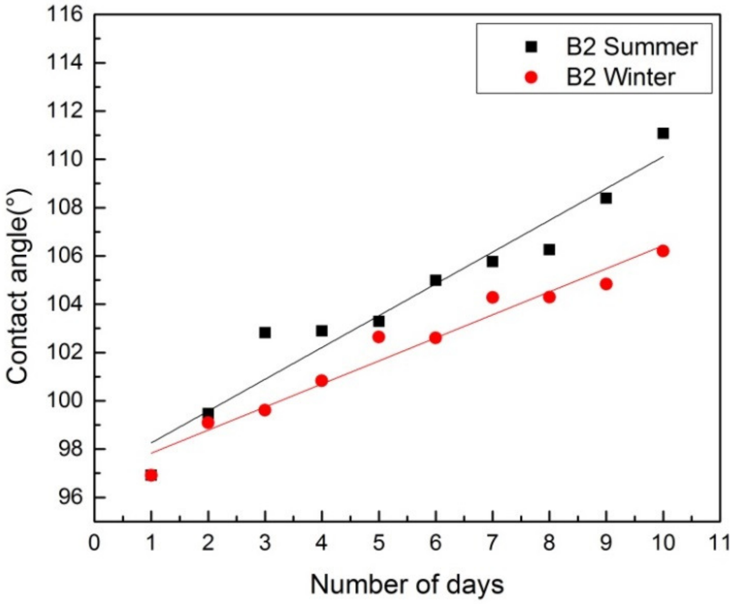

Figure 35: Graph comparing contact angles of sample B2 in both summer and winter condition from day 1 to day 10.

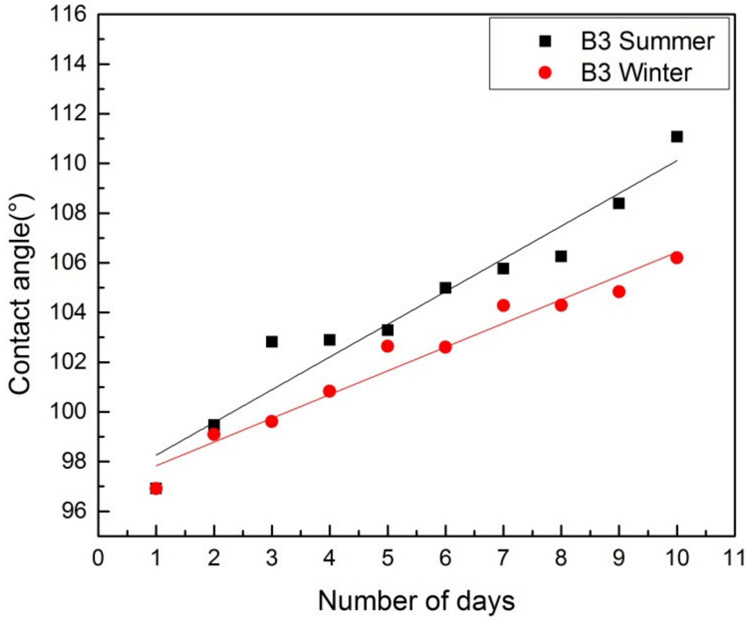

Figure 36: Graph comparing contact angles of sample B3 in both summer and winter condition from day 1 to day 10.

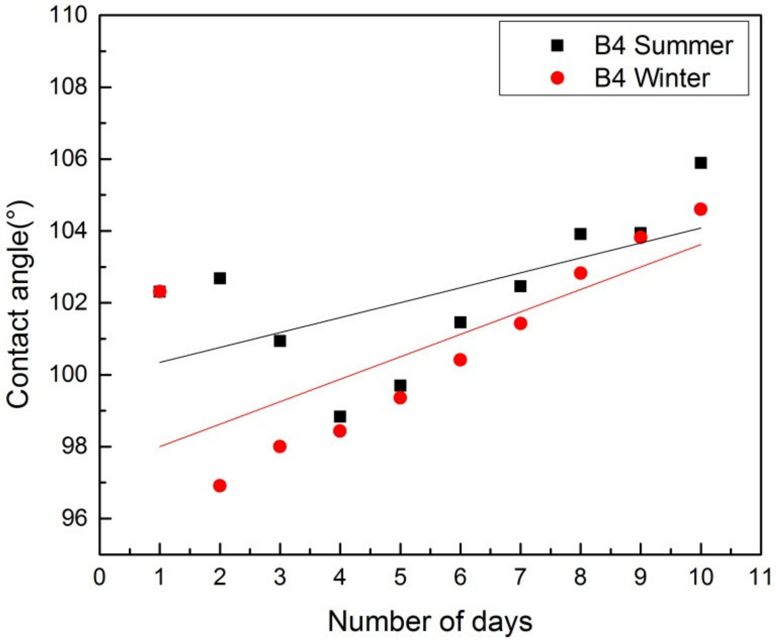

Figure 37: Graph comparing contact angles of sample B4 in both summer and winter condition from day 1 to day 10.

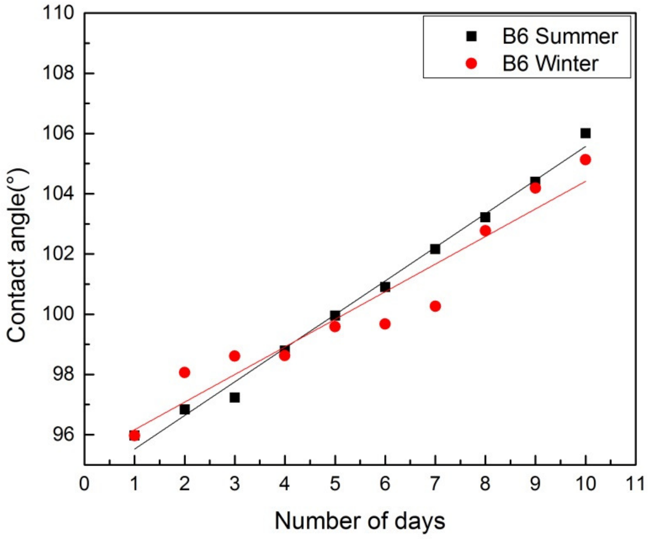

Figure 38: Graph comparing contact angles of sample B6 in both summer and winter condition from day 1 to day 10.

It can be observed that in all the cases the contact angle is higher in summer conditions and relatively lower in winter storage conditions. But in few cases especially in sample A the difference of contact angle between summer and winter condition is much higher. This can be also dependent on other factors apart from type of rubber, i.e. on type of wax and concentration of waxes.

As two different types of waxes were used namely paraffin wax and microcrystalline wax, the rate of desorption can be observed by comparing both waxes in A and B samples at highest concentration kept in summer condition (Figures 39 and 40).

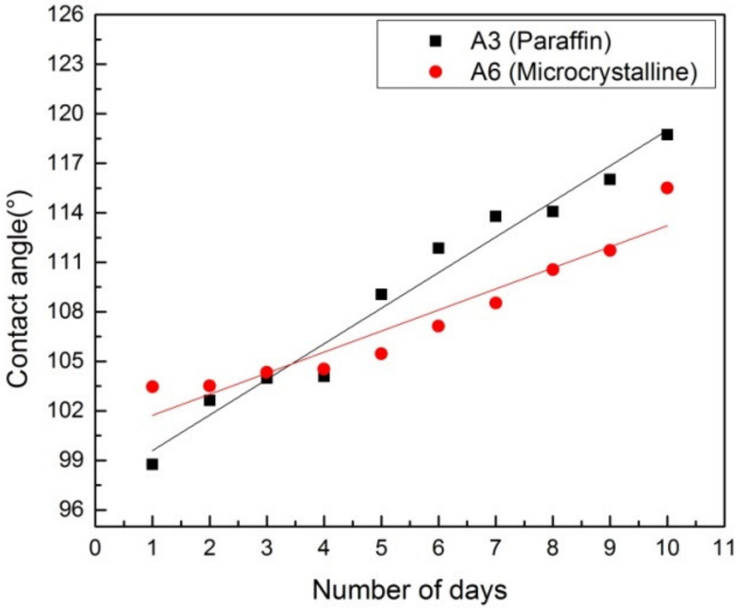

Figure 39: Contact angles of sample A containing highest concentration of paraffin wax (A3) and that of microcrystalline wax (A6) kept in summer condition.

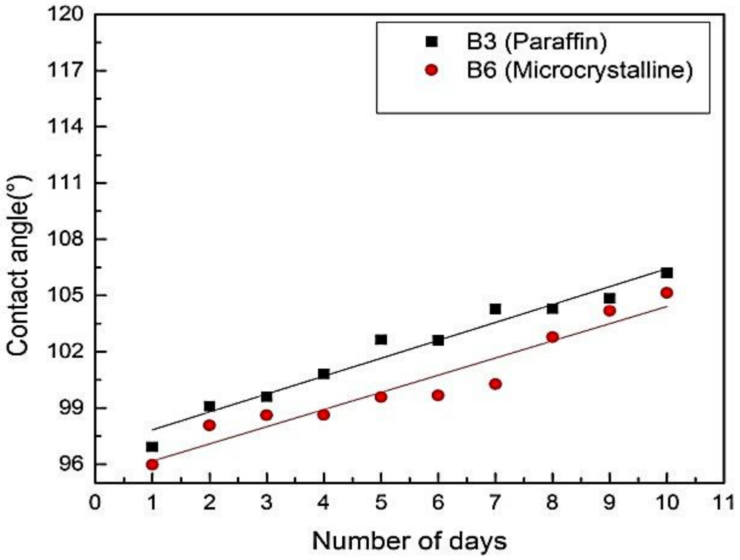

Figure 40: Contact angles of sample B containing highest concentration of paraffin wax (B3) and that of microcrystalline wax (B6) kept in summer condition.

It is quite clear from the above Figures that for both types of rubber, samples containing paraffin wax shows higher increase in contact angles as compared to microcrystalline wax. As expected paraffin wax having low molecular weight migrates to the surface easily.

Also it is possible that the increase in contact angle may vary on the type of rubber. Refer Figure 41- Figure 44 for comparing sample A with sample B for both types of wax at highest concentration both in summer and winter condition.

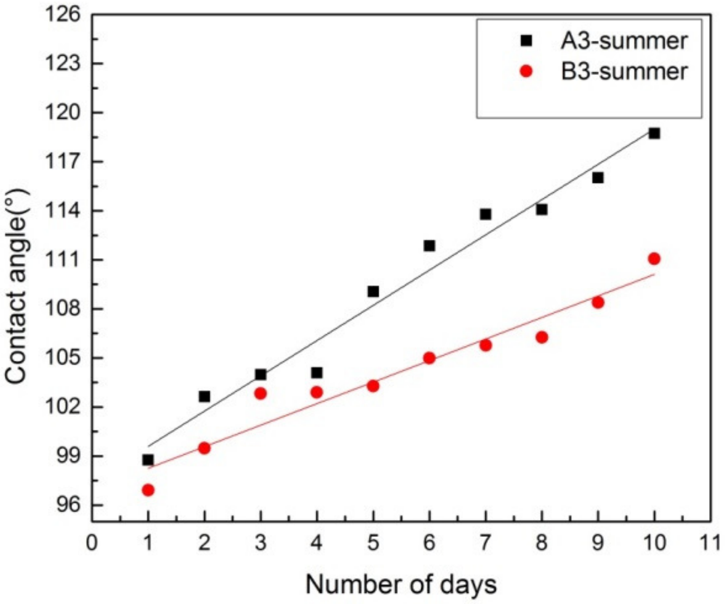

Figure 41: Comparison between sample A3 and sample B3 in summer condition.

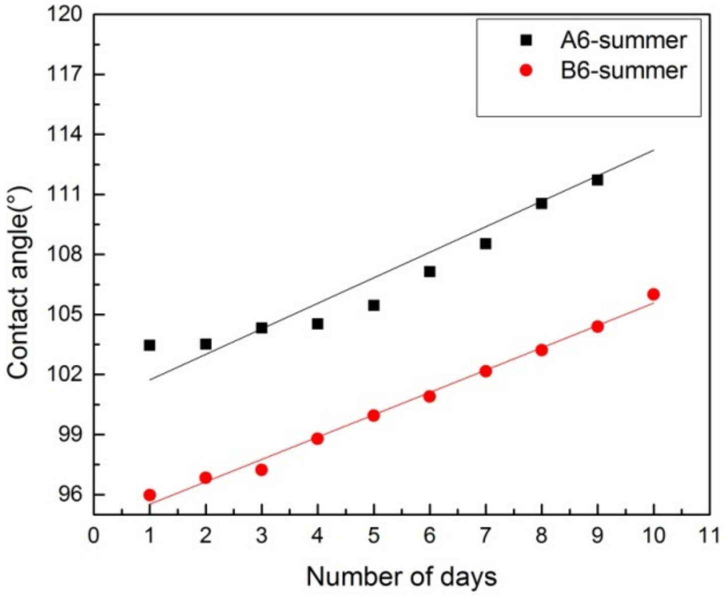

Figure 42: Comparison between sample A6 and sample B6 in summer condition.

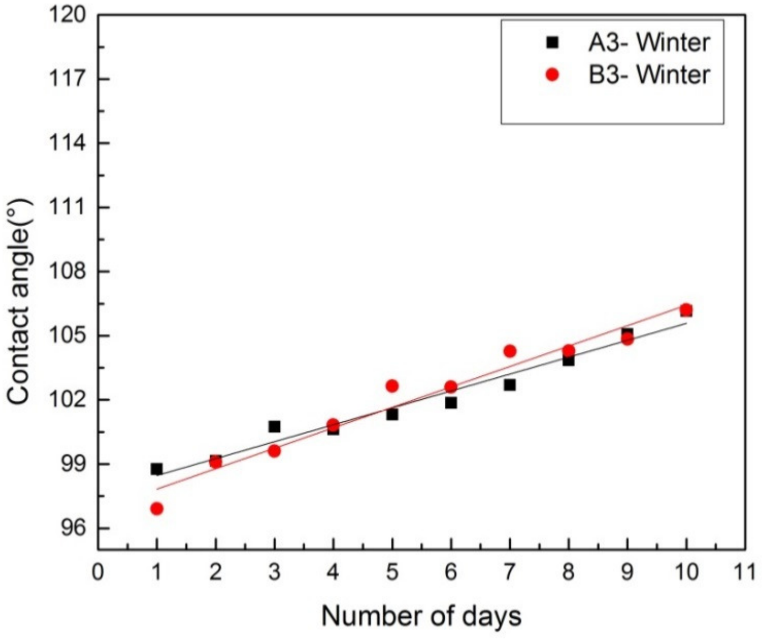

Figure 42: Comparison between sample A3 and sample B3 in winter condition.

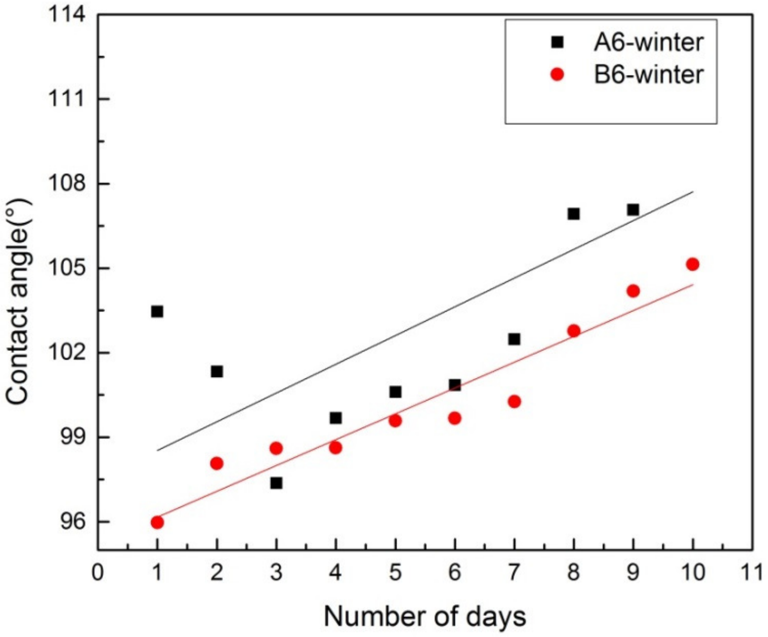

Figure 43: Comparison between sample A6 and sample B6 in winter condition.

During summer condition much more increase in contact angle was observed for sample A compared to sample B. Also in winter conditions it can be observed but it is not as significant as in summer condition.

Now three concentrations of both the waxes were used, in Figures 43–46 the comparison of the concentration would be done for both summer and winter condition and would be represented through 3-D graph. As expected at higher concentration the increase in contact angle is much higher for summer and winter condition, summer being more significant.

So as far as contact angle is concerned, it increases at higher rate for samples in summer condition, containing paraffin wax, at higher concentration for type A rubber, which is not at all favourable for rubber to metal adhesion.

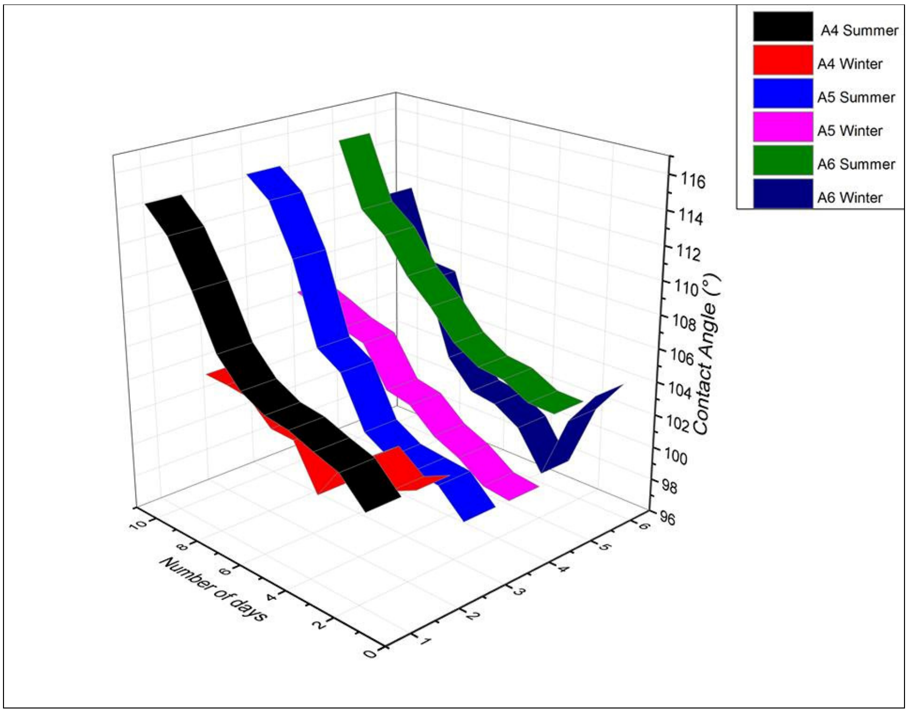

Figure 43: 3-D graph comparing 3 different concentration of paraffin wax A1, A2 and A3 in both summer and winter condition.

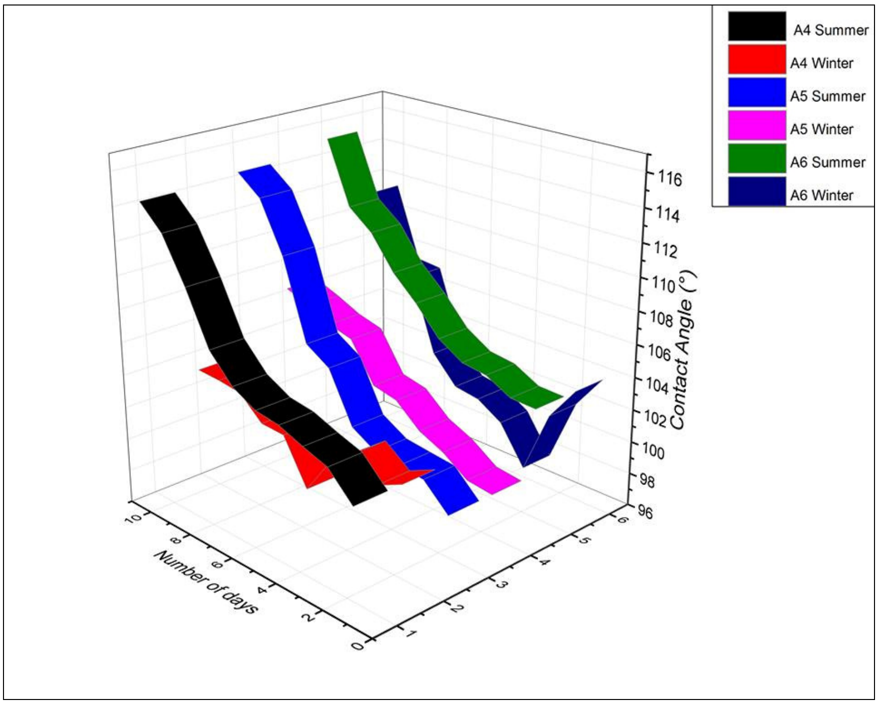

Figure 44: 3-D graph comparing 3 different concentration of microcrystalline wax A4, A5 and A6 in both summer and winter condition.

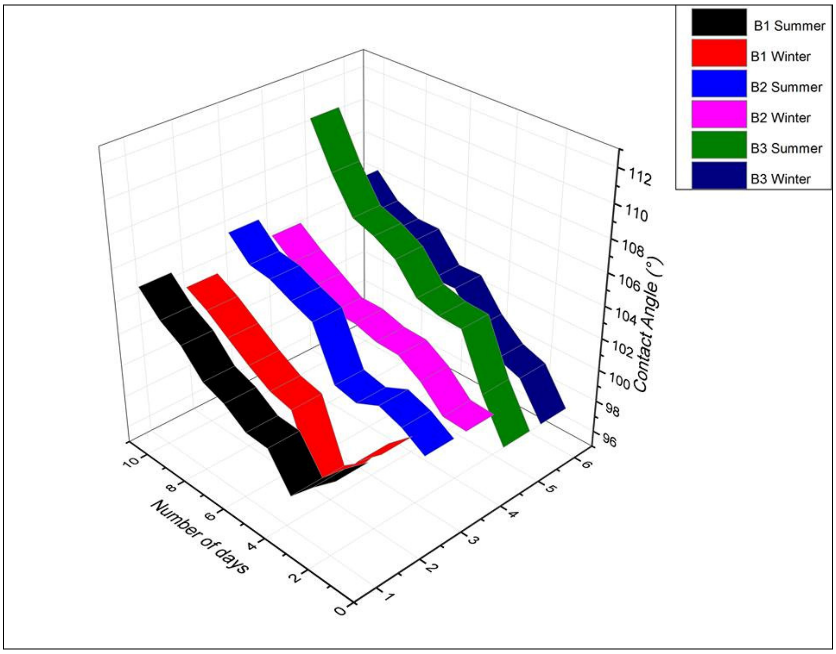

Figure 45: 3-D graph comparing 3 different concentration of paraffin wax B1, B2 and B3 in both summer and winter condition.

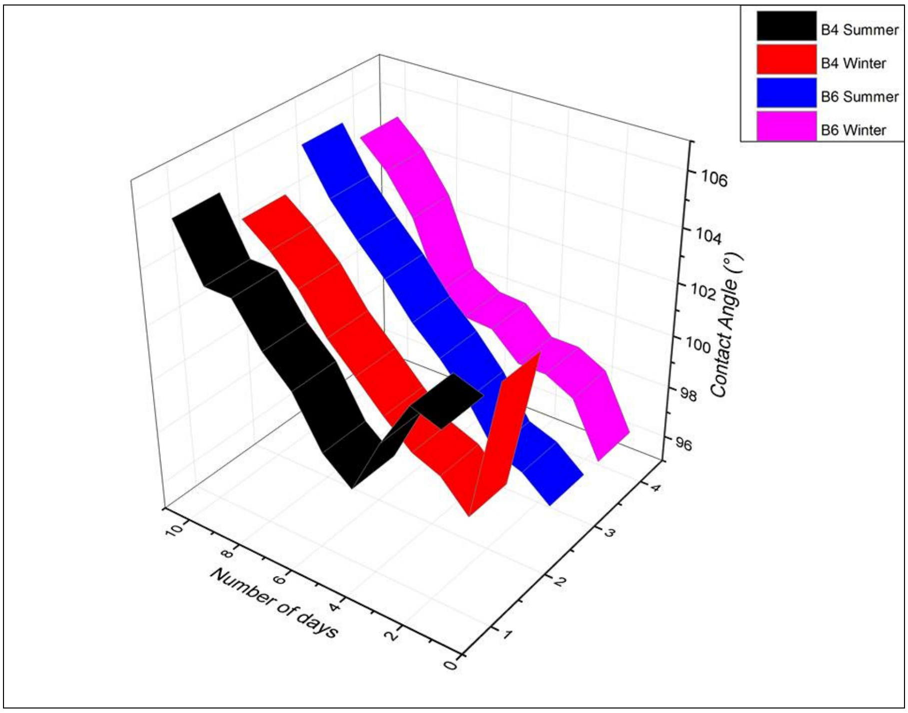

Figure 46: 3-D graph comparing 2 different concentration of microsrystalline wax B4 and B6 in both summer and winter condition.

6.3.3 Sorption

When rubber samples are heated around the melting point of wax, the crystals of waxes are supposed to melt resulting in decrease in thickness of wax on the surface.

Here sample A was heated at 80 °C for 0 min, 30 min, 60 min, 90 min and 120 min contact angle measurements were done just after that (Table 17).

Table 17: Contact angle of all the samples at 0 min, 30 min, 60 min, 90 min and 120 min at both the storage condition.

		Time(min)				
Sample	**Condition**	**0**	**30**	**60**	**90**	**120**
A1	**Summer**	118.93	104.84	106.51	101.91	100.72
	Winter	101.19	95.50	95.10	92.26	90.52
A2	**Summer**	111.02	109.56	103.56	102.12	100.96
	Winter	106.65	99.95	95.48	91.78	89.23
A3	**Summer**	112.36	105.49	105.12	103.98	102.54
	Winter	101.89	98.63	94.66	93.27	89.72
A4	**Summer**	104.34	102.95	101.67	100.73	98.27
	Winter	97.6	94.21	93.65	92.46	89.47
A5	**Summer**	110.20	106.48	104.45	99.41	99.16
	Winter	100.56	97.20	94.74	93.04	91.67
A6	**Summer**	113.75	106.88	100.33	99.65	97.53
	Winter	100.22	97.52	95.12	93.06	91.17
B1	**Summer**	103.42	100.54	99.75	95.47	88.83
B2	**Summer**	106.55	102.60	99.38	98.35	94.84
B3	**Summer**	108.88	101.27	97.75	95.76	93.53
B4	**Summer**	103.58	102.08	96.20	93.03	89.42
B5	**Summer**	105.06	97.18	93.41	91.41	90.83

For studying the comparison between rate of sorption of samples in both summer and winter condition, graphs were plotted for sample A (Figures 47–52).

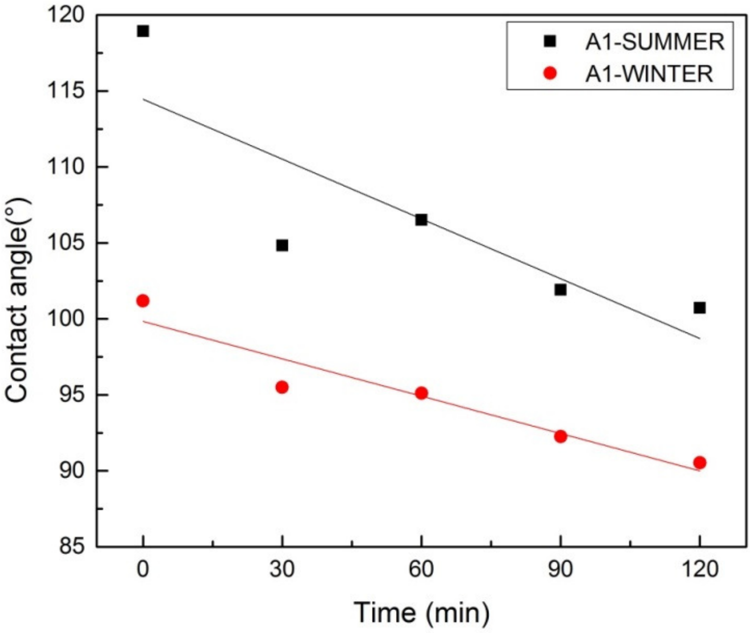

Figure 47: Comparison of decrease in contact angle in summer and winter condition for sample A1.

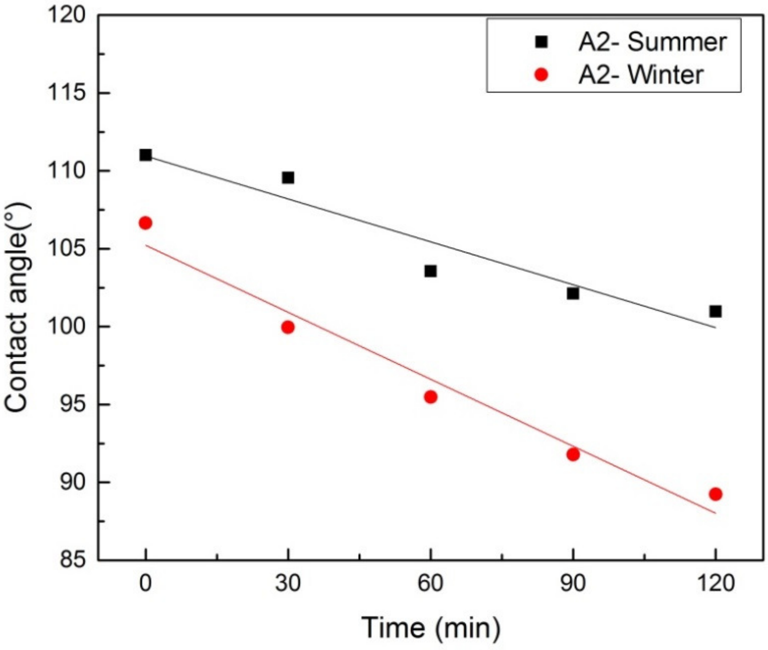

Figure 48: Comparison of decrease in contact angle in summer and winter condition for sample A2.

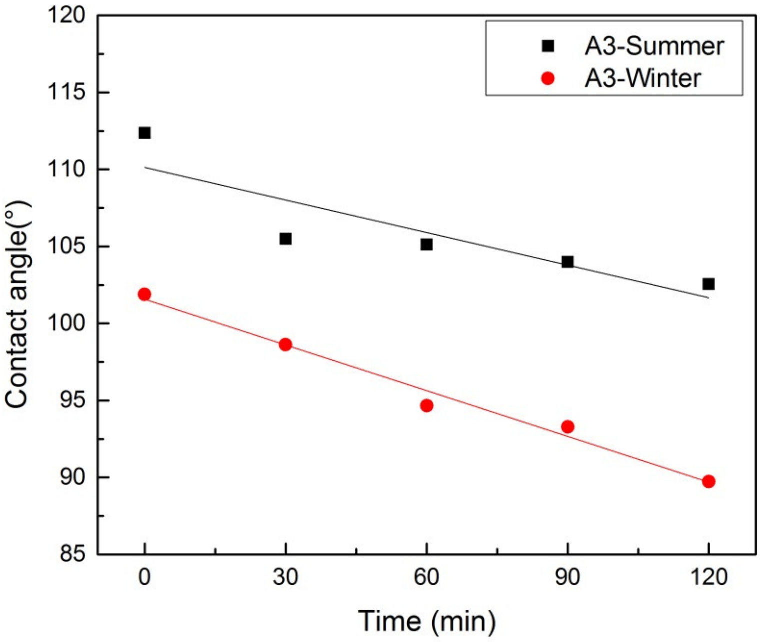

Figure 49: Comparison of decrease in contact angle in summer and winter condition for sample A3.

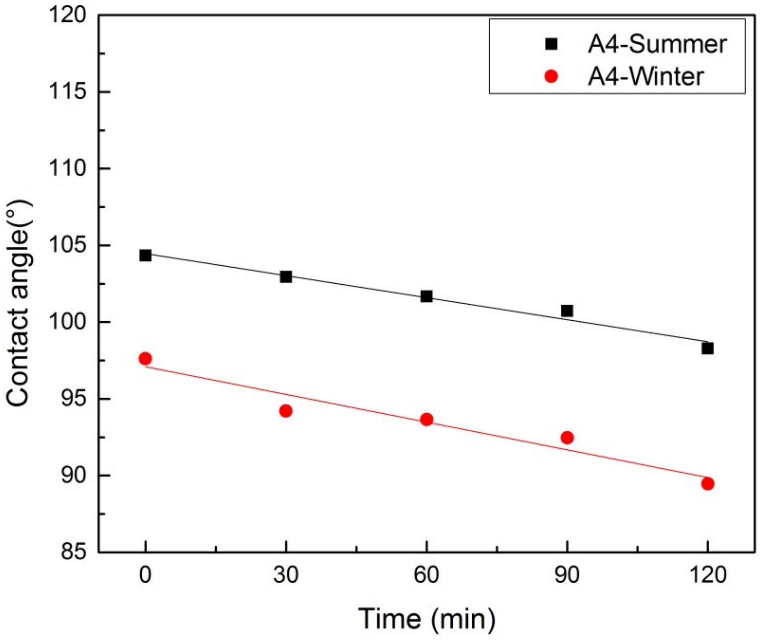

Figure 50: Comparison of decrease in contact angle in summer and winter condition for sample A4.

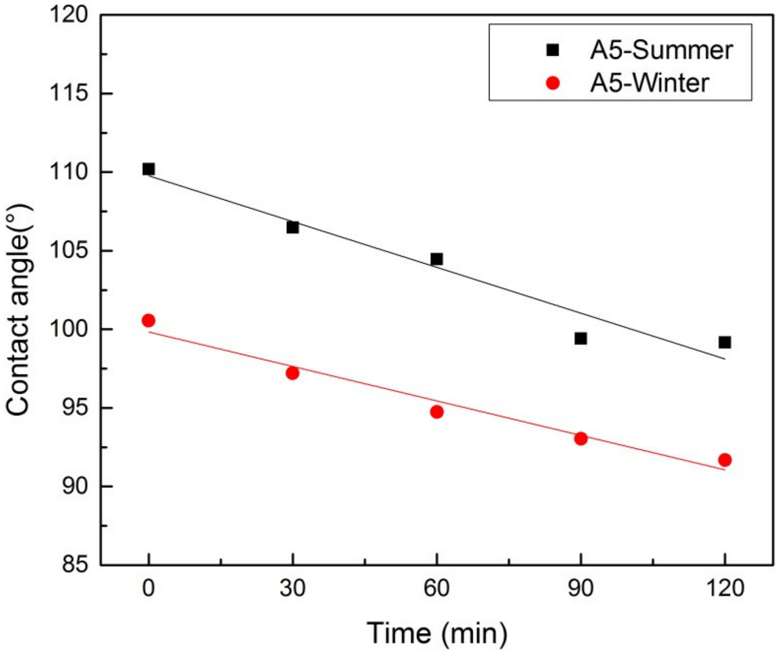

Figure 51: Comparison of decrease in contact angle in summer and winter condition for sample A5.

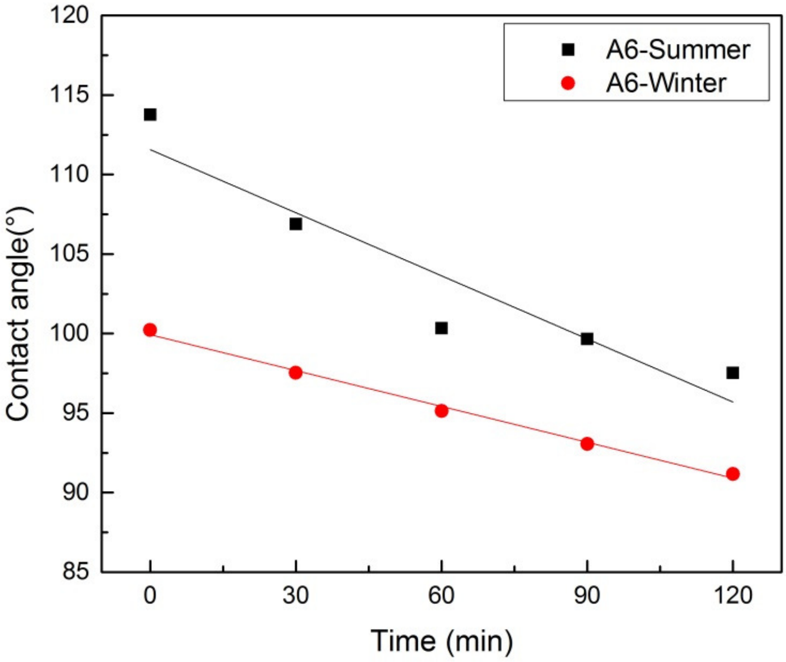

Figure 52: Comparison of decrease in contact angle in summer and winter condition for sample A6.

It can be again observed for sorption that samples kept in summer condition show more significant decrease in contact angle in comparison with sample kept in winter condition since more wax was desorped on the rubber surface enabling higher subsequent sorption. Although when sorption on basis of type of rubber, wax and its concentration are compared, no observable result was obtained.

6.4 Photography

Photographs were taken for 10 days after every 24 hours (±1 hr) for samples kept in summer and winter condition in order to observe any visible changes in appearance of rubber sample (Appendix III: Figures 87–97).

Evidently from photographs shown in Appendix II the amount of wax on the surface keeps on increasing. Also from these pictures it can be seen that for every sample in summer condition more visible wax on the surface of rubber can be observed.

6.5 Scanning electron microscopy

In order to study the topography of the rubber samples, SEM was performed. It was done for sample A and sample B after sorption and desorption (Appendix IV: Figures 98–103).

It can be seen that the rubber surface after sorption has traces of wax which is very less, but SEM micrographs shows presence of high amount of wax on the surface after desorption. It is also evident from SEM that more wax is migrated on the surface of sample A than that of sample B. In the case of sample A, wax particles are very densely spread on the surface and has globular shape. Moreover in case of sample B some cracks are observed on the surface of rubber and wax seems to migrate on the surface through it.

CONCLUSION

Two different behaviours have been observed for the effect of storage condition on sorption/desorption of wax on rubber surface:

- When samples were stored in both summer and winter condition, wax tends to migrate on the rubber surface (desorption). But the amount and rate of desorption phenomena depends on the storage condition. When samples were stored in summer condition there was quite high amount of wax because its migration to the surface of rubber was facilitated. Where as in winter conditions desorption was at a slower rate and comparatively lower amount of wax was observed on the rubber surface than in summer storage condition.
- When samples stored in winter and summer condition were observed after 10 days and heated at 80 °C, wax sorption phenomena has been also confirmed, as the wax crystals on the surface were melted at this temperature, and partial removal of wax from the surface of rubber is observed. The amount of the wax on the surface decreased significantly till 2 hours. This behaviour was also dependent on the storage conditions, summer condition again shows more reduction of wax on the surface.

Other factors responsible for wax desorption/sorption has also been observed in this Master Thesis. Migration of wax occurs when the solubility of wax in rubber is decreased; the small size of wax molecules permits them to form a film on the rubber surface. Hence paraffin wax shows more desorption as its low molecular weight and lower melting point facilitates the migration of wax crystals than microcrystalline wax. Also as expected it is observed that higher the concentration of wax the more the migration. It is observed that sample A shows more migration compared to sample B.

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LIST OF ABBREVIATIONS

3-D	3-Dimentional
IIR	Butyl rubber
SBR	Styrene-butadiene rubber
EPDM	Ethylene-propylene diene monomer rubber
NR	Natural rubber
IR	Polyisoprene
CR	Chloroprene rubber
NBR	Nitrile rubber
ISO	International standard organization
ASTM	American Society for Testing and Materials
EV	Elevated pressure
DTA	Dynamic thermal analysis
TGA	Thermogravimetric analysis
ATR- FTIR	Attenuated total multiple reflection – infra-red spectroscopy
SEM	scanning electron microscopy
phr	Parts per hundred

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Appendix I: ATR-IR spectra of samples under investigation during desoprtion in summer and winter conditions.

In each Figure the following boxes corresponds to peaks of wax, zinc stearate and rubber (which includes silica filler as well) respectively:

Wax Zinc strearate Rubber

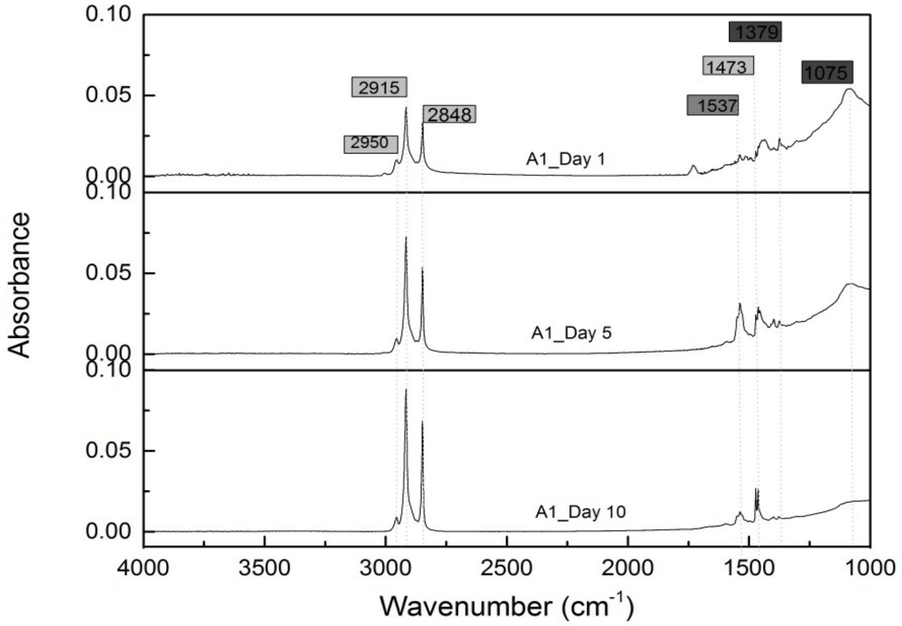


Figure 53: ATR- IR spectra of sample A1 kept in summer condition at day 1, day 5 and day 10.

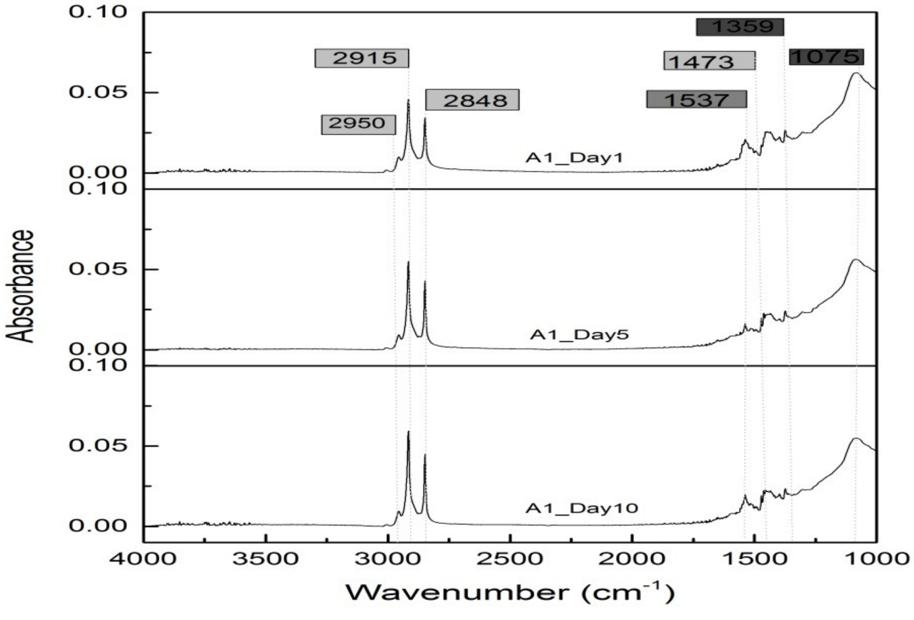


Figure 54: ATR- IR spectra of sample A1 kept in winter condition at day 1, day 5 and day 10.

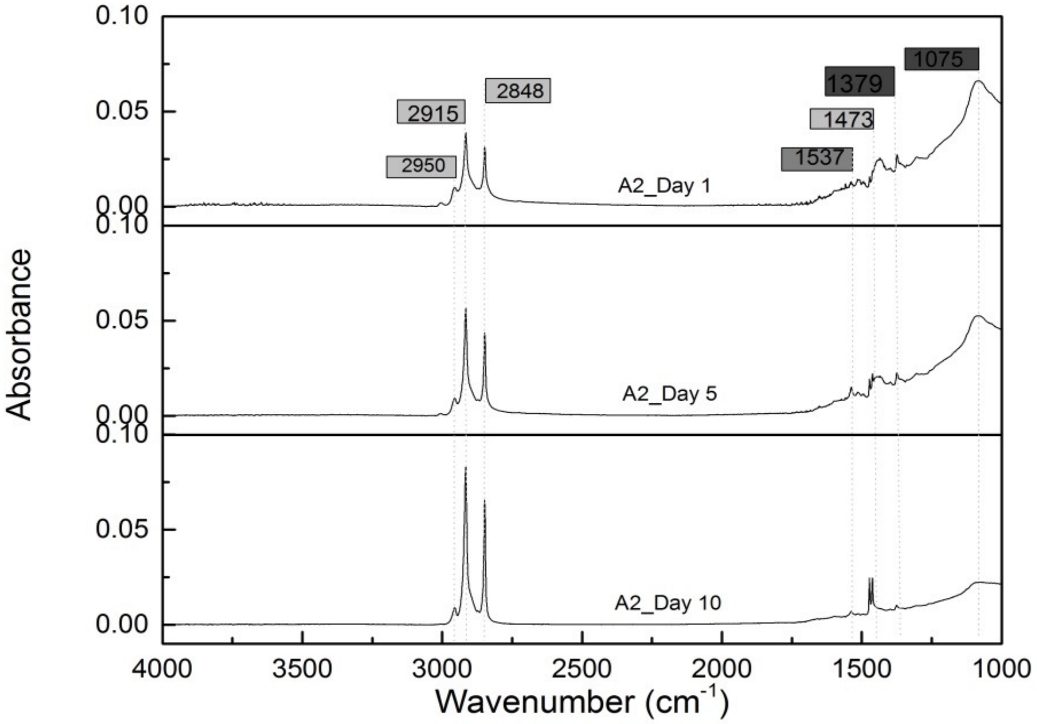


Figure 55: ATR- IR spectra of sample A2 kept in summer condition at day 1, day 5 and day 10.

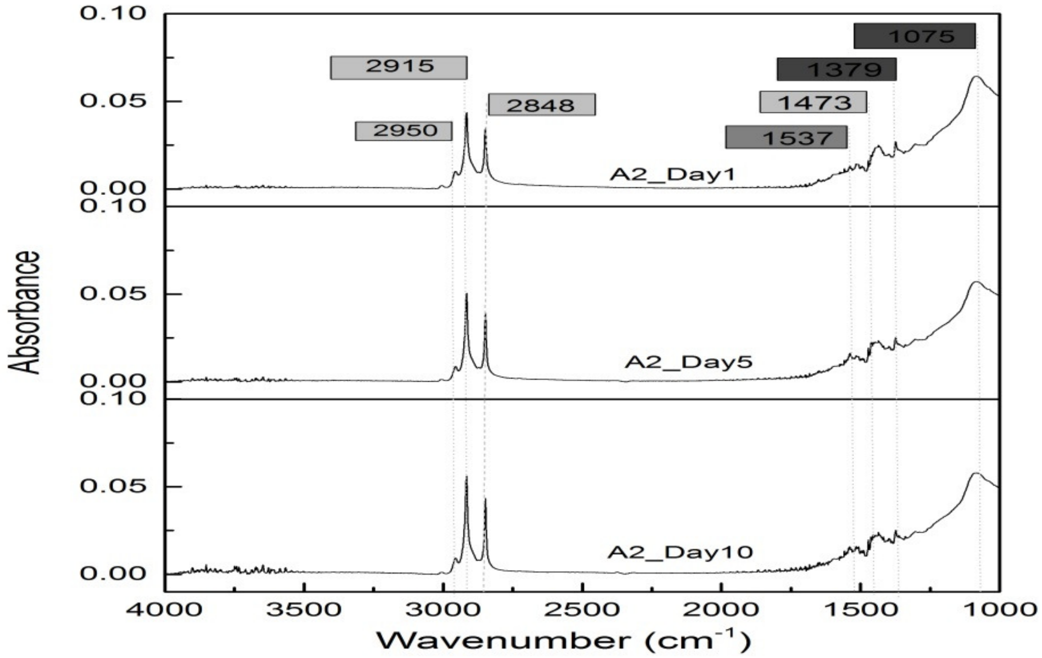


Figure 56: ATR- IR spectra of sample A2 kept in winter condition at day 1, day 5 and day 10.

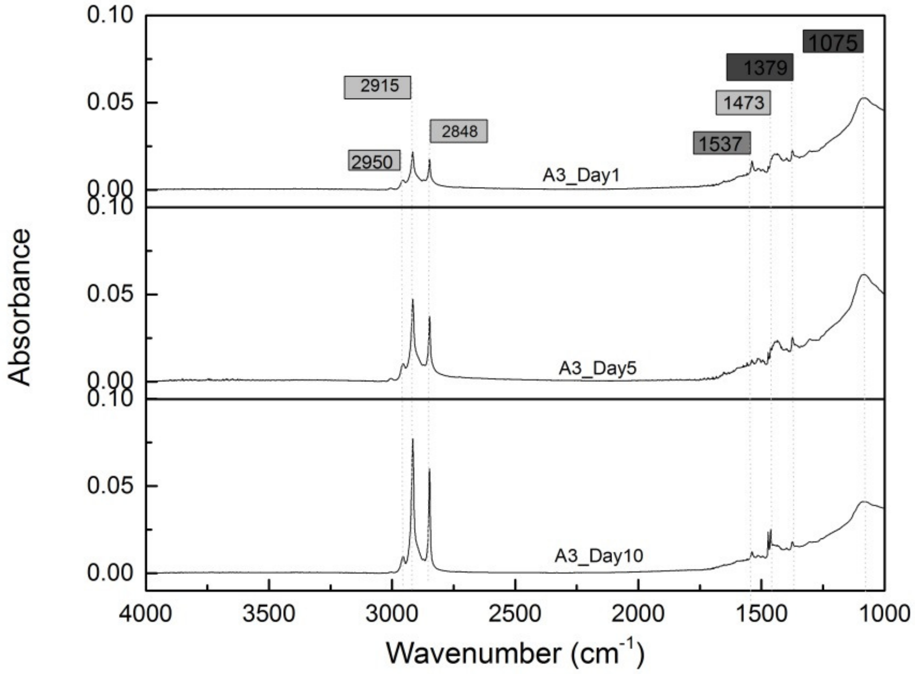


Figure 57: ATR- IR spectra of sample A3 kept in summer condition at day 1, day 5 and day 10.

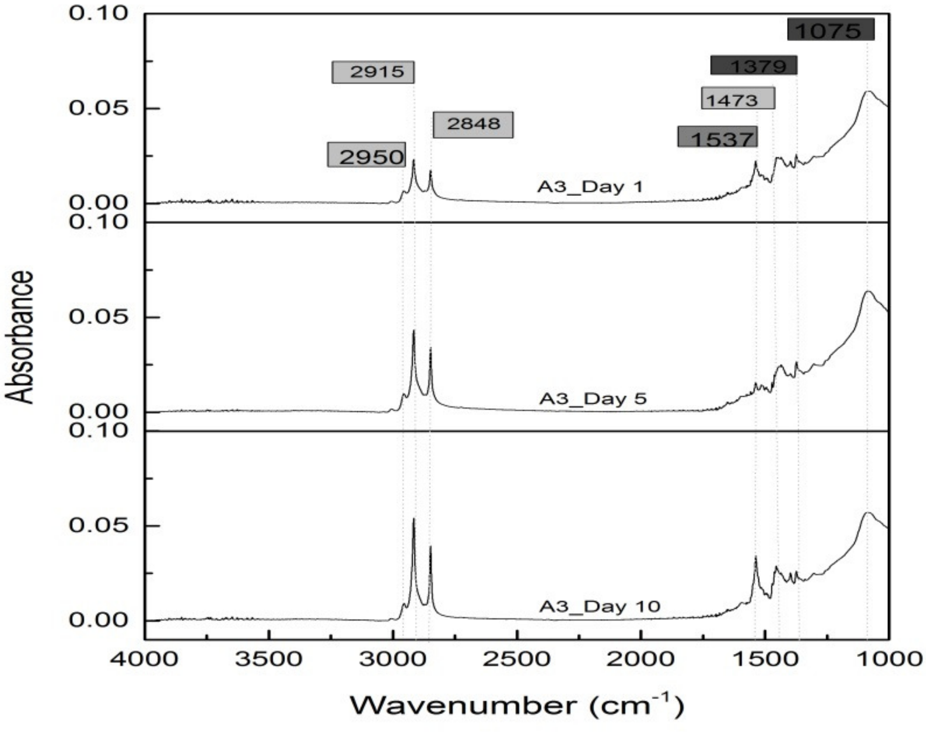


Figure 58: ATR- IR spectra of sample A3 kept in winter condition at day 1, day 5 and day 10.

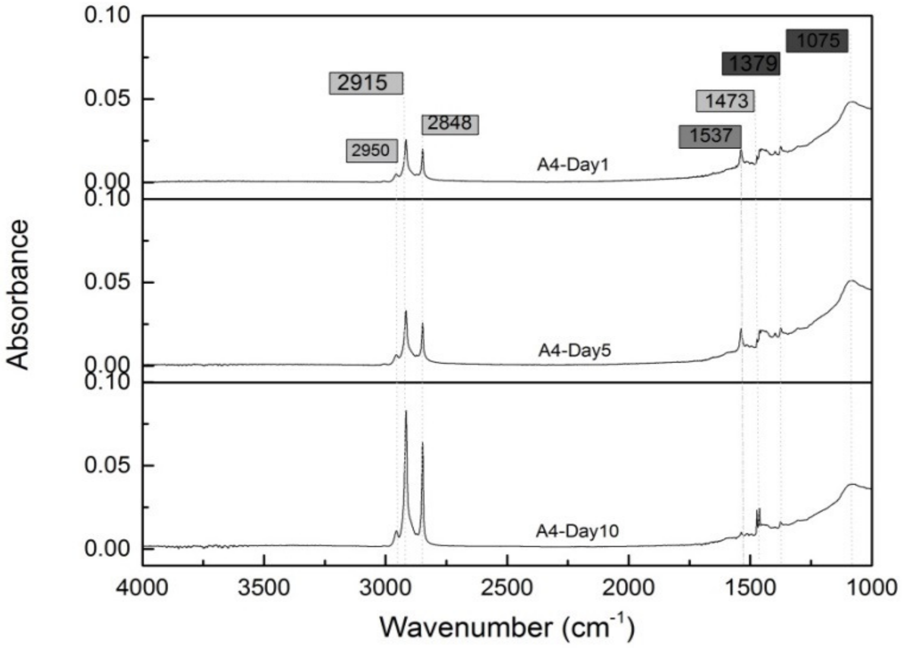


Figure 59: ATR- IR spectra of sample A4 kept in summer condition at day 1, day 5 and day 10.

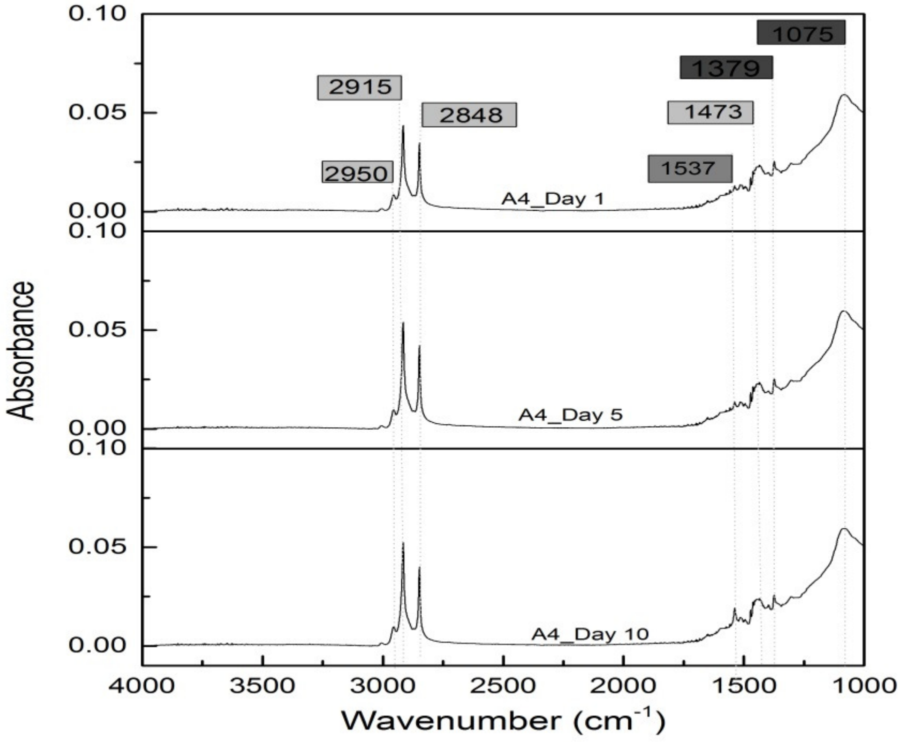


Figure 60: ATR- IR spectra of sample A4 kept in winter condition at day 1, day 5 and day 10

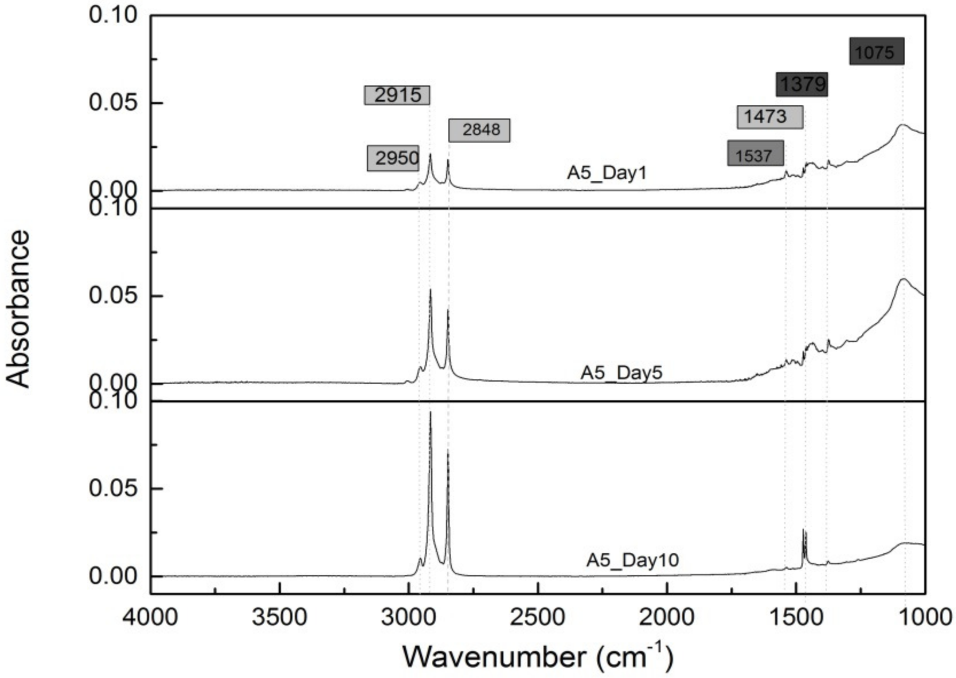


Figure 61: ATR- IR spectra of sample A5 kept in summer condition at day 1, day 5 and day 10.

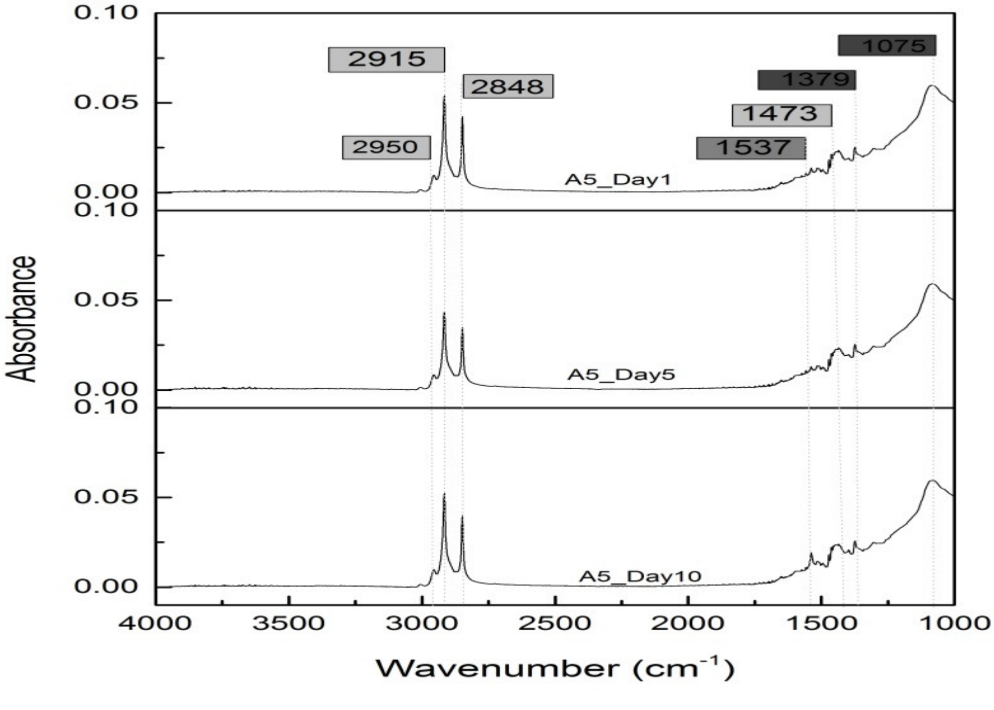


Figure 62: ATR- IR spectra of sample A5 kept in winter condition at day 1, day 5 and day 10.

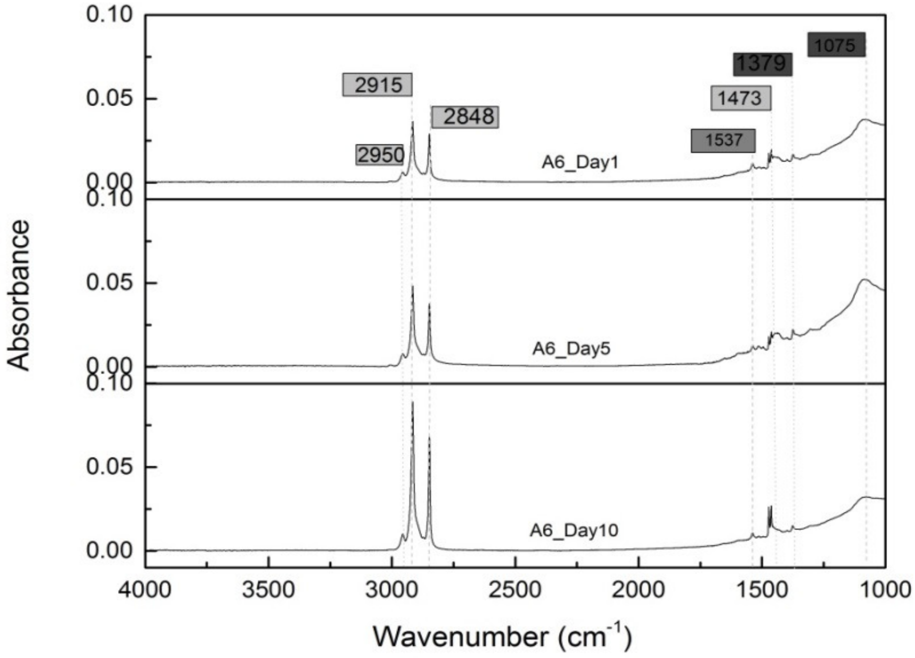


Figure 63: ATR- IR spectra of sample A6 kept in summer condition at day 1, day 5 and day 10.

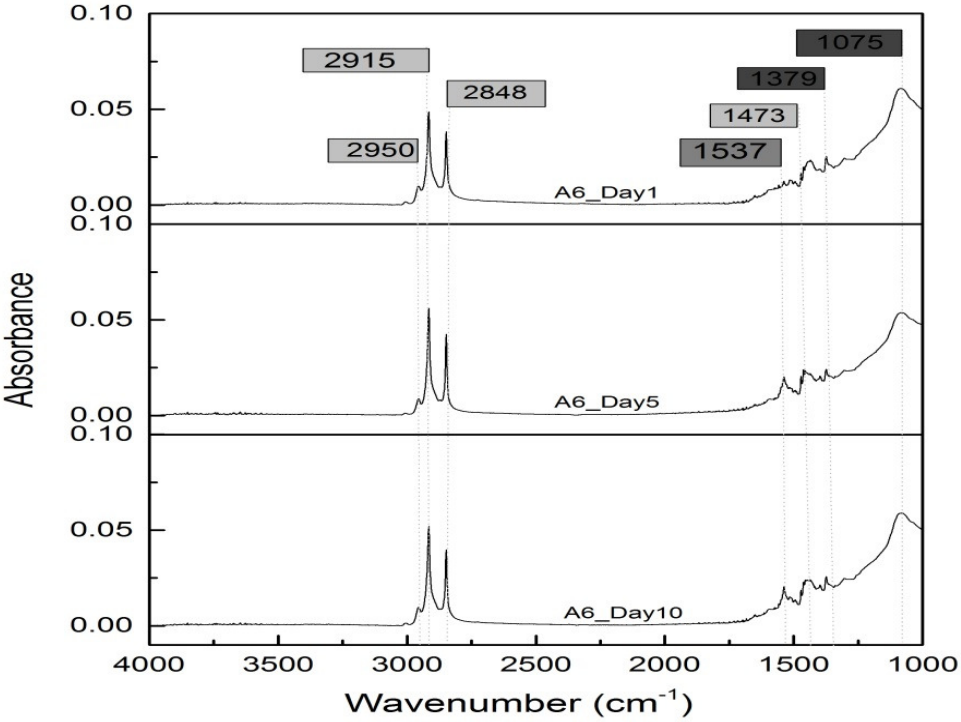
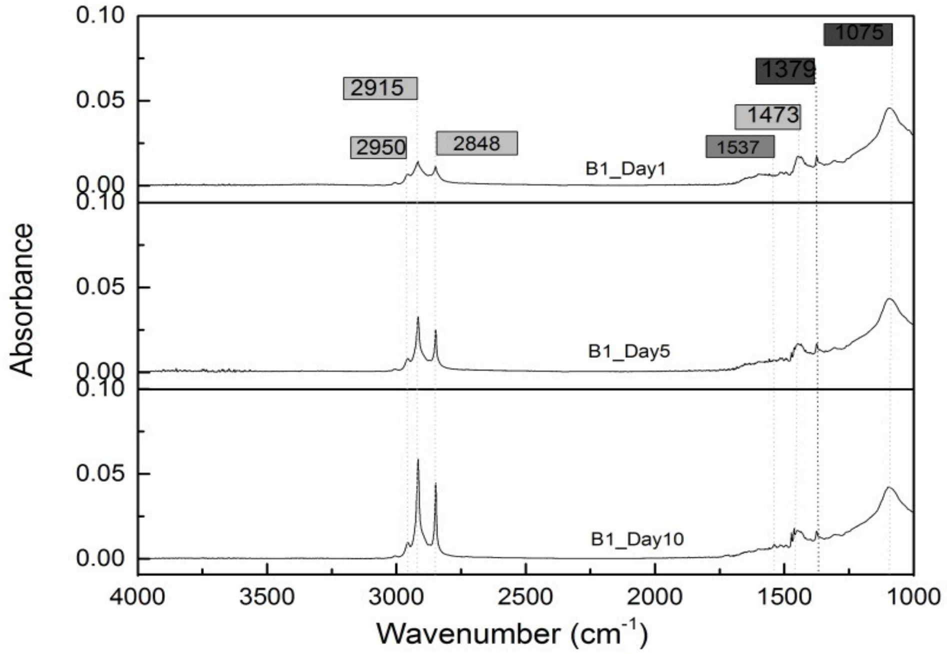


Figure 64: ATR- IR spectra of sample A6 kept in winter condition at day 1, day 5 and day 10.



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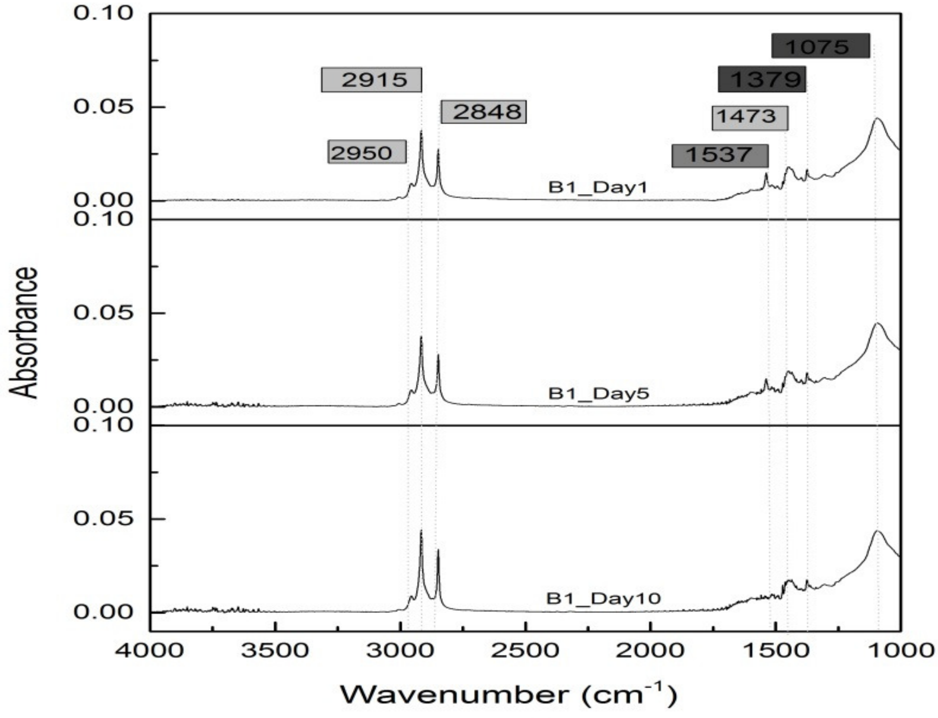

Figure 66: ATR- IR spectra of sample B1 kept in winter condition at day 1, day 5 and day 10.

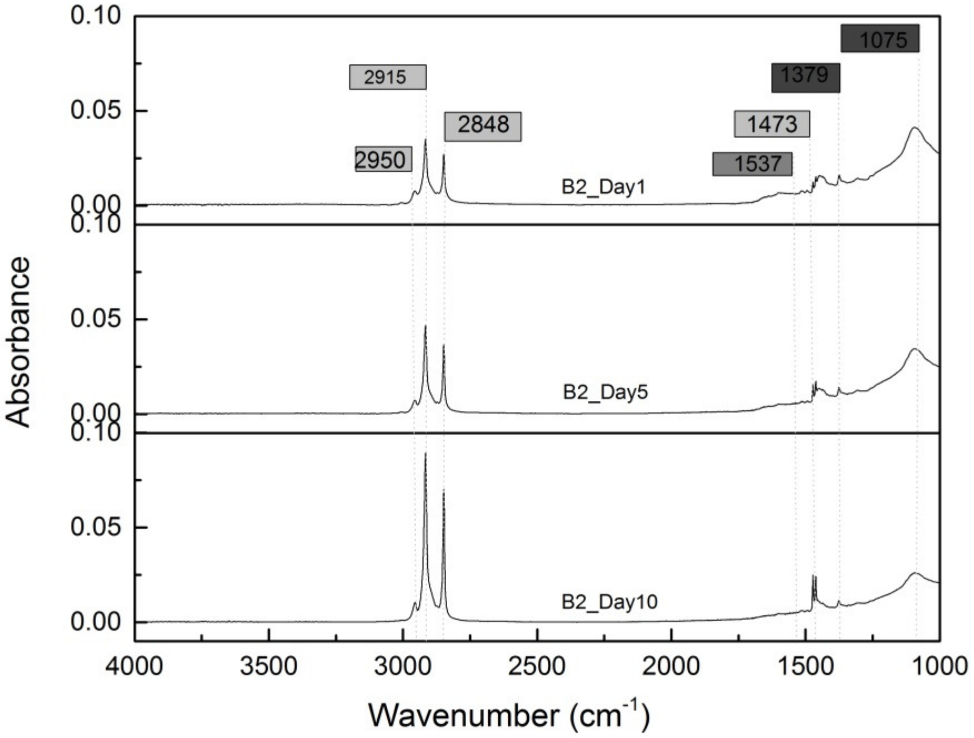

Figure 67: ATR- IR spectra of sample B2 kept in summer condition at day 1, day 5 and day 10.

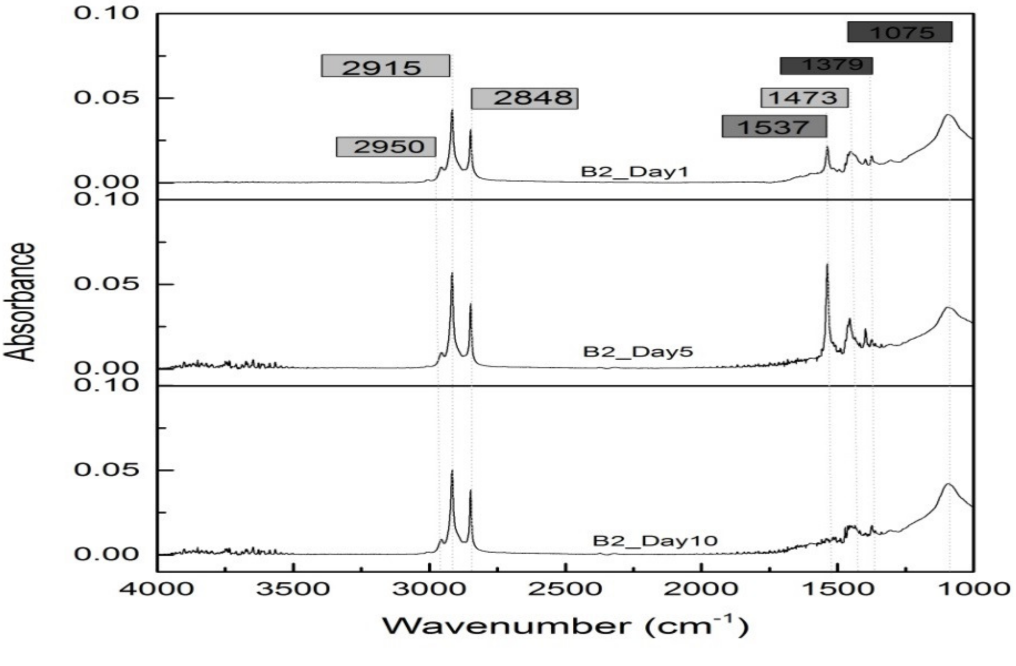

Figure 68: ATR- IR spectra of sample B2 kept in winter condition at day 1, day 5 and day 10.

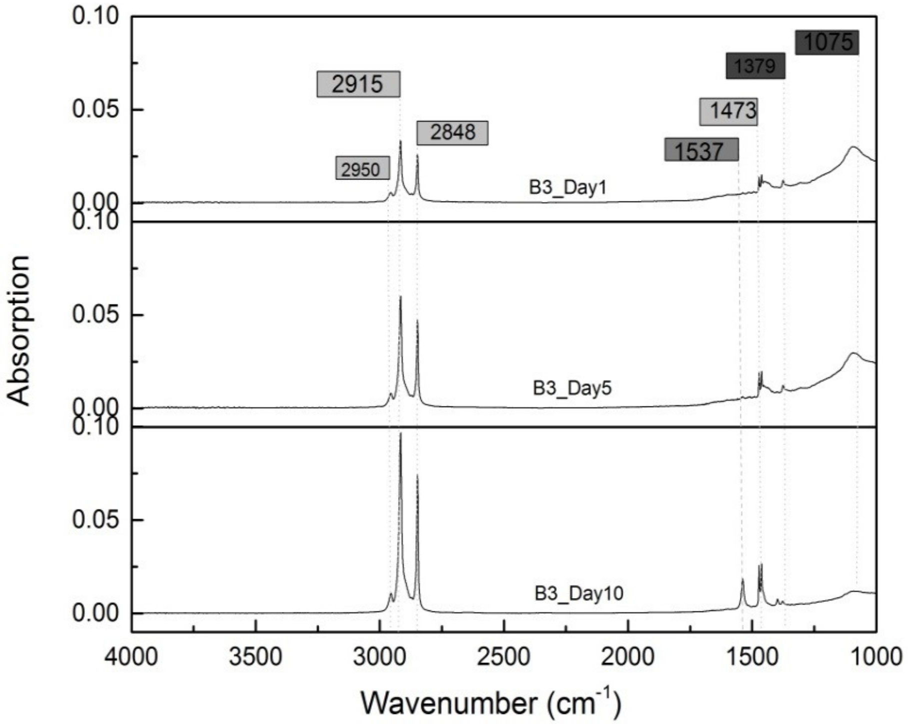

Figure 69: ATR- IR spectra of sample B3 kept in summer condition at day 1, day 5 and day 10.

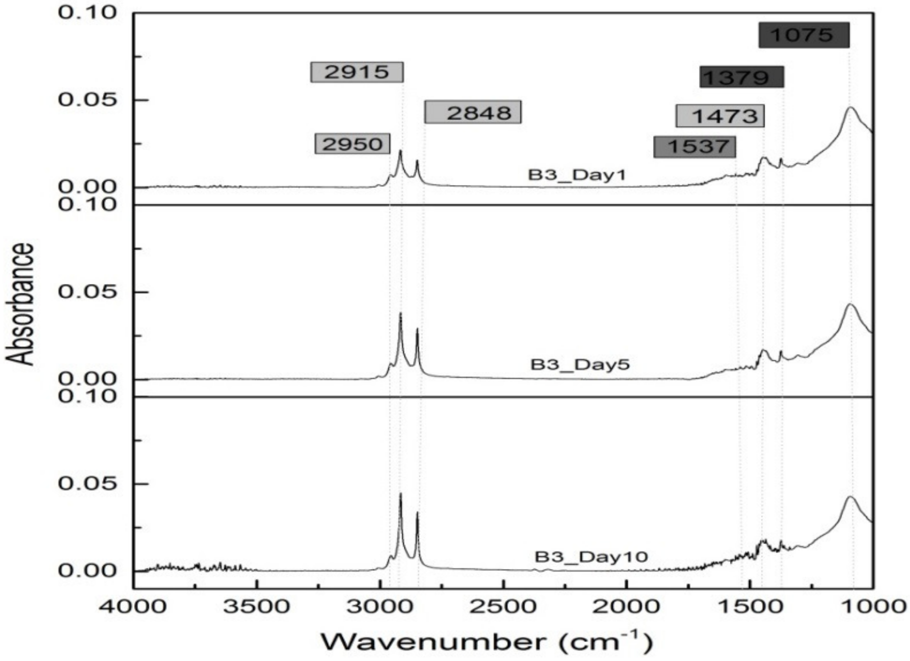

Figure 70: ATR- IR spectra of sample B3 kept in winter condition at day 1, day 5 and day 10.

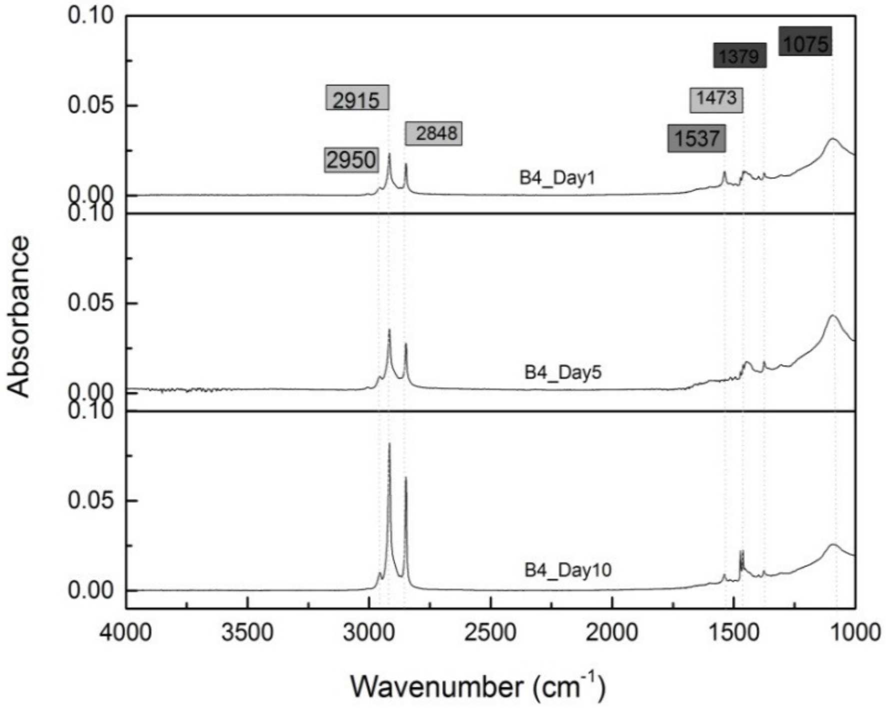

Figure 71: ATR- IR spectra of sample B4 kept in summer condition at day 1, day 5 and day 10.

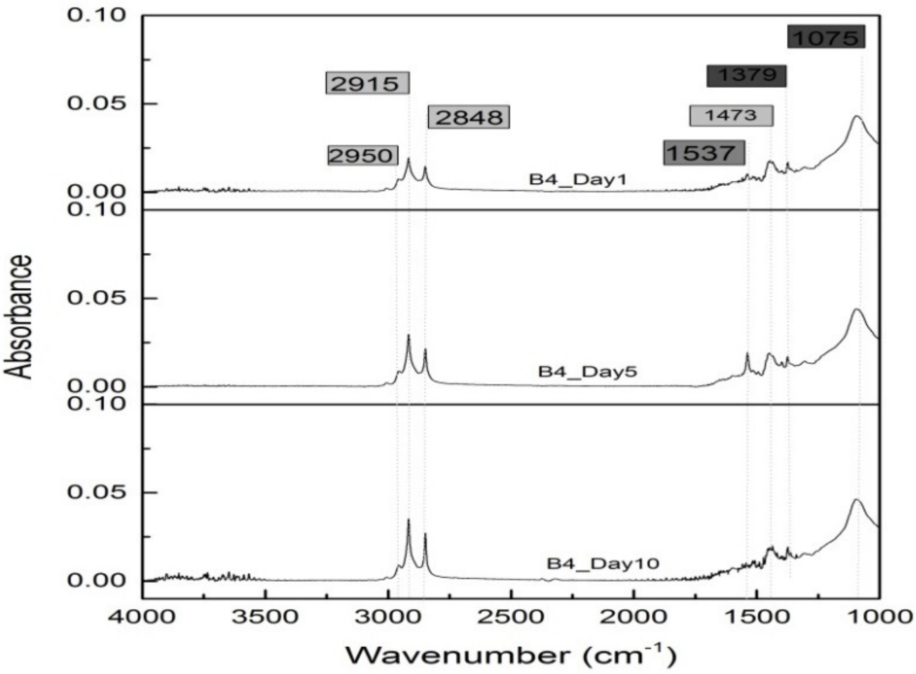

Figure 72: ATR- IR spectra of sample B4 kept in winter condition at day 1, day 5 and day 10.

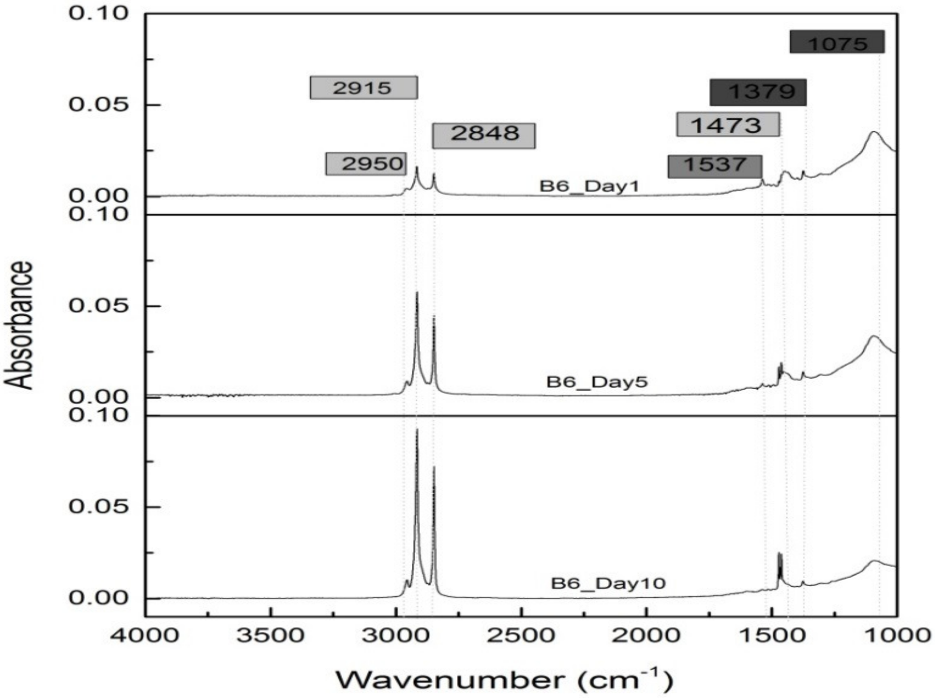

Figure 73: ATR- IR spectra of sample B6 kept in summer condition at day 1, day 5 and day 10.

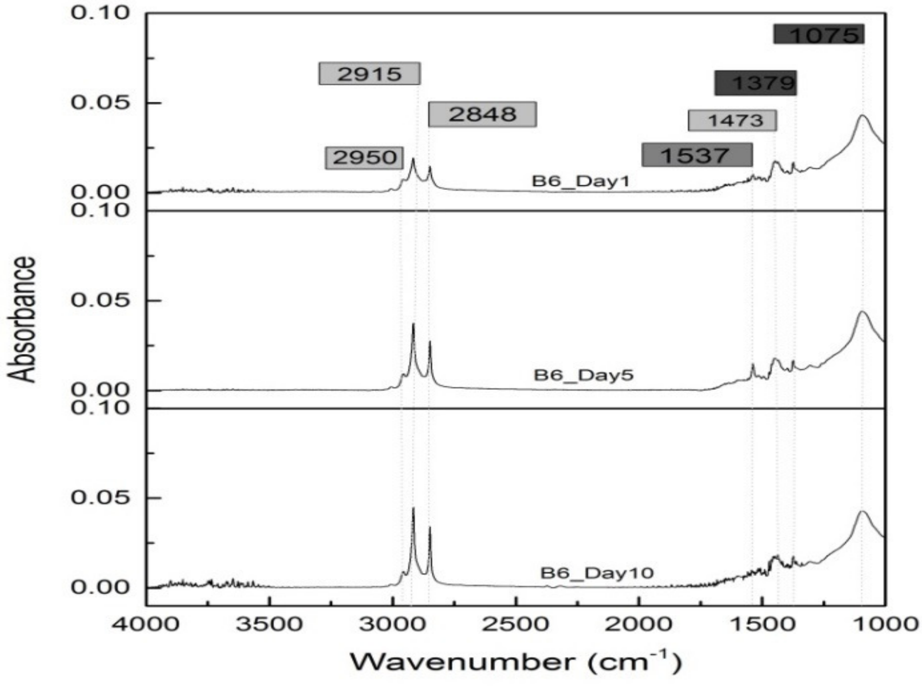

Figure 74: ATR- IR spectra of sample B6 kept in winter condition at day 1, day 5 and day 10.

Appendix II: ATR-IR spectra of sample A during soprtion of the wax.

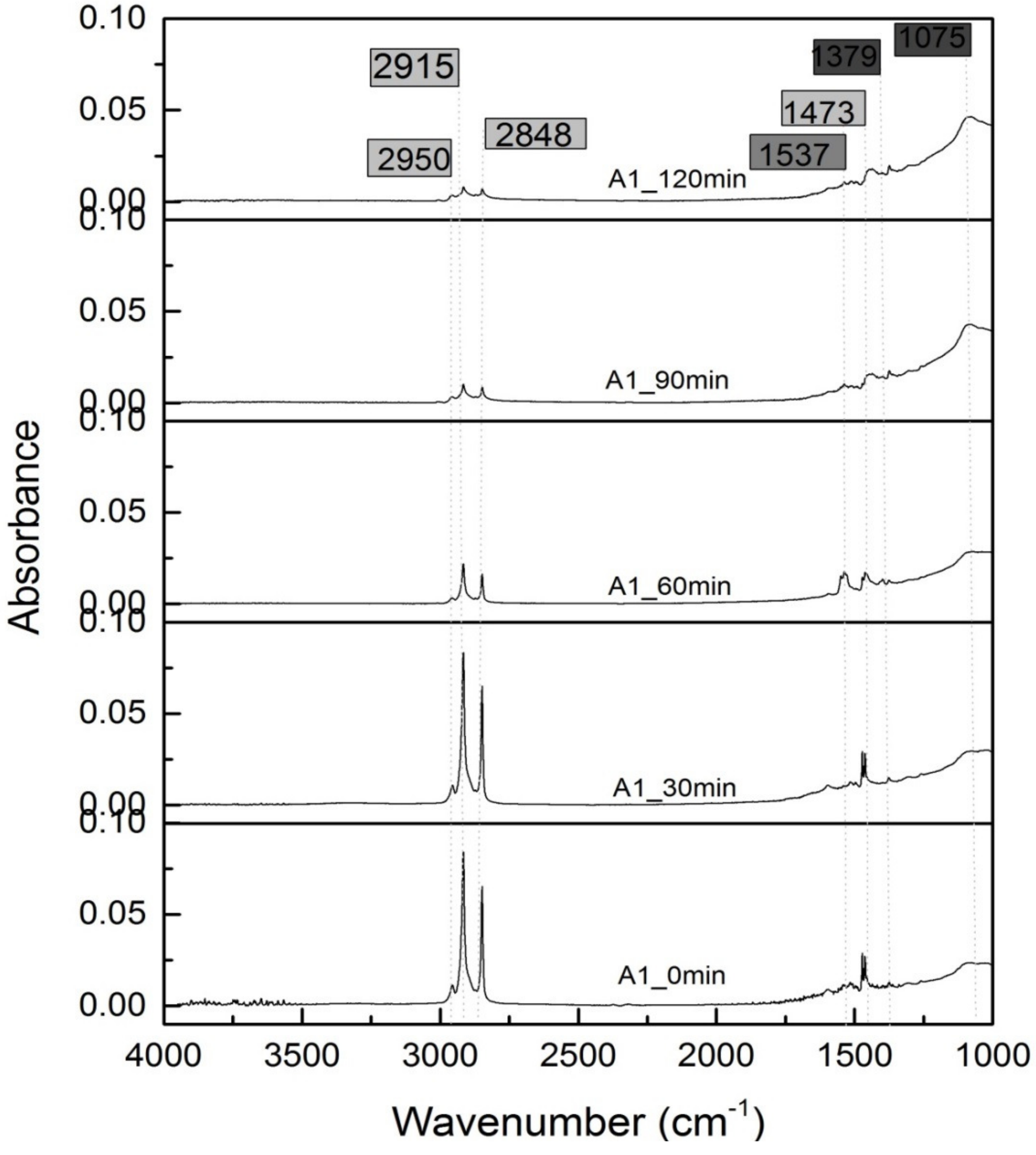

Figure 75: IR spectra of A1 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition.

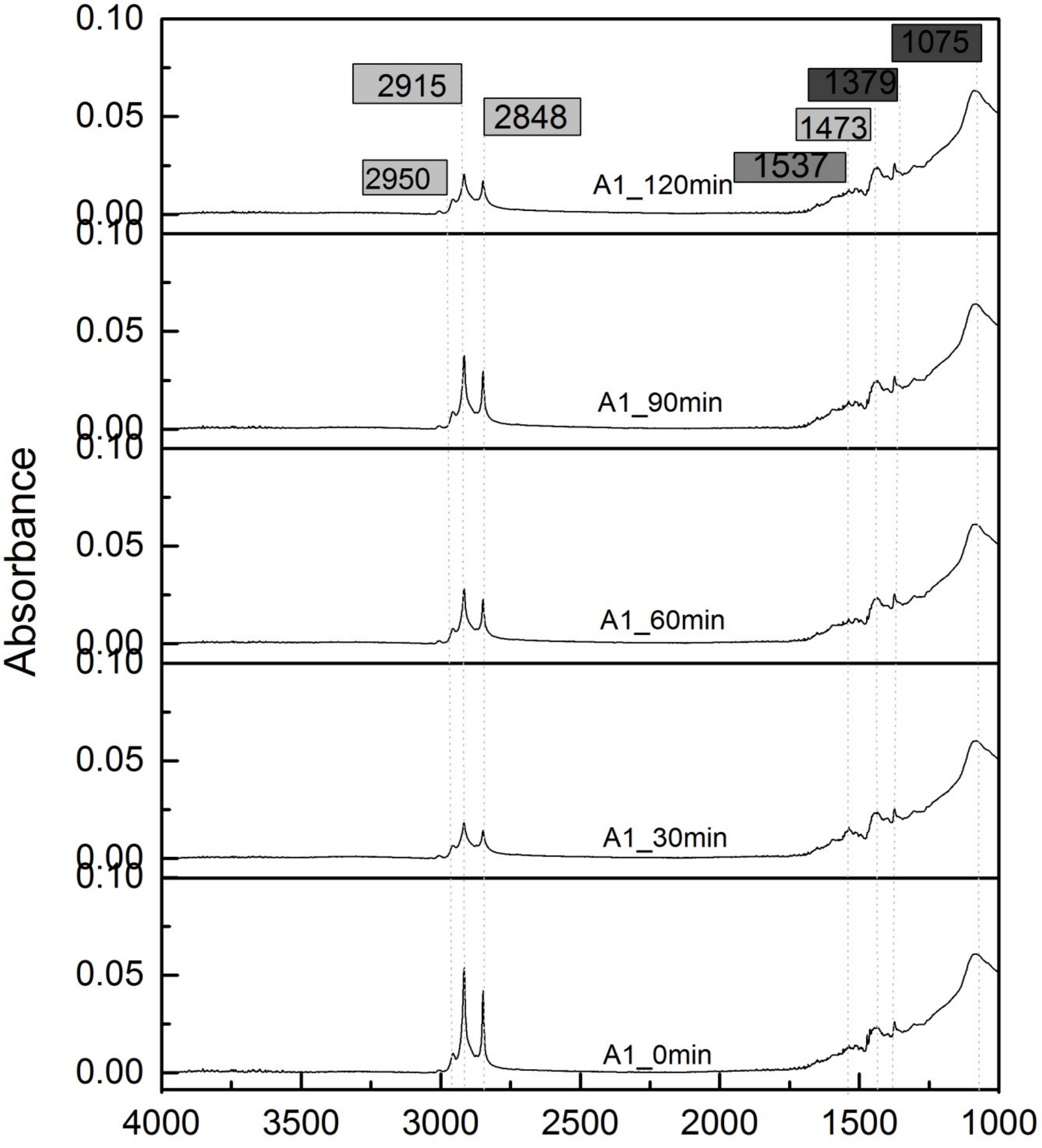

Figure 76: IR spectra of A1 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

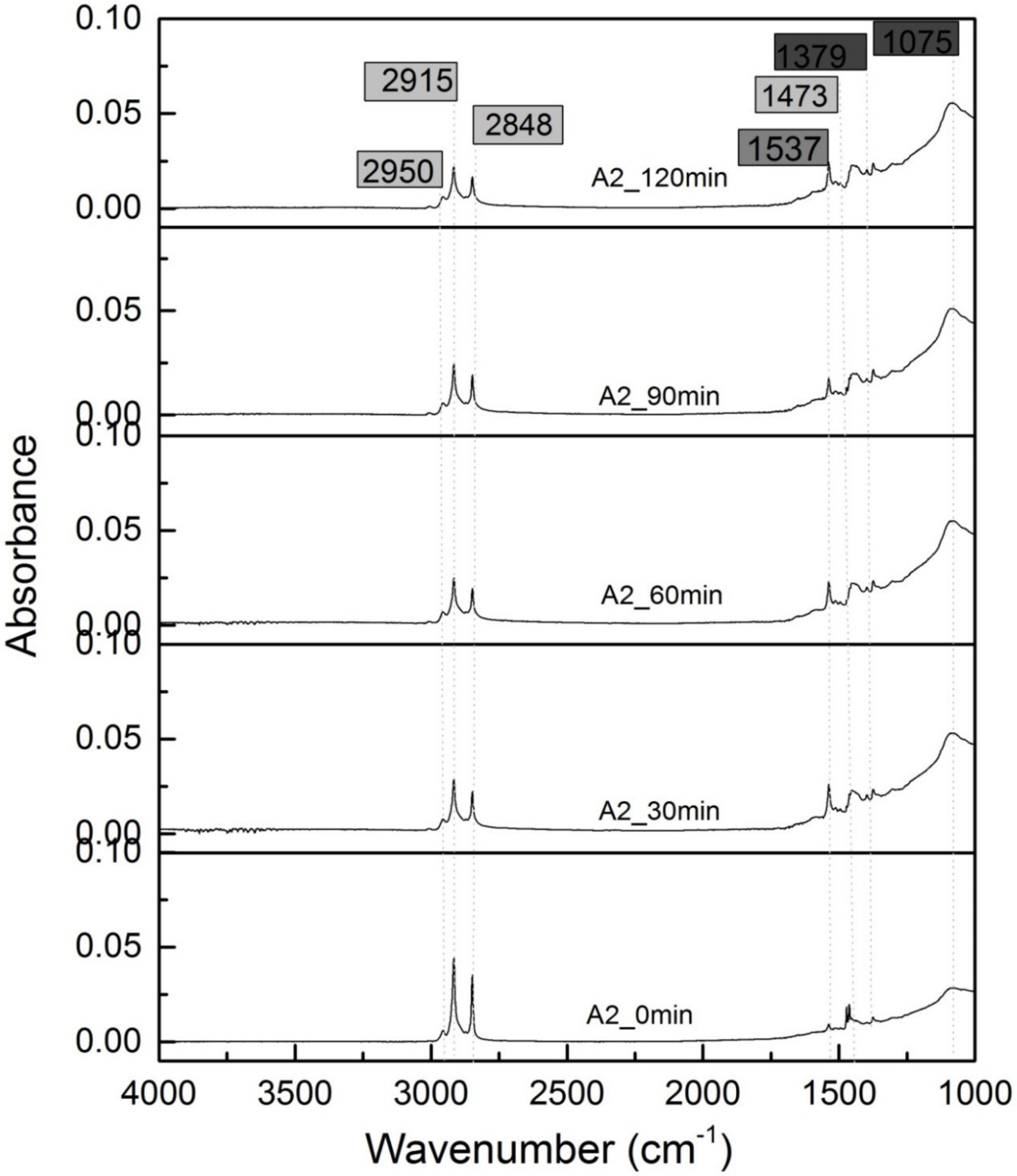

Figure 77: IR spectra of A2 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition

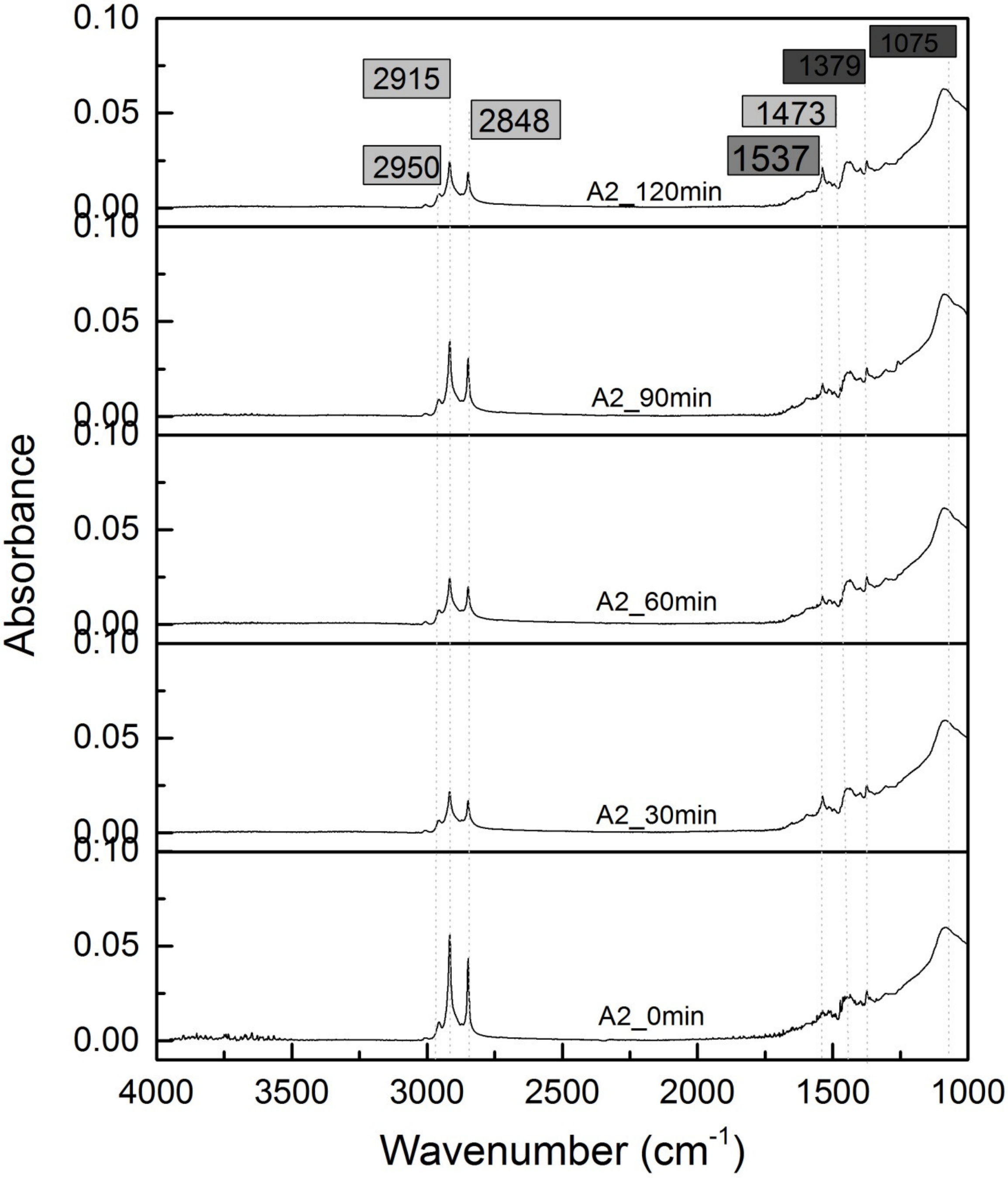

Figure 78: IR spectra of A2 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

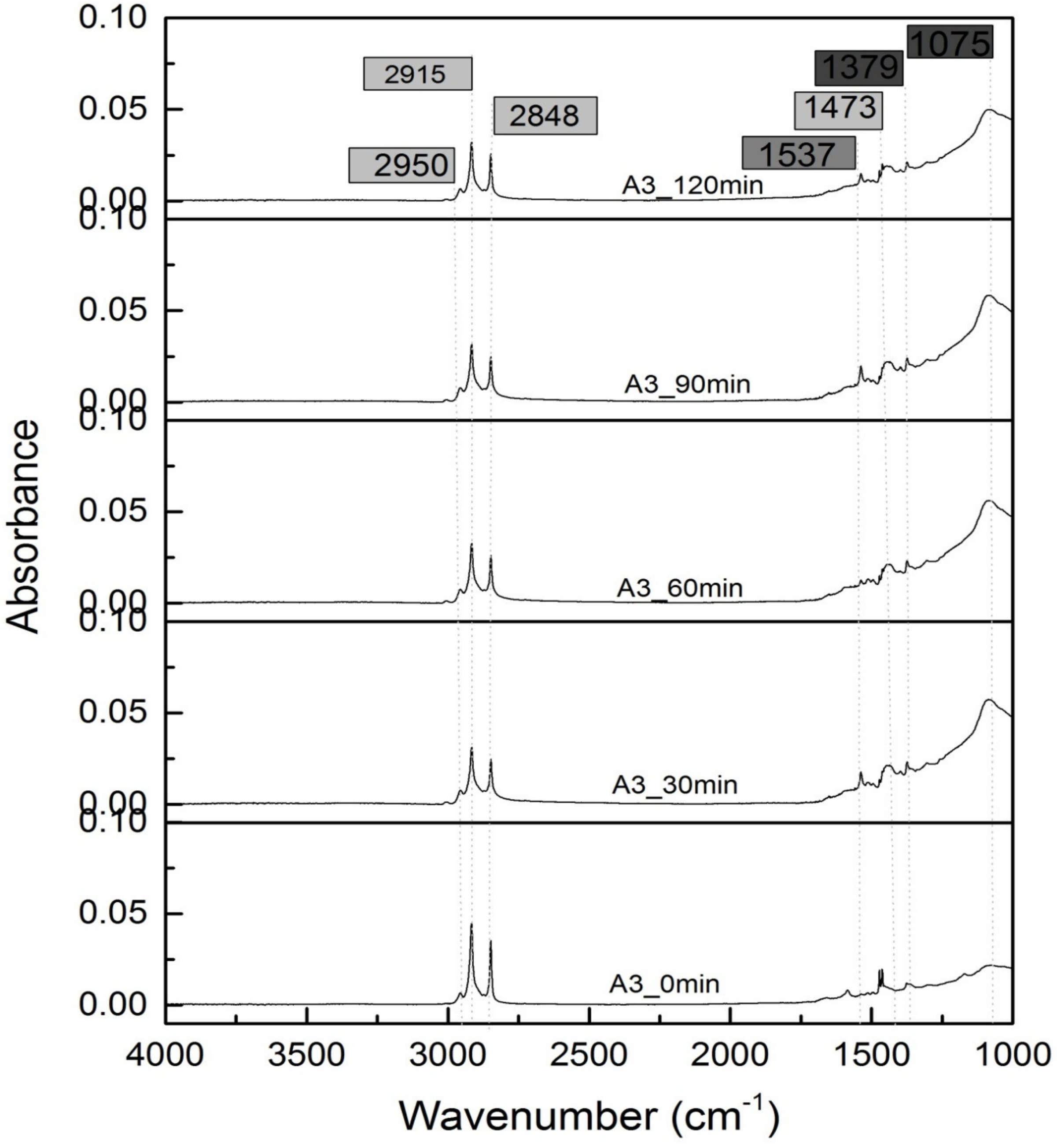

Figure 79: IR spectra of A3 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition.

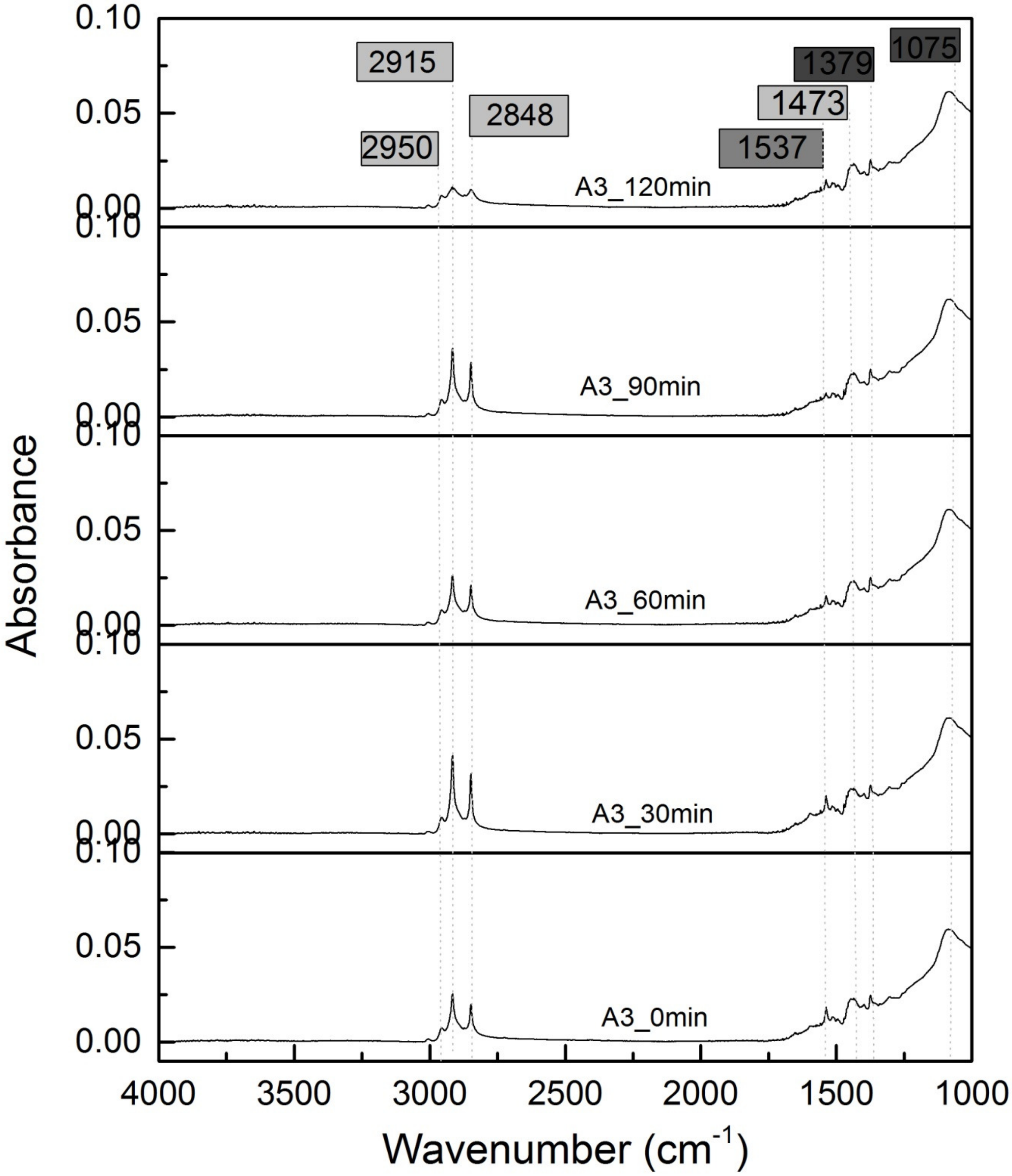

Figure 80: IR spectra of A3 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

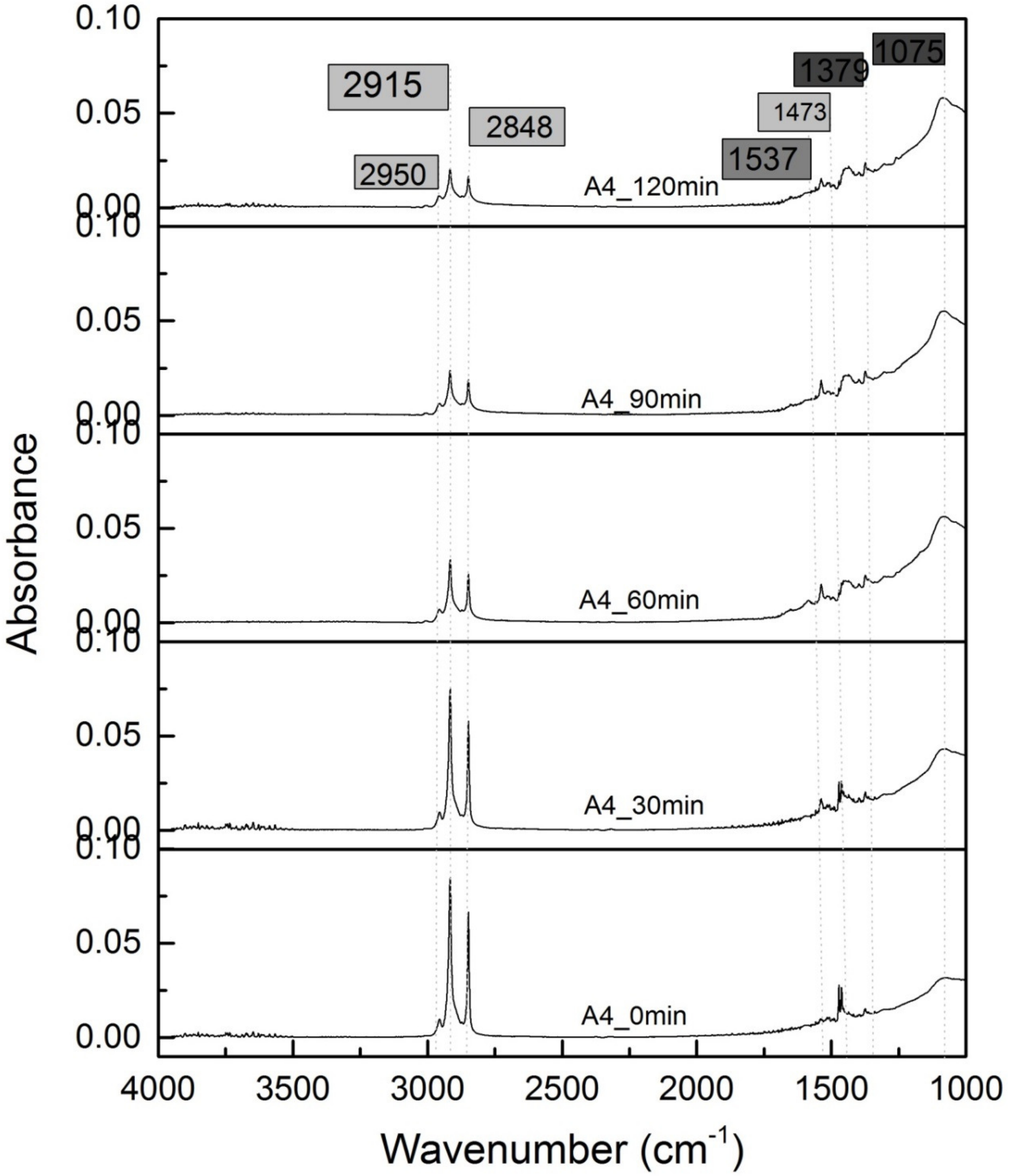

Figure 81: IR spectra of A4 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition.

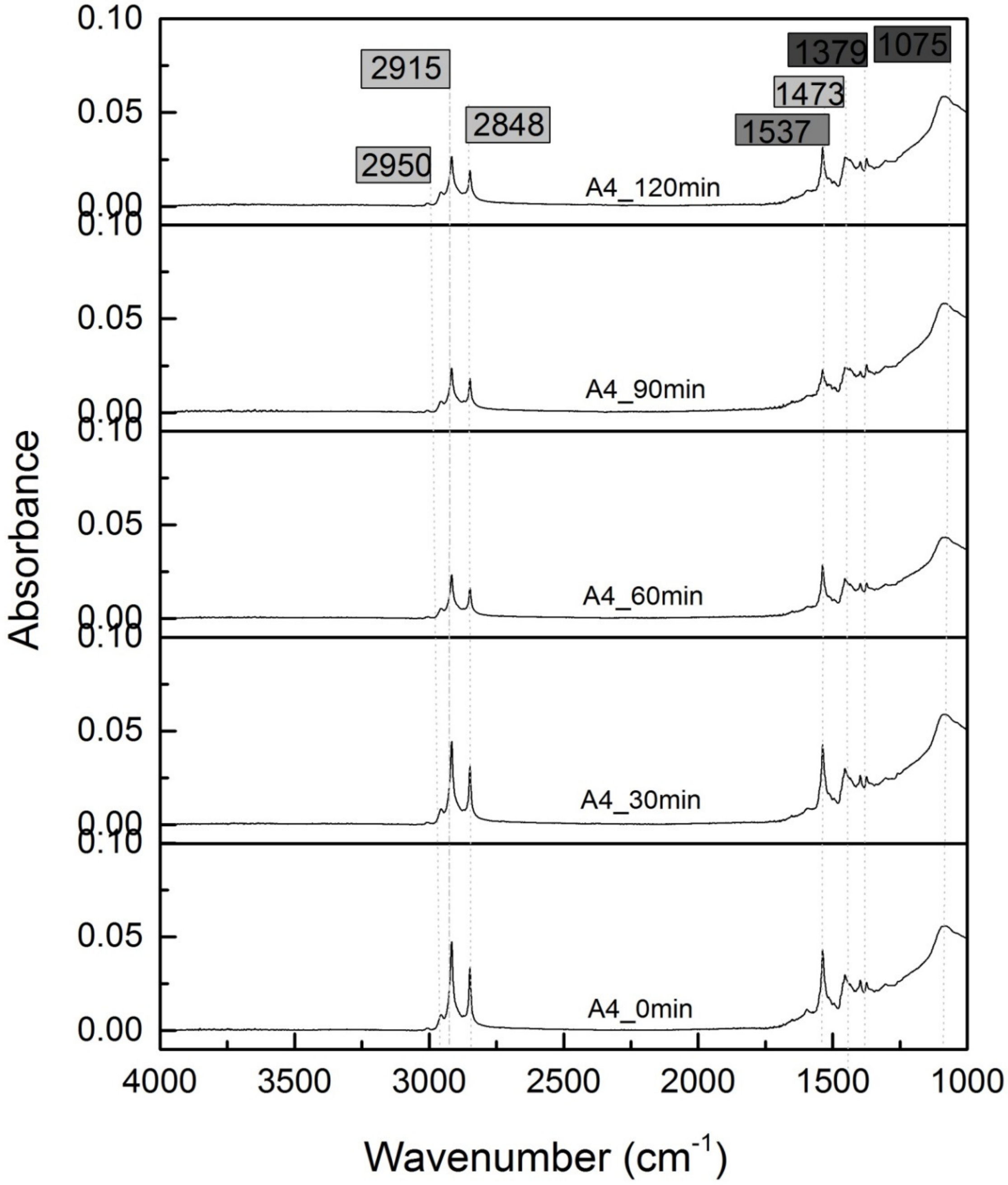

Figure 82: IR spectra of A4 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

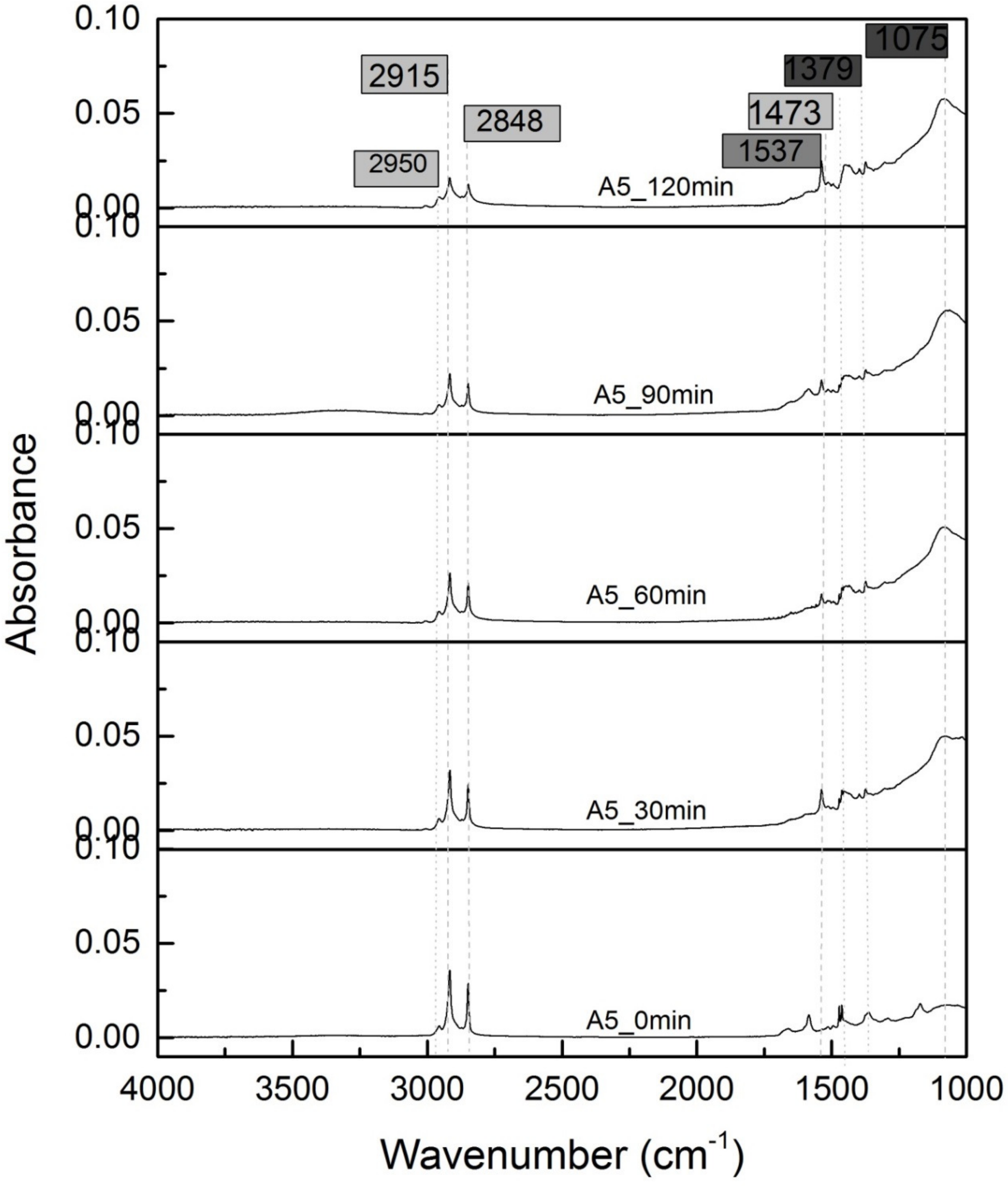

Figure 83: IR spectra of A5 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition.

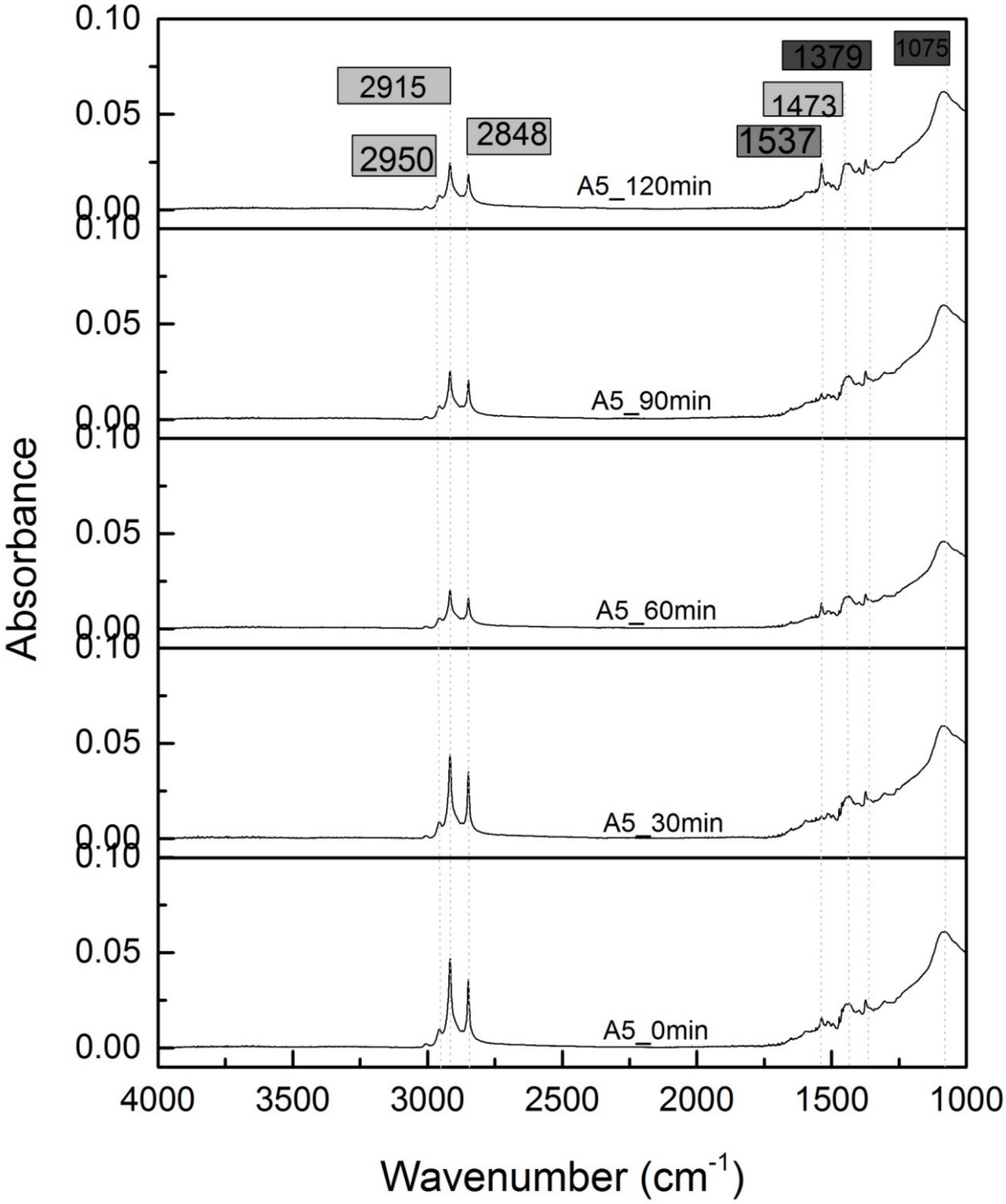

Figure 84: IR spectra of A5 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

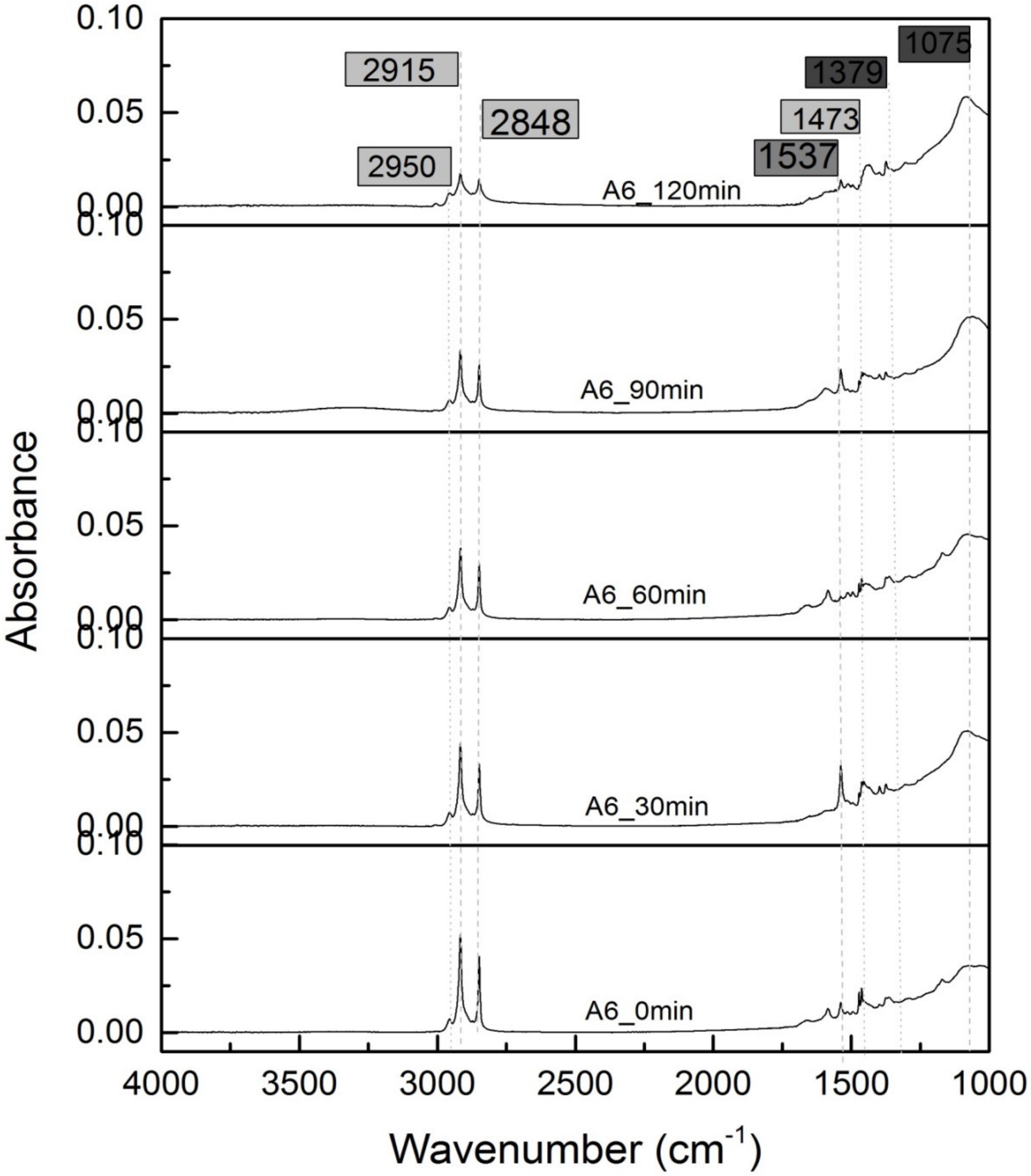

Figure 85: IR spectra of A6 at 0 min, 30 min, 60 min, 90 min and 120 min kept in summer condition.

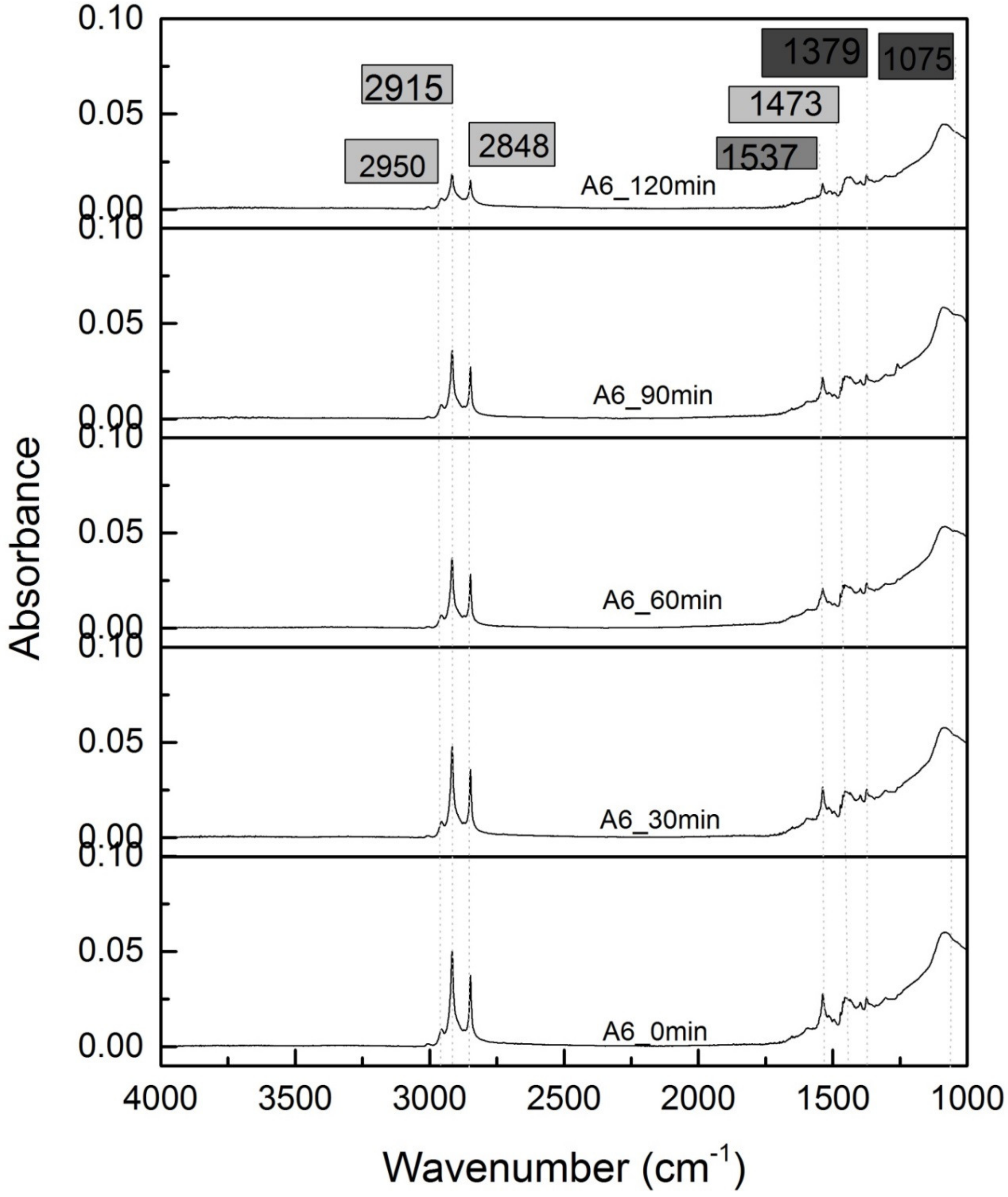

Figure 86: IR spectra of A6 at 0 min, 30 min, 60 min, 90 min and 120 min kept in winter condition.

Appendix III: Photographs of rubber samples under investigation stored at summer and winter conditions.

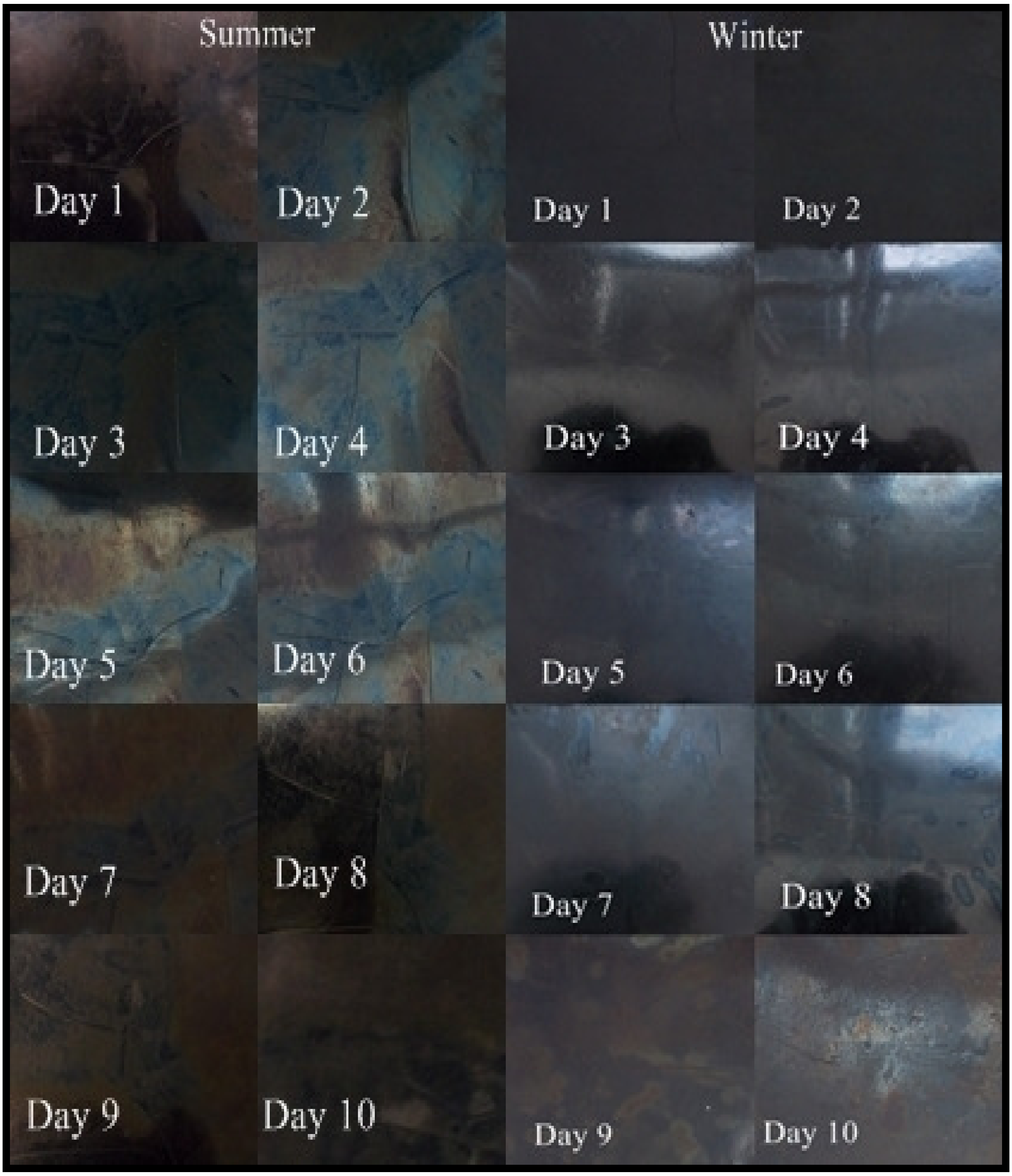

Figure 87: Photographs of sample A1 in summer and winter condition from day 1 to day 10.

Figure 88: Photographs of sample A2 in summer and winter condition from day 1 to day 10.

Figure 89: Photographs of sample A3 in summer and winter condition from day 1 to day 10.

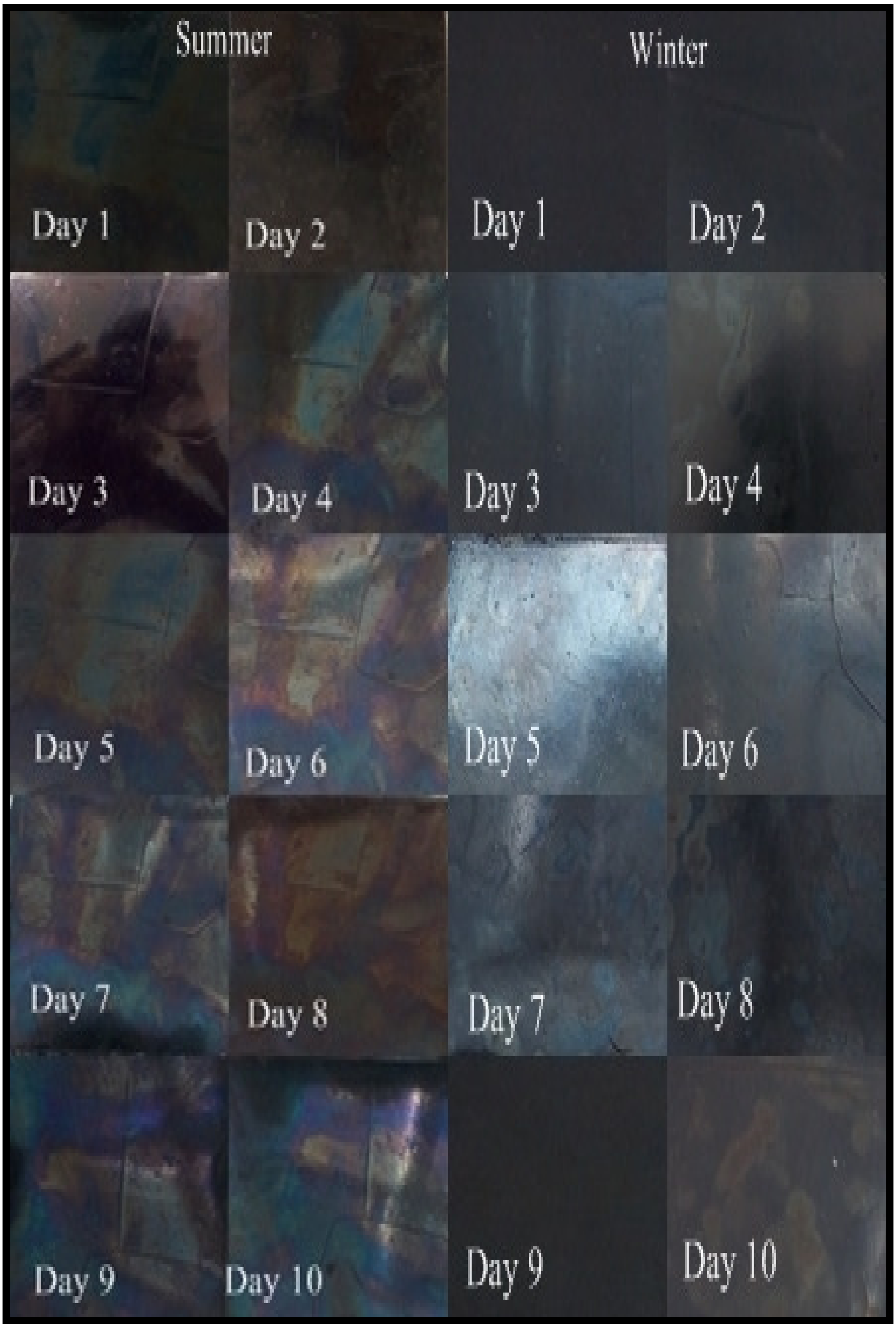

Figure 90: Photographs of sample A4 in summer and winter condition from day 1 to day 10.

Figure 91: Photographs of sample A5 in summer and winter condition from day 1 to day 10.

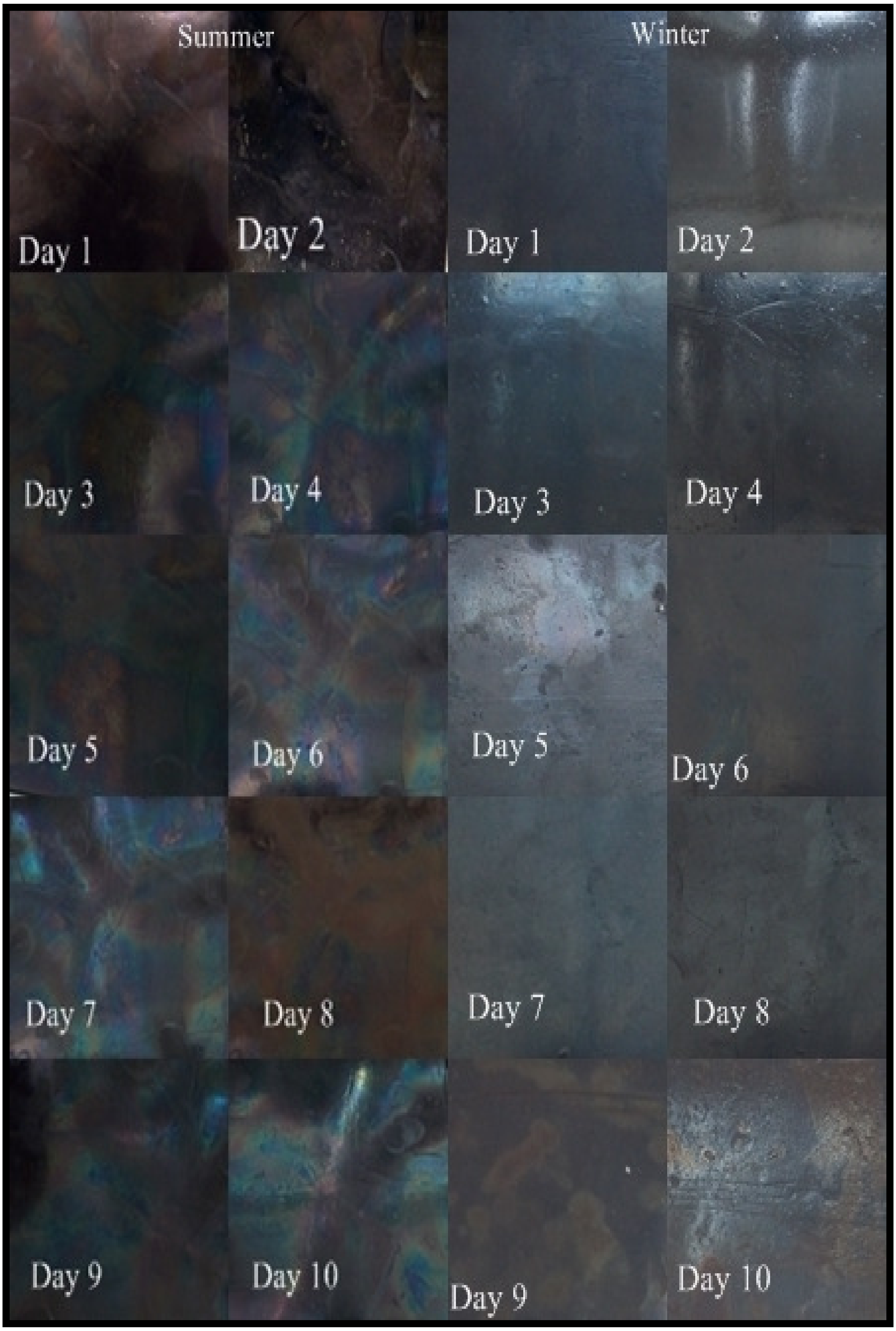

Figure 92: Photographs of sample A6 in summer and winter condition from day 1 to day 10.

Figure 93: Photographs of sample B1 in summer and winter condition from day 1 to day 10.

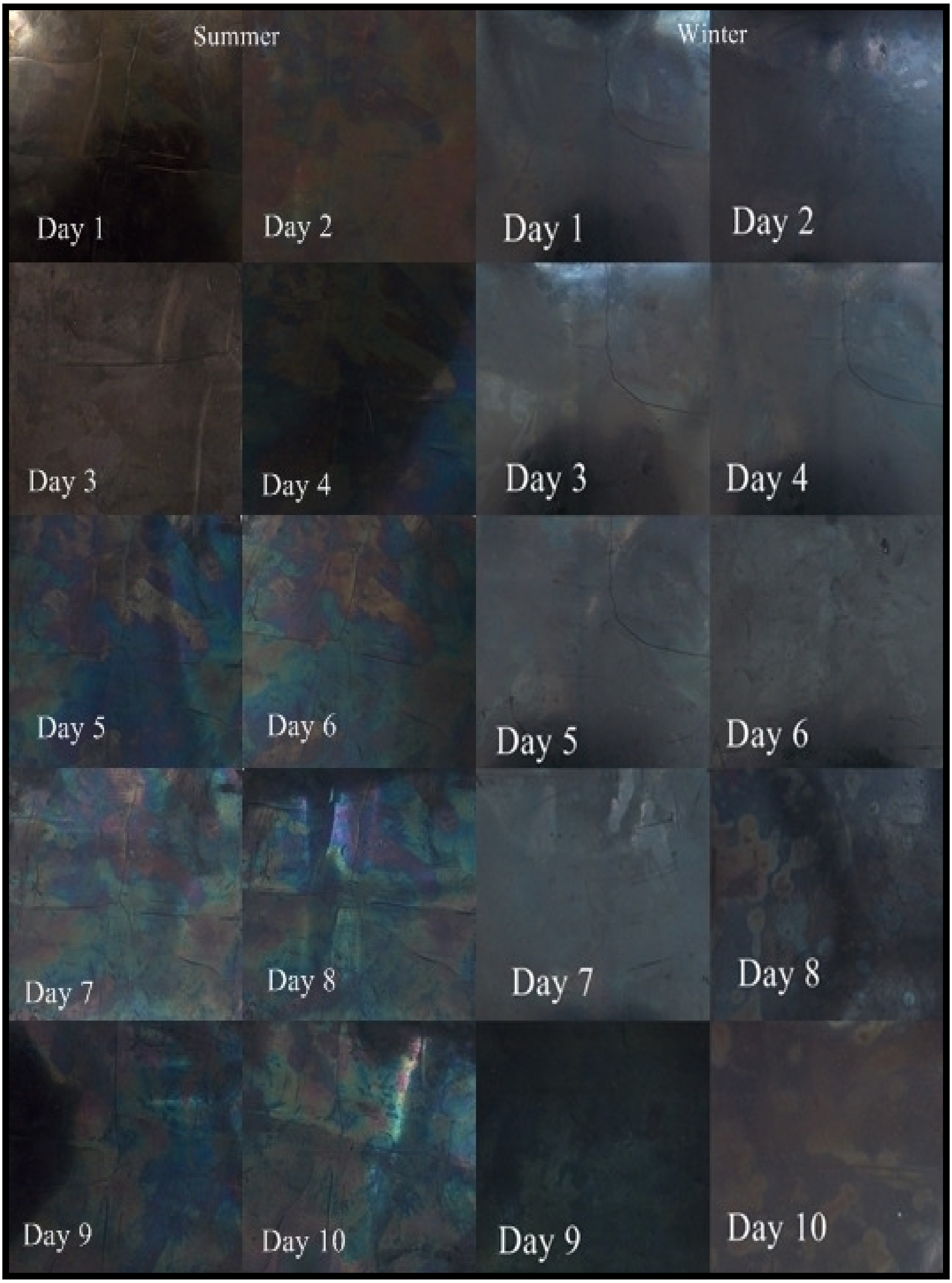

Figure 94: Photographs of sample B2 in summer and winter condition from day 1 to day 10.

Figure 95: Photographs of sample B3 in summer and winter condition from day 1 to day 10.

Figure 96: Photographs of sample B4 in summer and winter condition from day 1 to day 10.

Figure 97: Photographs of sample B6 in summer and winter condition from day 1 to day 10.

Appendix IV: SEM images of rubber samples after desorption and sorption.

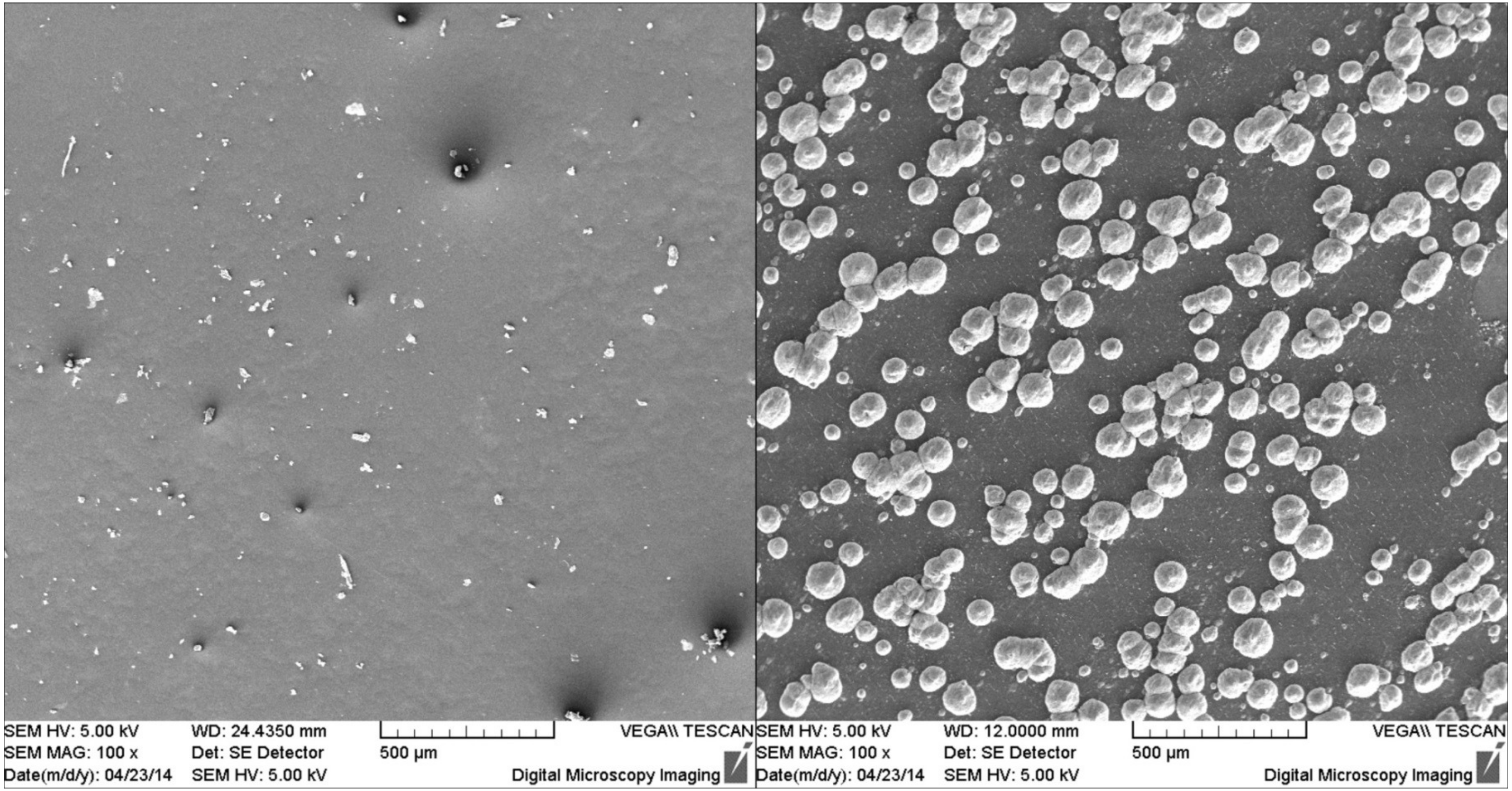

Figure 98: SEM micrograph (magnification 100x) of sample A1 after sorption (left) and after desorption (right).

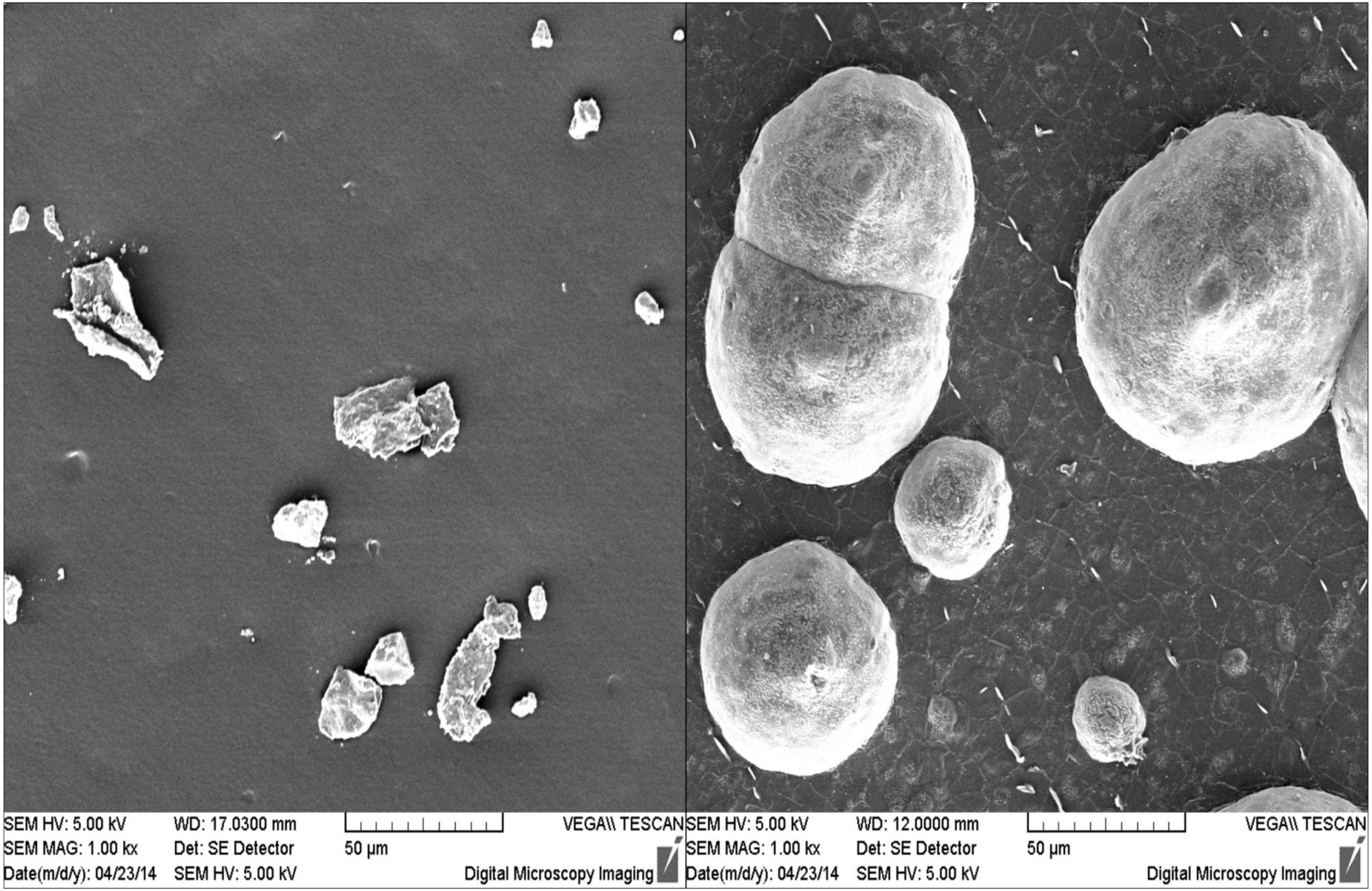

Figure 99: SEM micrograph (magnification 1000x) of sample A2 after sorption (left) and after desorption (right).

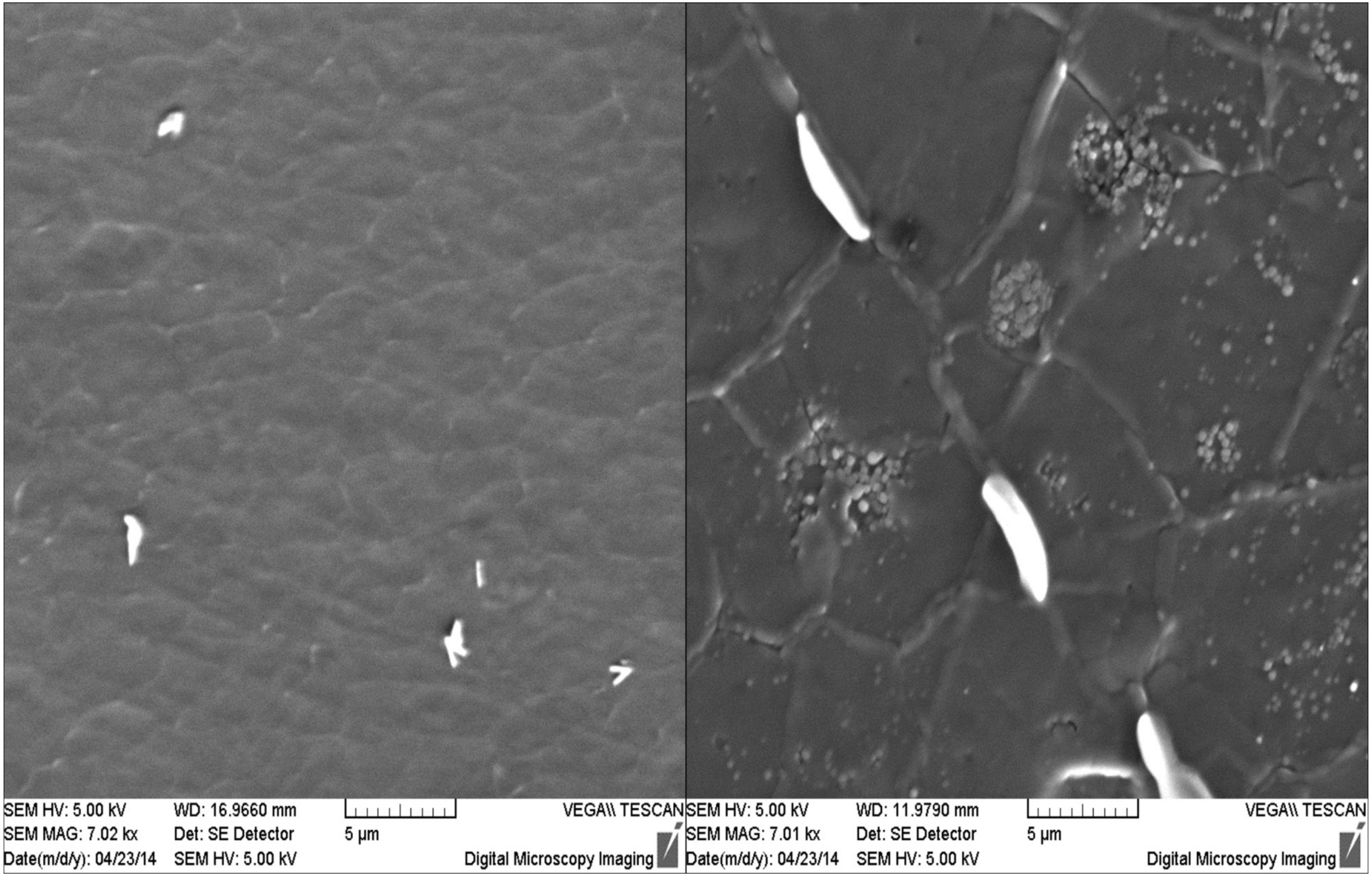

Figure 100: SEM micrograph (magnification 100x) of sample A3 after sorption (left) and after desorption (right).

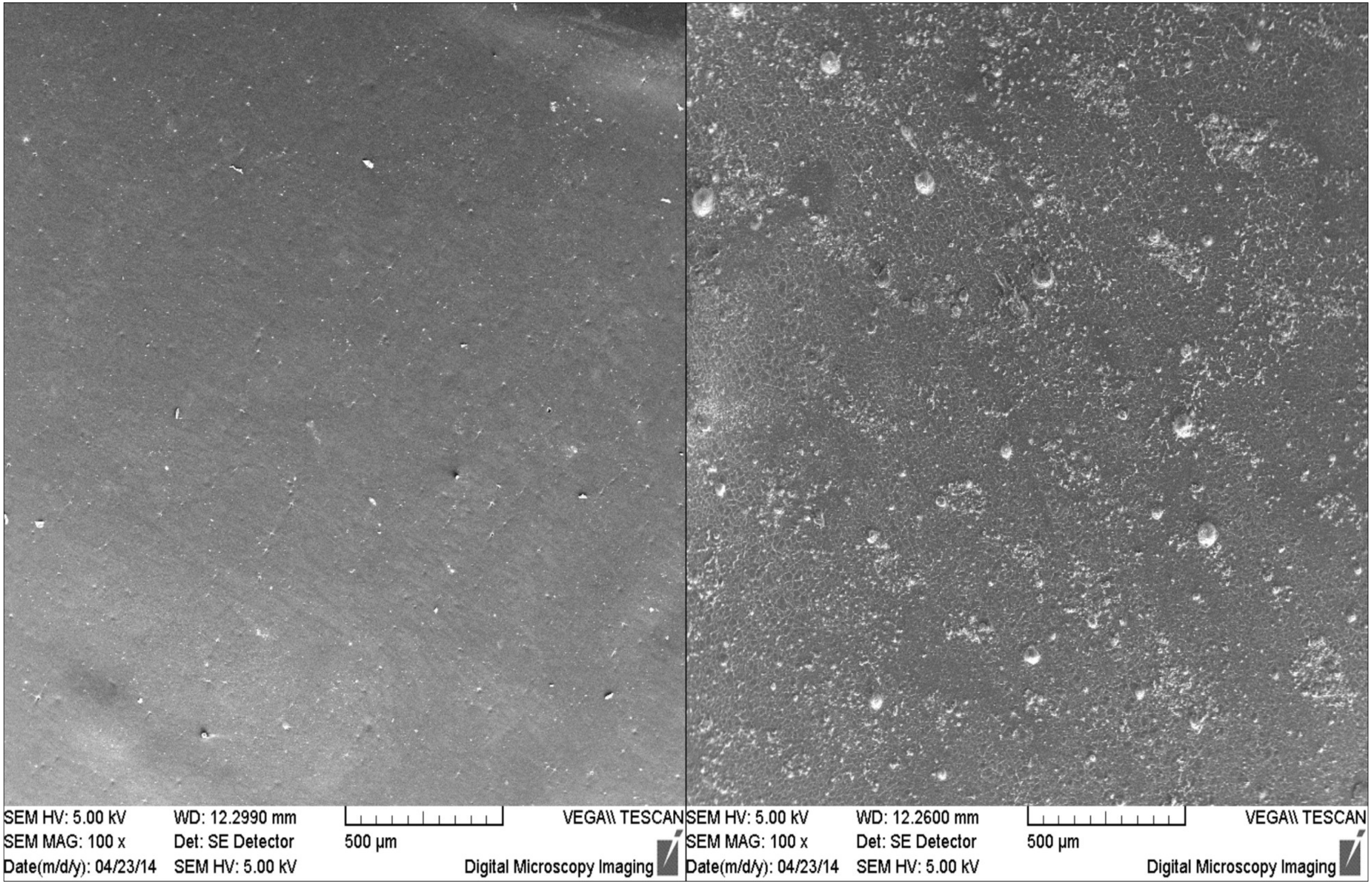

Figure 101: SEM micrograph (magnification 100x) of sample B1 after sorption (left) and after desorption (right).

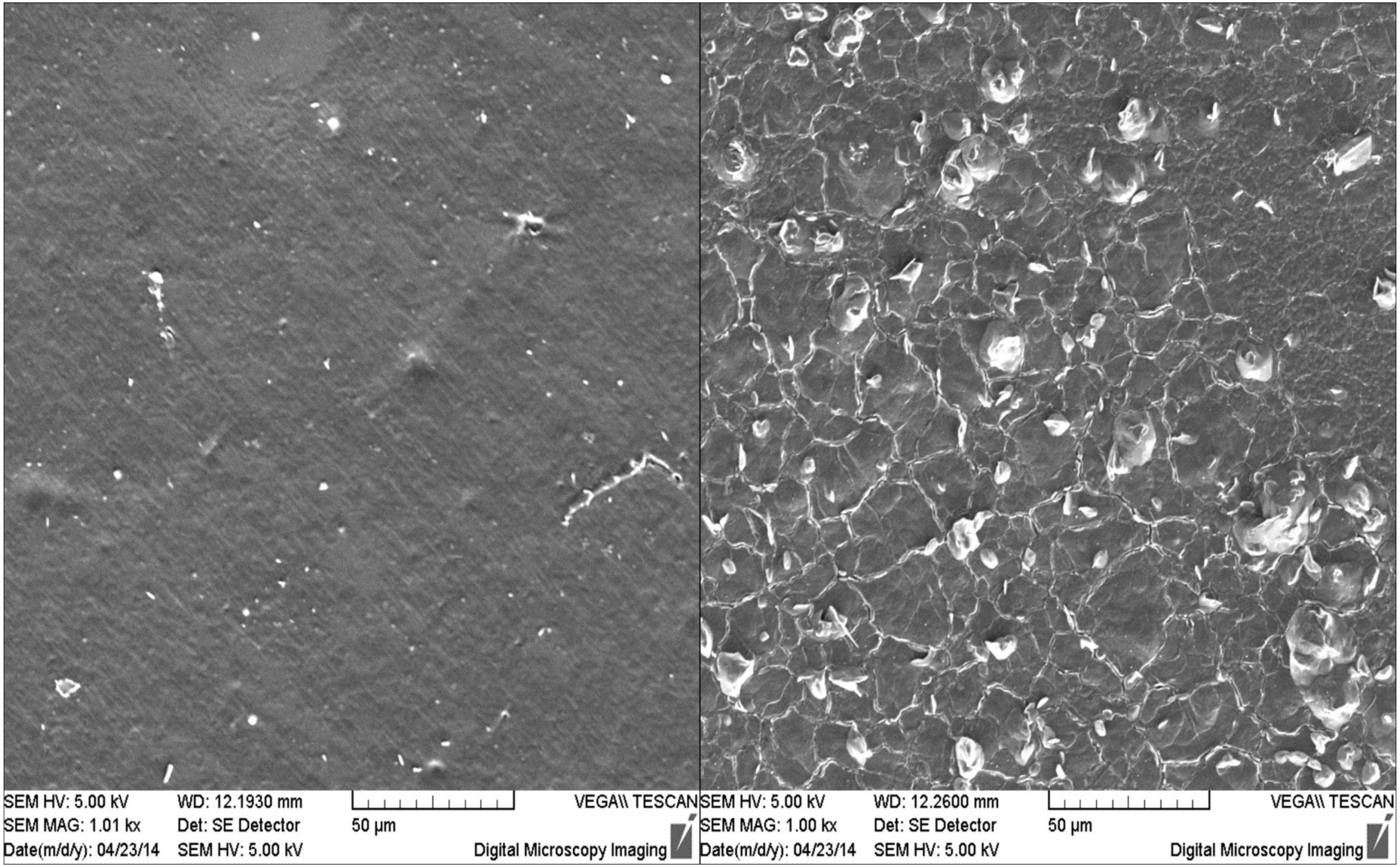

Figure 102: SEM micrograph (magnification 100 x) of sample B2 after sorption (left) and after desorption (right).

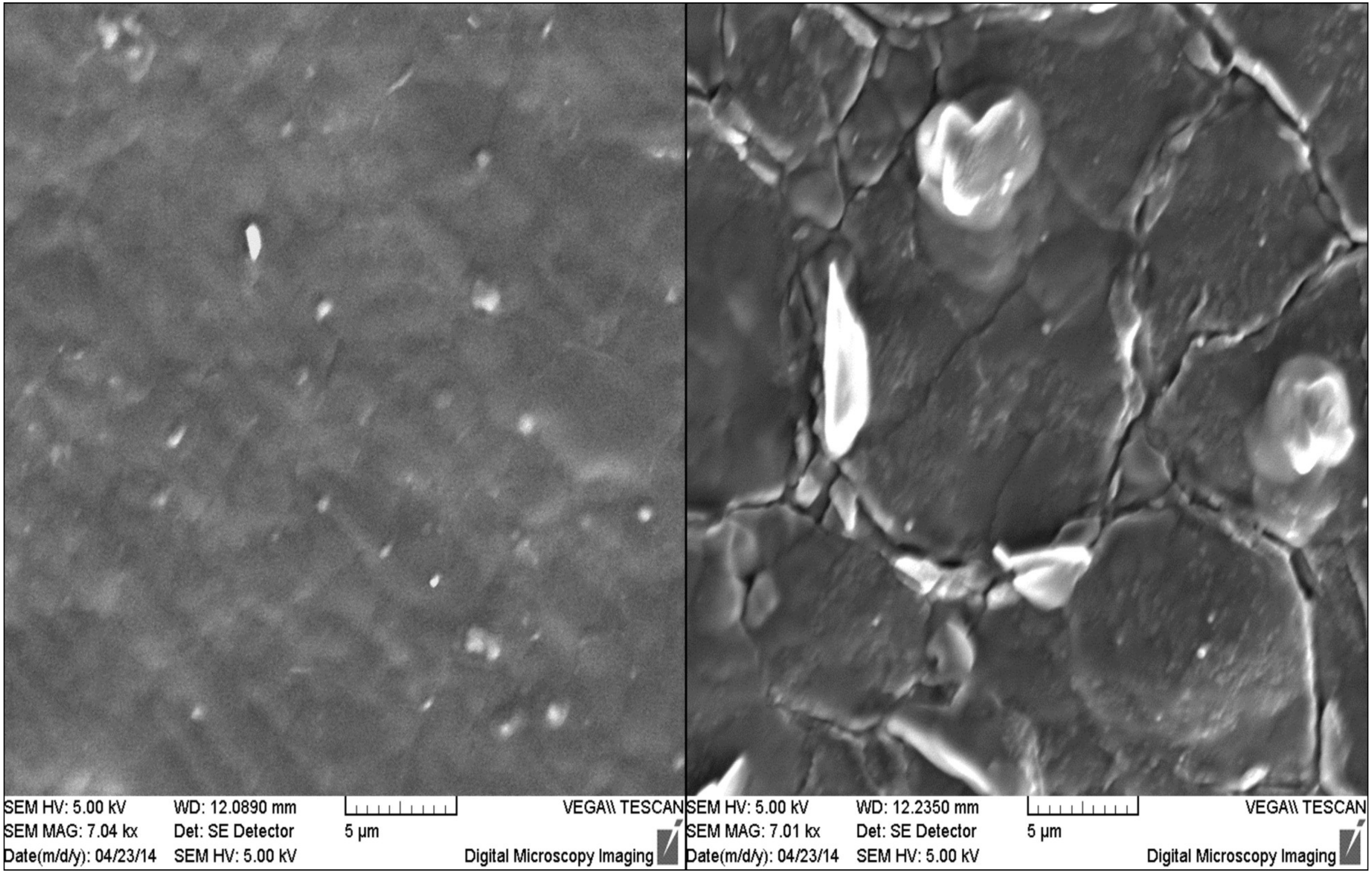

Figure 103: SEM micrograph (magnification 100 x) of sample B3 after sorption (left) and after desorption (right).