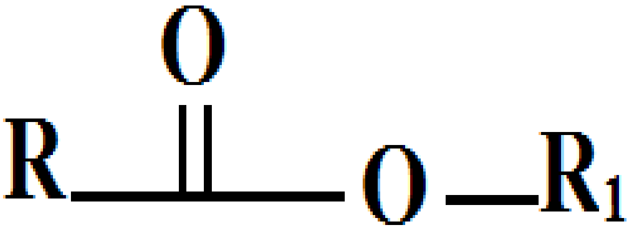

$\mathrm{R}-\overset{\mathrm{O}}{\|}-\mathrm{O}-\mathrm{R}_1$

Biodiesel

Aging of polymer in diesel and biodiesel blended fuel

Master of Science Thesis in the Master's Programme Innovative and Sustainable Chemical Engineering

KALIM ULLAH

Department of Chemical and Biological Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY
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Examiner: Börje Gevert

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ABSTRACT

As access to oil-derived fuels decreases, it increases the need to find new alternative fuels. Biodiesel is one of the promising fuels, having several advantages compared with fossil fuels. Biodiesel is an alkyl ester of long chain fatty acids derived from vegetable oil by trans-esterification reaction. Rapeseed methyl ester, RME, is one popular biodiesel in Europe. Biodiesel is very aggressive in nature as it readily oxidizes, producing highly acidic constituents which degrade polymers, soften rubber materials and corrode metal over time. It is miscible with petro-diesel in any key; one way of decreasing its aggressiveness is to make a blend with petro-diesel.

The project work is performed in two parts, the main objective of first part to find out preeminent level of biodiesel in petro diesel which follows the ASTM specifications. To achieve the desired level, various blends of fuel (B10, B20 and B30) are thermally aged for 100 hours at 85 ^{0}C. Various products of the fuel are characterized by analysing acid number, hydro peroxide number and water contents. The effect of antioxidants is also investigated by using two types of RME, one with 1.6 hour and the other with 9 hour stability. It is concluded that fuel B10 follow the ASTM specifications without adding any antioxidants. B20 is less oxidized than B30 with 1.6 hour stable RME and can be used in car engines by adding antioxidants or creating inert system (oxygen-free environment).

In the second part, the fuels are aged in "nearly car-like environment" i.e. with polymeric material using same conditions of time and temperature. Objective of this part is to see how the polymer affects the fuel and further to inspect the polymer compatibility in the fuel. POM (Polyoxymethylene) is the polymeric material chosen which is also used in car parts. Four different schemes (open & nitrogen system with and without antioxidants) are created. There is no change observed in the fuel when aged in the presence of polymer. The polymer is then further aged for 1600 hours changing the fuel each week (after 100 hours) and taking the sample after 400 hours. The change in chemical structure-using IR spectroscope and scanning electron microscope, material swelling, penetration of fuel inside the polymer and residue on the polymer surface are analysed at each aging time.

No significant changes are observed at entire aging period while using the inert system. The amount of residue observed more in open system and furthermore these residues are polymerized on the polymer surface after 1200 and 1600 hours of aging. The material is swelled more in 1.6 hour stable fuel than 9 hour fuel. The appearance of cracks on the polymer surface using open system significantly lessens its strength (almost 35 % increase in fragility), which is substantiated by charpy impact test.

Contents

Acknowledgment

I would like to thank my examiner Börje Gevert for giving me the opportunity to work on this project and guided me nicely throughout entire work. I also express my special thanks to supervisor Mauricio Jimenez for the daily discussion and kind suggestions in this work. I cannot forget all the helpful people of fuel system department in Volvo Cars Corporation (VCC) who helped me a lot in the thesis. Special thanks to Stig Andersson, Kai J. Kallio and Sabina Fleiss whose suggestions and assistance have been valuable for this project.

I would also thank my friends for their support and motivation. Finally I would like to thank my parents for their love and prayers.

Göteborg February 2013

Kalim Ullah

Notations

Terminology

RME	Rapeseed Methyl Ester, Biodiesel
MK1	Miljöklass 1, Swedish environmental class 1 diesel
POM	Polyoxymethylene
PY	Pyrogallol
GA	Gallic acid
BHA	Butylated hydroxyanisol
BHT	Butylated hydroxyl toluene
TBHQ	t- Butyl hydroquinone

Specifications

1.6 hr fuel	1.6 hour stable RME
9 hr fuel	9 hour stable RME
B10	10% biodiesel and 90 % petro-diesel
B20, B30	20% and 30% biodiesel mix with petrodiesel

1 Introduction

1.1 Background

The humankind is increasingly approach towards high energy crisis, on account of greater energy consumption than its supply. The demand is increasing further because of the world becoming more developed in new technologies. Plentiful and economical energy is the lifeblood of current nation. The world presently meets the energy requirements majorly from fossil fuels. These fuels include liquid fuel mostly petroleum based, solid fuel (coal) and natural gas. Liquid fuel predominantly remains the leading source of energy, which is expected to contribute the energy need for limited duration. The transition to alternative energy resources is required due to the fact that fossil fuel reservoirs are diminishing and trend in cost is rising. The environmental consequences from exhaust emission have further speed up the switch to alternative renewable fuels.

Biofuels, fuels derived from biomass have been gaining the attention as of highly renewable, biodegradable and locally available. Biomass liquid fuels are Bio alcohols; ethanol is the most common, Biodiesel; obtained from vegetable oil or animal fats and Bio crude; synthetic oil. Biofuels are carbon-neutral, nontoxic and reduce emission of volatile organic compounds. These fuels are not only green in nature but also help to reduce dependence on imported oil.

1.2 Objective and scope

Along with numerous advantages, biofuels have some negative aspects. This project work is concerned with biodiesel, which is surrounded by negative sentiment. Pure biodiesel and blend above B20 causes degradation of elastomers soften rubber material and corrode metals over time. Understanding the compatibility between polymer material and conventional diesel is long-established; however less information is available about the interaction with biodiesel. Polymer POM (Polyoxymethylene), the most essential part in car components is highly compatible with petro diesel. However it is necessary to look over its compatibility with biodiesel blended fuels, as inspected in this work using blend B20.

2 Literature review

2.1 Vegetable oil

Crude vegetable oil is mostly (about 95%) composed of triglyceride and some free acids like monoglycerides and diglycerides [1]. Triglyceride contains long chain-acids generally called fatty acids; the structure is given in Figure 2.1. These long chains are unbranched, containing 16 to 18 carbons which have similar properties to petro diesel like cetane number, a dimensionless number which indicate fuel ignition quality. These long chains of hydrocarbon in similar properties make a substitute of diesel fuel.

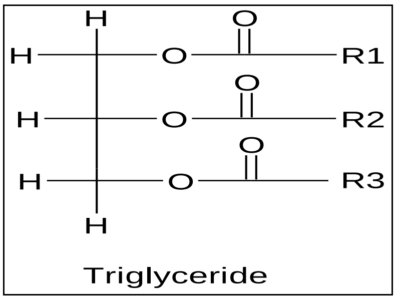


Figure 2.1 Triglyceride.

There are mainly five types of carbon chain of each fatty acid moiety in the oil derived from soybean or animals fats. It is designated by two numbers; the first number shows the number of carbon while the second number shows the number of double bonds. These fatty acid chains are given below in more detail [2].

Palmitic: R= $(CH_2)_{14}$-CH_3. It is designated as (16:0). The number of carbons is 16 (including the one where R is attached to) and no double bonds.

Stearic: R= $(CH_2)_{16}$-CH_3. It is also fully saturated; the numbers of carbons is 18 and designated as (18:0).

Oleic: R= $(CH_2)_7CH{=}CH\ (CH_2)_7CH_3$. It is unsaturated; the number of carbons is 18 with 1 double bond, and designated as (18:1).

Linoleic: R= $(CH_2)_7CH{=}CH$-CH_2-$CH{=}CH\ (CH_2)_4CH_3$. The number of carbons is 18 with two double bonds and designated as (18:2).

Linolenic: R= $(CH_2)_7CH{=}CH$-CH_2-$CH{=}CH$-CH_2-$CH{=}CH$-CH_2-CH_3. It is highly unsaturated with 18 carbons having three double bonds, designated as (18:3).

Vegetable oil can be used directly in diesel engine, but it needs high modification in engine. The problem is caused by high viscosity of vegetable oil. The high viscosity restricts the flow of oil through the fuel line, causes problem in fuel injection and form some deposits [3]. To avoid the operational problems and to make possible their use like diesel, the oil needs to be modified to low viscosity. Four methods are generally used to decrease its viscosity, these are: to make their blend with petrodiesel, microemulsification, hydrogenation, pyrolysis, and trans-esterification [4]. The most common method used is the trans-esterification, which produce alkyl ester (having low viscosity) from vegetable oil.

It is important to realize that the fatty acids moiety in vegetable oil/ Alkyl ester has different melting point than corresponding esterified fatty acids like methyl ester of fatty acid (melting point of oleic acid is 16 ^{0}C, while the corresponding methyl oleate is -20 ^{0}C). So the presence of free fatty acid in oil can change its physical and chemical properties.

As the vegetable oil is a mixture of different form of fatty acids, each fatty acid has different physical and chemical properties because of different number of carbon and double bond. So if the mixture contains high amount palmitic acid or methyl palmitate will have different melting point than the mixture concentrated in methyl linoleate. The chemical formula and melting point of each fatty acids and their corresponding ester are shown in Table 2.1[2].

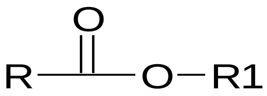
Table 2.1 Characteristics of common fatty acids and their methyl ester

Fatty acid Methyl ester	Common acronym	Formula	Melting point [^{0}C]
Palmitic acid Methyl palmitate	C 16:0 C17:0	$C_{16}H_{32}O_2$ $C_{17}H_{34}O_2$	63-64 30.5
Stearic acid Methyl stearate	C 18:0 C19:0	$C_{18}H_{36}O_2$ $C_{19}H_{38}O_2$	70 39
Oleic acid Methyl oleate	C18:1 C19:1	$C_{18}H_{34}O_2$ $C_{19}H_{36}O_2$	16 -20
Linoleic acid Methyl linoleate	C18:2 C19:2	$C_{18}H_{32}O_2$ $C_{19}H_{34}O_2$	-5 -35
Linolenic acid Methyl linolenate	C18:3 C19:3	$C_{18}H_{30}O_2$ $C_{19}H_{32}O_2$	-11 -52/-57

2.2 Basics of biodiesel

2.2.1 Biodiesel

Biodiesel is a substitute of fossil fuel for diesel engine and defined as: a fuel comprised of mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats [5].Biodiesel, also known as “mono-alkyl ester” is the product of the reaction of alcohol, such as methanol or ethanol with oil or fats (triglyceride) by trans-esterification reaction. It is designated as B100 and the chemical structure is given below.

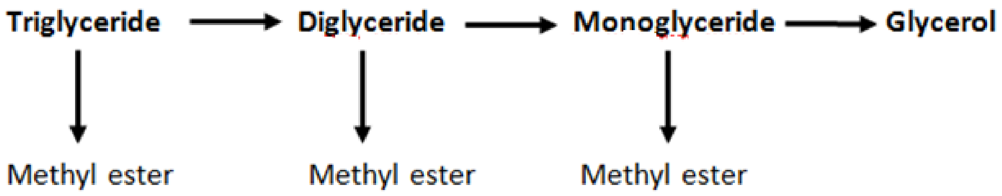


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R1$$

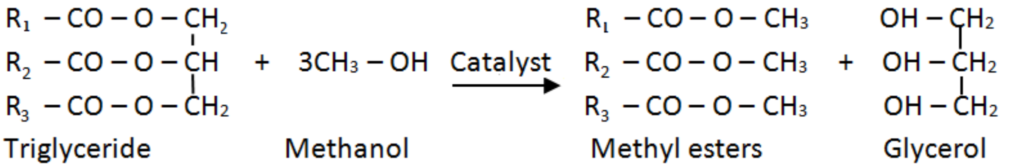
R is methyl or ethyl from methanol and ethanol respectively, used in the reactant. R1 is a long chain of fatty acids having 16 to 18 carbons. The long unbranched hydrocarbon chain of fatty acid methyl ester similar to long-chain of petro-diesel makes it an alternative diesel fuel [2].

2.2.2 Trans-esterification

Tranesterfication is the equilibrium organic reaction, which involves the transformation of an ester in to another by substitution of alkoxy moiety. The original ester is reacted with alcohol in the presence of catalyst (strong acid or base); the reaction is also called alcoholysis. This reaction involves the conversion of triglyceride to diglycerides, the diglycerides then converted in monoglycerides, the reaction further followed by conversion to glycerol. Each of these three consecutive steps produces mono-alkyl (methyl in case of methanol) esters. The reaction consumes three moles of methanol for every one mole of triglyceride. In order to precede the reaction to maximum completion, 100 % excess of methanol i.e. 6 moles is used. The excess of alcohol increases the yield of alky ester and also make its separation easy from glycerol. Three mole of alkyl ester is produced when triglyceride converts to glycerol.



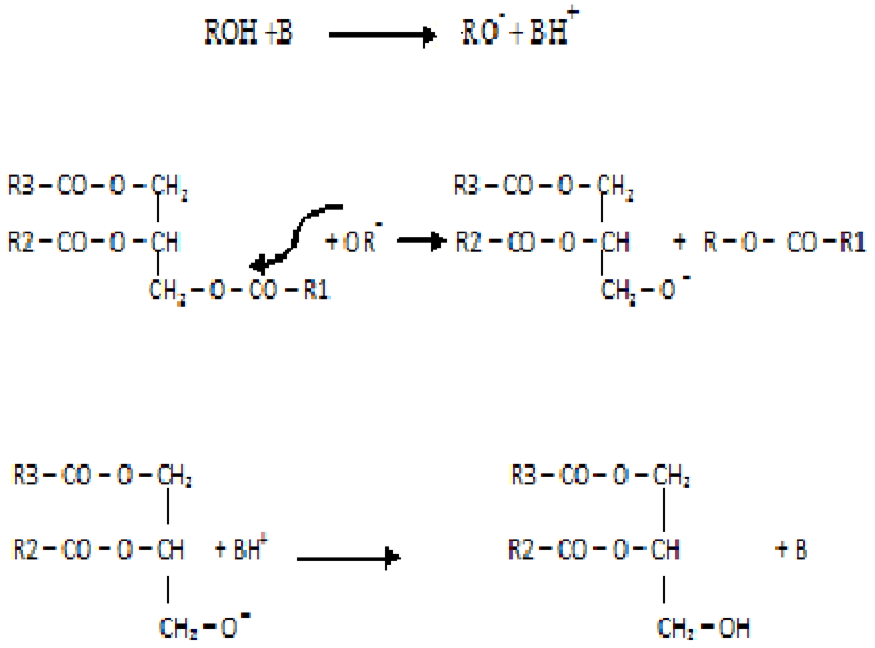
To increase the reaction rate, alkaline or acidic based catalyst is used. Alkaline catalyst is more favoured for industrial production, because it has more advantages over acidic catalysts. Basic catalyst is less corrosive, high reactive (more rapid reaction) and less time to complete the conversion. Acidic catalyst mostly sulphuric acid requires 3 hours and more than 100 ^{0}C to complete the reaction [6].



$$\begin{array}{l} R_1-CO-O-CH_2 \\ R_2-CO-O-CH \\ R_3-CO-O-CH_2 \\ \text{Triglyceride} \end{array} + \begin{array}{c} 3CH_3-OH \\ \text{Methanol} \end{array} \xrightarrow{\text{Catalyst}} \begin{array}{l} R_1-CO-O-CH_3 \\ R_2-CO-O-CH_3 \\ R_3-CO-O-CH_3 \\ \text{Methyl esters} \end{array} + \begin{array}{l} OH-CH_2 \\ OH-CH_2 \\ OH-CH_2 \\ \text{Glycerol} \end{array} \qquad \mathbf{2.1}$$

2.2.3 Reaction mechanism

The reaction converts one ester to another by replacing alkoxy moiety from methanol to triglyceride. The reaction catalysed with alkaline medium like sodium or potassium hydroxide is described in this mechanism. The first step produces alkoxide (R-O $^-$) and protanated catalyst from methanol by reacting with base (NaOH or KOH). In the second step alkoxide attack on triglyceride which produce anion of diglyceride and alkyl ester (methyl ester). Diglyceride anion regenerates the catalyst and diglyceride, (intermediate product of the reaction) is produced by taking proton from protanated catalyst.



2.2

2.3

2.4

Figure 2.2 Reaction mechanisms.

The regenerated catalyst work by the same mechanism as explained in the steps above, convert diglyceride to monoglyceride, then produce mono alkyl ester from monoglyceride [6].

2.2.4 Selection of alcohol for the reaction

The alcohol used in the trans-esterification reaction can be methanol, ethanol or butanol. Methanol is more preferred because of least expensive alcohol. The higher alcohol requires high temperature i.e. 75 ^{0}C and 114 ^{0}C for ethanol and butanol respectively, it also promote higher soap and gel formation and make problem in phase separation from glycerol. Methanol rapidly reacts with triglyceride and dissolves easily in base catalyst. It has lower flash point of 8 ^{0}C and toxic which have need of safe handling [2][4][7].

2.3 Biodiesel oxidation

Vegetable oil (Triglyceride) is a mixture of different fatty acids which are explained earlier in detail. The trans-esterification reaction does not change the fatty acid profile, so the fatty acid moiety connected to mono alkyl ester (Biodiesel) are same as in parent oil. The fatty acid chains are highly unsaturated which makes it prone to oxidation; multiple double bonds present in the chain like in linoleic or linolenic acid are more susceptible towards oxidation. The chemical nature of the fuel is changed with oxidation which produces hydropeoxides, which in turn produce short fatty acids chain and aldehydes. The acid value is increased due to oxidation as of highly acid formation which causes corrosion of metals. The hydroperoxides can also polymerize to produce gums and sediments which plug the fuel filter and make deposits on fuel system, and also very destructive to elastomers [3]. The olefinic unsaturated fatty acid present in alkyl ester occurs in methylene-interrupted configuration. The structure given in Figure 2.3 is for linolinic acid, having three double bonds. The rate of oxidation increases with increasing number of double bonds; the relative oxidation rate for methyl oleate, linoleate and linolenate is 1:12:25 [8].

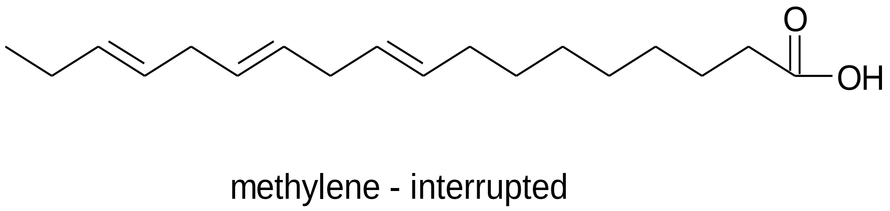


Figure 2.3.

2.4 Oxidation mechanisms

2.4.1 Primary oxidation

Primary oxidation occurs in series by a set of free radical reactions characterized as initiation, propagation and termination.

Initiation $RH + I \rightarrow R^{\cdot} + IH$ (2.5)

Propagation $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ (2.6)

$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$ (2.7)

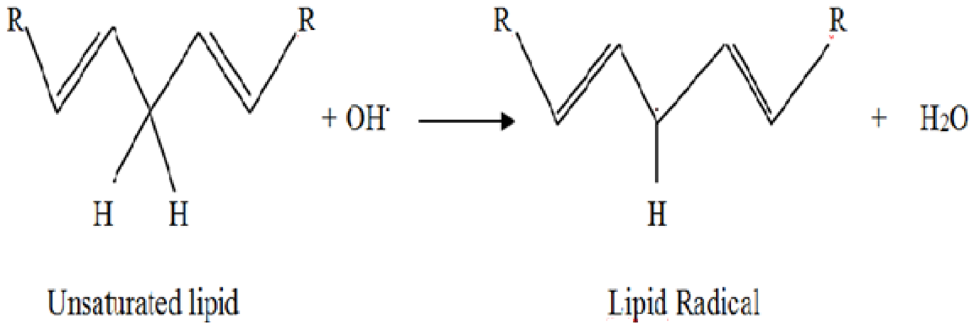
Termination $R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R$ (2.8)

$ROO^{\cdot} + ROO^{\cdot} \rightarrow \text{Stable product}$ (2.9)

The first step leads to abstraction of hydrogen from carbon atom to produce free radical. The initiator involve in the first step is produced by photoxidation or existing hydroperoxide can be decompose to give free radical [9]. Oxygen present in the vicinity, reacted with free radical (alylic radical), generating a peroxy radical. This step is much faster as to not allow any alternative for the free radical, produced in first step. The peroxy radical abstracts hydrogen from another carbon which produces hydroperoxide and additional carbon free radical. The process thus works in cycle producing more and more hydroperoxide. The last step is the termination, which prevent further oxidation. The reaction is either terminated when the two radicals combine or antioxidant is used to form a stable product. Initially hydroperoxides (ROOH) concentration is very low; until a period of time called induction period is reached. It is the time which determines the oxygen stability of biodiesel. Later on when the induction period attains, the hydroperoxides concentration increases.

The oxidation mechanism explained above involves hydrogen abstraction in the first two steps, which create free radicals and oxidation is caused. The fatty oil is olefinic unsaturated which involve allylic carbon (CH2=CH-C*) in their chain. The adjacent olefin group contain pi electron which impart resonance stability to the molecule. This is the reason, hydrogen attach to allylic carbon is easily removed. The presence of two double bonds (CH2=CH-CH_2*-CH=CH2), which delocalize the allylic carbon over five carbon are more prone to hydrogen abstraction [10].

The initiation step can also occur if hydroxyl ion (OH^-) is present, which attack on allylic carbon to abstract the hydrogen. The hydrogen removed by this mechanism produce water and hydrocarbon free radical. The free radical generated work on the same way as explained earlier. This is one indication that water may possibly produce during oxidation. This mechanism given below is explained for lipid oxidation [11].



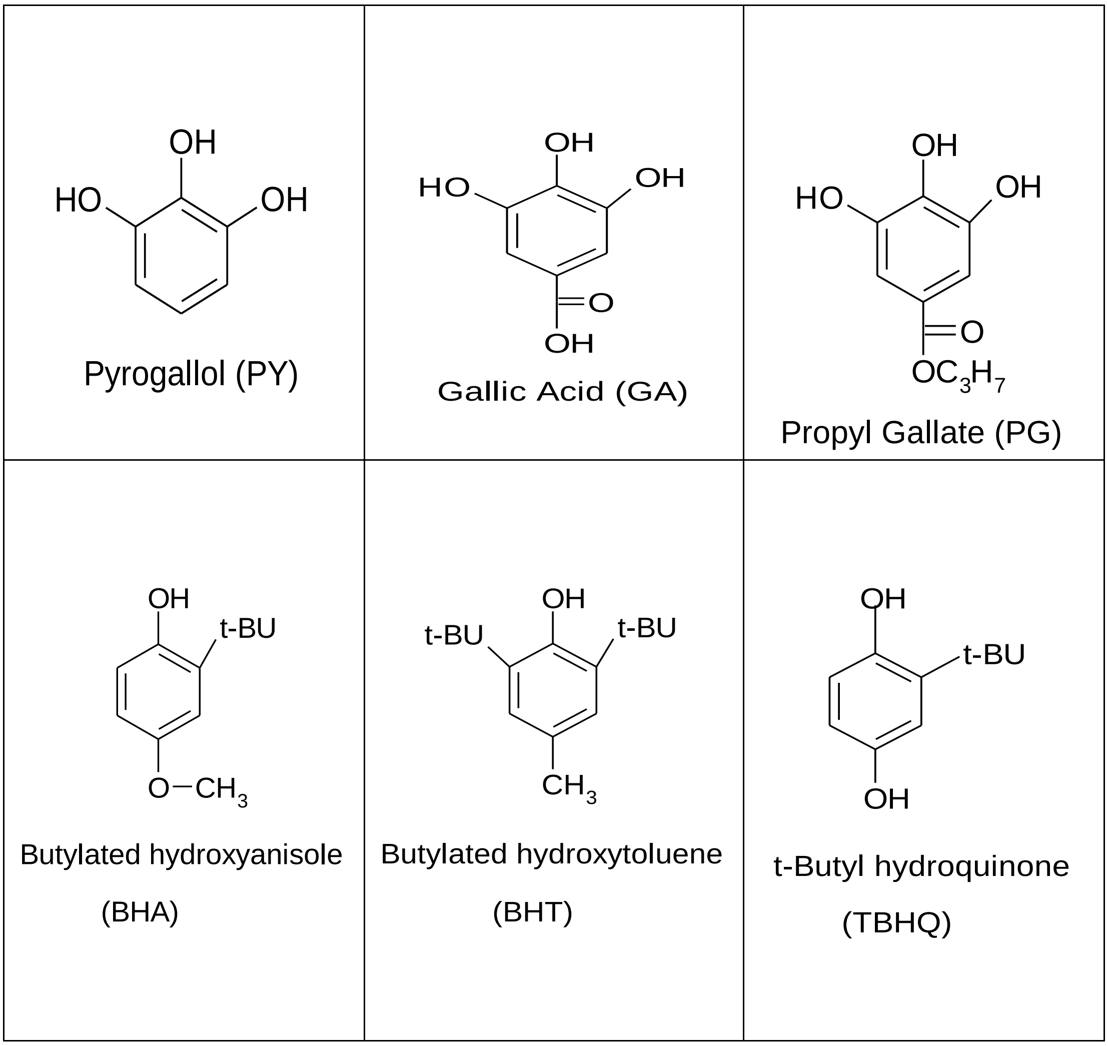
2.10

2.4.2 Secondary oxidation

The hydro peroxides formed during primary oxidation, are very reactive and decompose easily to form alkoxy and hydroxyl radicals, which further initiate primary oxidation. Presence of some metal ions like Cu^{2+} / Fe^{3+} catalyzes the process more [9]. Decomposition of hydroperoxides leads to the formation aldehydes (such as hexanals and heptanals), alcohols and shorter fatty acid chain like formic acid, which results in high acid value. It also causes to polymerize the chain by oxidative linking of fatty acid called oxidative polymerization, to form high molecular weight species. The polymerization products increase the biodiesel viscosity which makes it unable to use as a fuel, i.e. thrashing the gain of trans-esterification.

2.5 Antioxidant

Antioxidants are the type of chemicals use to inhibit oxidation of biodiesel to increase its stability. The addition of antioxidants does not affect the fuel quality, i.e. the viscosity, density remains same, and no filter plugging is observed, except acid value which is slightly increased [8]. The most common antioxidants are phenolic types which are given in the Figure 2.4.



Pyrogallol (PY)

Gallic Acid (GA)

Propyl Gallate (PG)

Butylated hydroxyanisole (BHA)

Butylated hydroxytoluene (BHT)

t-Butyl hydroquinone (TBHQ)

Figure 2.4 Antioxidants

2.5.1 Mechanism and relative effectiveness

Antioxidants contain highly labile hydrogen which can easily abstracted by peroxy radical as compared to hydrogen abstracted from fatty oil /ester chain. The antioxidant free radical thus formed is either stable or combine to form a stable product. The general mechanism by which the antioxidants work is given in the fig below.

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot} \qquad (2.11)$$

$$A^{\cdot} \rightarrow \text{stable product} \qquad (2.12)$$

The phenolic antioxidant contains active hydroxyl group which easily liberate hydrogen to combine with the free radicals thus lessen the oxidation rate. These antioxidants contain benzene ring and have different functional group at ortho-, metaand pera- position, illustrating different effectiveness from each other. Effectiveness of these antioxidants in decreasing order is shown below. Hydrogen is easily abstracted from Pyrogallol (PY), Gallic acid (GA) and propyl Gallate (PG), as of having three active hydroxyl groups in their ring. These three types of antioxidants are more effective than the rest. The carboxyl group at pera position of PG makes it less effective as compared to PY. BHA and BHT contains mono-hydroxyl group shows less effectiveness, the two tertiary butyl (t-Bu) in BHT is the reason of less effective as compare to BHA. The hydroxyl at pera position of TBHQ is less electron with drawing than –CH3 and O-CH3 in BHT and BHA respectively [12].

2.5.2 Effectiveness decreasing order

PY > GA > PG > BHA > BHT > TBHQ

2.6 Water contents

Water can be present in biodiesel, the most housekeeping issue for fuel; it could present in dissolved form or suspended droplets. The water might produce in the initiation step of oxidation if the initiator is hydroxyl ion ($OH^{\cdot}$) as explained earlier in biodiesel oxidation. The presence of methanol in the fuel can also make possible its production. As the oxidized biodiesel already contain free fatty acids which can react with methanol to form water and ester, the reaction is given below. Biodiesel contain more water contents than petrodiesel, the ASTM standard for water content is 500 ppm. The presence of water is highly problematic; it can corrode the fuel injection system and can also support the microbial growth [4]. Biodiesel has high capacity of moisture absorption (15 to 25 times higher) than petro-diesel, the maximum absorption observed is from 1000 to 1700 ppm [13].

$$\underset{\text{FFA}}{\text{R-CO-OH}} + \underset{\text{alcohol}}{\text{CH3OH}} \rightarrow \underset{\text{ester}}{\text{R-CO-O-CH3}} + \underset{\text{water}}{\text{H2O}} \qquad (2.13)$$

2.7 Swedish Environmental Classification of Diesel fuel

The engine technology has larger impacts on several emissions like particulate, sulfur, lead and some aromatics. The worldwide focus on local and regional emissions initiated from 1970. Later on the Sweden become the top leading country in Europe on emission regulation connected to automobile fuels. The Swedish Environmental Protection Agency regulations have reduced the emissions from new engines by implementing some tougher regulations. The old vehicles had to take more time on emission control; as a result the diesel fuel is classified in to different classes in 1991. These classes are MK3, MK2, and MK1, which drastically improved the emission in all vehicles old and new. MK3 has similar requirements as the European standard diesel EN 590. MK2 has some strict requirements for some oil refineries to produce fuels with minor upgrades. Whereas the MK1 has more significant results as required large upgrade of fuel for all refineries [14].

2.7.1 Swedish environmental class 1 diesel (MK1)

The MK1 diesel substantially reduced both the regulated and unregulated emissions. It has more benefits on control emissions of sulfur, aromatics, NOx and PAH. The MK1 diesel has less viscosity, less density, lower distillation curve and high cetane number. The lesser density decreases the high boiling components and increases the energy contents. High cetane number not only increases the fuel ignition quality but also reduces NOx emissions. When MK1 diesel came into view in 1991, it was the cleanest fuel in the world; afterward the European diesel gets ahead and reached some specifications near to MK1. Still there is some difference (MK1 is greener than EU diesel) in comparison of both these fuels. The diesel fuel sold today in Sweden is of MK1 quality, the main specifications are given in the table below [14].

Table 2.2 Specifications of Swedish environmental class 1 diesel

Fuel property	**MK1, 2010 (SS 155435)**		**Analyzing method**
	Specifications	Unit	
Cetane number	≥ 51	-	ISO 5165
Desity at 15 ^{0}C	800 – 830	Kg/m^{3}	ISO 5165, ISO 4264
Sulfur	≤ 10	mg/kg	SS 15 51 16
Aromatics	≤ 5	Vol %	ISO 3675, ISO 12185
PAH	≤ 0.02	Vol %	SS 15 51 16
Viscosity at 40 ^{0}C	1.4 – 4	cSt	ISO 3104
FAME	5	Vol %	EN 14078

2.8 Polyoxymethylene (POM)

POM is an engineering thermoplastic derived from formaldehyde; consist of repeating carbon-oxygen linkage therefore also known as polyacetal. It is highly crystalline with linear shape which gives it high rigidity, more stiffness and good chemical resistance. Along with many other applications, it is used to replace metal as of low weight, corrosion resistance, ease of fabrication, low coefficient of friction, and resistance to fatigue [15]. It is available both as a homopolymer and copolymer. The polymer analyzed in this work is POM-copolymer of trade name Hostaform.

2.8.1 Homopolymer

The homopolymer consists of repeated unit of (-CH_2O-), and produced by polycondensation of aqueous solutions of formaldehyde. A very high molecular weight polymer is obtained by cationic or anionic polymerization of formaldehyde [16]. It has high tensile strength, greater surface hardness and more resistance to organic solvents. It is not degraded in water but can swell if kept for longer time at high temperature. The resistance to inorganic solvent is however not so excellent, which makes it less usable in strong acids, strong alkalis or oxidizing agents [15].

Homopolymer POM has high tendency to depolymerize liberating formaldehyde monomers. This propensity is more found in hydroxyl end groups polymer. One way to reduce the depolymerization reaction is to capping the end groups with ester or ether group and the other way is to co polymerize the formaldehyde with cyclic ether to make a copolymer POM [17]. The hompolymer structure is given below.

$$[\text{-}CH_2O\text{-}CH_2O\text{-}\ CH_2O\text{-}\ CH_2O\text{-}\ CH_2O\text{-}\ CH_2O\text{-}]$$

POM Homopolymer

2.8.2 Copolymer

The copolymer, in addition consists of randomly distributed comonomer (CH_2-CH_2) unit with repeated -CH_2O- units. It is produced by cationic polymerization of trioxane with cyclic ether such as ethylene oxide or 1, 3 dioxalane. This polymer offer great stability towards alkalis, hot water and other chemical as a result carbon-carbon bond in its polymer chain. The copolymer POM can also degrade like homopolymer, but in lesser extent as the comonomer unit holds back the unzipping of whole chain. As soon as the depolymerization of polymer starts, the c-c bond in the chain is accountable to stop the reaction [18].

The thermal and chemical stability depends more on the end groups. The diols end group is thermally unstable as compared to diacetates end group. The thermal stability is increased further with dimethyl ether-ending group, which in addition increases the stability to alkali [16]. The structure of copolymer POM is given below.

$$[\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}\ \underline{CH_2\text{-}\ CH_2}\text{-}O\text{-}\ CH_2\text{-}O\text{-}\ CH_2\text{-}]$$

POM copolymer

The copolymer POM is further differentiated on its good physical properties like high toughness, more hardness, high rigidity, and excellent resistance to chemicals, e.g. to solvents, strong alkalis and fuels. The polymer is resistive to both petrol and diesel and even to fuels containing 15 to 20 % methanol. Though it is used in fuel system-components like fuel pump, consequently raise the importance to recognize its compatibility with fuel. One changing property is the degree of swelling while immersed in fuels for longer time. The swelling in petrol depends on immersion time but observed less than in mix with methanol. The absorption level does not increase than 2 % when immerse in 85:15 % petrol/methanol mixture [19].

2.9 Ageing of the copolymer (POM)

2.9.1 Autoxidation

The copolymerization and capping the end groups with ester or ethers stops the depolymerization reaction. But the polymer is still susceptible to oxidation as the adjacent oxygen atoms in the chain act a labializing effect on methylenic hydrogen, which makes it more susceptible to a free radical formation and subsequently oxidation take place. The mechanism of the oxidation reaction can be explained in three steps, the first step is chain initiation step, then chain propagation and finally chain termination. These steps are explained below with the corresponding reactions involved [17].

2.9.2 Chain initiation

This step generates free radicals by liberating hydrogen from the chain. These radicals formation is either due to action of heat or mechanical stress combined with heat. Moreover the presence of oxygen in the environment is also a source of free radical formation.

$$\mathrm{PH} \rightarrow \mathrm{P}^{\cdot} + \mathrm{H}^{\cdot} \qquad (2.14)$$

$$\mathrm{PH} + \mathrm{O}_2 \rightarrow \mathrm{P}^{\cdot} + \mathrm{HO}^{\cdot}_2 \qquad (2.15)$$

2.9.3 Chain propagation

The free radicals thus formed are easily attacked by oxygen present in the environment, which in turn form free radicals and sequentially produce hydroperoxides. The free radicals again initiate the first step and the process continues as long as the oxygen is available.

$$\mathrm{P}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{PO}_2^{\cdot} \qquad (2.16)$$

$$\mathrm{PO}_2^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^{\cdot} \qquad (2.17)$$

2.9.4 Chain termination

As the amount of oxygen in the vicinity decreases, the reactions are then stopped by reacting the free radicals and form stable products. These stable products can raise the molecular weight of the polymer and also give raise to gel formation.

$$\mathrm{PO}_{2^{\cdot}} + \mathrm{PO}_{2^{\cdot}} \rightarrow \mathrm{POOP} + \mathrm{O}_2 \qquad (2.18)$$

$$\mathrm{P}^{\cdot} + \mathrm{PO}_2^{\cdot} \rightarrow \mathrm{POOP} \qquad (2.19)$$

$$\mathrm{P}^{\cdot} + \mathrm{P}^{\cdot} \rightarrow \mathrm{P\text{-}P} \qquad (2.20)$$

3 Experimental work

3.1 Biodiesel blends

Biodiesel blend is a mix of biodiesel in petro diesel; it is represented by “B” followed by a number which shows the percentage of biodiesel in the fuel. Different blends i.e. B2 to B30 can be made, blends higher than B20 may be problematic and may need engine modification; the main purpose of this work is to investigate some of the problems. B2 means 2% of biodiesel in the fuel; it can be made by mixing 2ml of biodiesel in 98 ml of petro diesel to make 1 liter of blend. Three blends (B10, B20, and B30) are used in this project work. Swedish environmental class 1 diesel (MK1) is used as a petro diesel and rapeseed methyl ester (RME) is a biodiesel. The various blends made are given in the Table 3.1.

Table 3.1 Biodiesel Blends

Test liquids	MK1 (L)	RME (L)	Total volume (L)
B10	2.25	0.25	2.50
B20	2.00	0.50	2.50
B30	1.75	0.75	2.50

3.2 Part first-Aging of fuel without polymer

In the first part of this thesis work, these blends are thermally aged at 85 ^{0}C for 100 hours without polymer. The samples are taken after six and eighteen hours, in that way the total aging time became around 5 days (100 hours). These blends are made of using two types RME, one with 1.6 hour stability and the other is 9 hour stable. The stability temperature of the RME is 110 ^{0}C. The experimental setup is made both with open and N_2 system.

The properties measured for fuel are:

1. Acid number
2. Hydro peroxide number
3. Water contents

3.3 Analysis of fuel

3.3.1 Acid Number

This analysis is carried out with ASTM D 974-08 Standard Test Method for Acid and Base Number by Color-Indicator Titration.

Definitions: The amount of hydroperoxide required in milligram per gram of the sample to neutralize the acid constituents present.

Reagents:

Methyl Orange Indicator Solution– 0.1 gram of methyl orange is dissolved in 100 ml of water.

Potassium Hydroxide Solution 0.1 M– 6 gram of KOH is added to approximately 1 L of anhydrous isopropyl alcohol in a 2-L conical flask. The mixture is boiled for 10 to 15 minutes with stirring to prevent the formation of solid cake on the bottom. 0.2 g of Barium hydroxide ($Ba(OH)_2$) is added, and again the mixture is boiled for 10 to 15 min. The solution is then filtered through porcelain filtering funnel.

Titration Solvent– it is prepared by mixing toluene, water and anhydrous isopropyl alcohol in ratio 100: 1: 99.

Procedure and calculation:

A weight quantity of sample is taken in conical flask, 100 ml of titration solvent and 0.5 ml of indicator is added, the solution is continuously swirled to dissolve the solvent in the sample. Yellow-orange color appeared which is titrated with 0.1 M KOH solution at room temperature. The solution is vigorously shaken until green-brown color appeared which indicates the end point.

Acid number is calculated as follows:

Acid number in mg of KOH/g = [(A-B) M × 56.1]/W

A = KOH used in ml to titrate the solution,

B = KOH required in ml to titrate the blank,

“M” is the molarity of KOH solution and “W” is the weight of sample.

3.3.2 Hydroperoxide Number

This analysis is carried out with ASTM D 3703-07, Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels.

Hydroperoxide number- it measures the oxidizing constituents present in the sample, expressed in mg/kg. The higher the number more is the fuel oxidized, more the quality become worst. The hydroperoxides have damaging effect on fuel system like fuel tank and pump made of polymer.

Reagents:

Acetic Acid Solution- 4 ml of concentrated hydrochloric acid is mixed with 996 ml of glacial acetic acid.

Potassium Dichromate Solution, 0.1N- when 2.452 gram of dried potassium hydroxide is diluted in 500 ml of water, 0.1 N solution will obtained. 0.01N solution is attained by diluting 100 ml of 0.1 N in 100 ml of water.

Potassium iodide solution- 120 g of potassium iodide (KI) is dissolved in 100 ml of water. If blue color develops can be discharged by using 0.005N $Na_2S_2O_3$

Sodium Thiosulfate solution, 0.1 N- 12.5 g of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) and 0.1 g of sodium carbonate (Na_2CO_3) is dissolved in 500 ml of water. The solution is stand for a weak or more before using. The 0.005 N solutions is obtained by diluting the 0.1 N to twenty fold in distilled water; it is obtained by adding 100 ml of 0.1 N solutions with water to 2000 ml.

Starch solution- A paste of 6 g of arrowroot starch is made in cold water, then poured into 1 L of boiling water. 20 g of potassium hydroxide is mixed; the solution is allowed to stand for 1 hour. 6 ml of glacial acetic acid is added, the solution is then adjusted to pH of 4 by adding sufficient HCl.

Procedure and calculations:

A weight quantity of sample is taken in conical flask of 500 ml capacity, which was flushed with nitrogen before putting the sample. 25 ml of 2,2,4- trimethylpentane is added and vigorous flow of nitrogen is passed, then 20 ml of acetic is added and the flow of gas is reduced. 2 ml of KI solution is mixed shaking for at least 30 sec, the reaction is completed by setting the flask aside for 5 min. The flow of gas is stopped after adding 100 ml of distilled water. 5 ml of starch solution is added and the whole solution is titrated with 0.005 N Na_2SO_3 until the blue color disappeared.

Peroxide number is calculated as follows:

Hydroperoxide number, mg/kg = $[(A-B) \times N \times 1000 \times 8]/S$

A = ml of Na_2SO_3 solution used to titrate the sample,

B = ml of Na_2SO_3 required for the titration of blank,

S = weight of the sample in gram,

N is the normality of Na_2SO_3 solution,

8 is milliequivalent of hyroperoxide number.

3.3.3 Water Determination

3.3.3.1 Karl Fisher Titration

Karl Fischer Titration method is used to determine water contents, even at mico level in various products like hydrocarbons, plastics, paints and some other solvents. The basic principle in which it works is based on Bunsen reaction which involves the reaction of iodine with sulfur dioxide in aqueous medium, shown below.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \qquad (3.1)$$

This reaction is used to measure SO_2 in aqueous solutions, later on modified for water measurement if excess of sulfur dioxide is present and base is added to neutralize the solution. In general two methods volumetric and coulometric titration are used for water determination. In volumetric method the iodine is dissolved in the sample which react with water, the amount of consumed iodine is used to analyze the water contents.

The coulometric titration method is used in this project work; it works on the principle that electric current is used to produce Iodine by electrolysis of iodide containing regent. The following reactions occur at the cathodes:

Cathode: $I_2 + 2e^- \rightarrow 2I^-$ (reduction) (3.2)

Anode: $2I^- - 2e^- \rightarrow I_2$ (oxidation) (3.3)

The iodine is generated when iodide ion is oxidized at anode, gives two electrons. The iodine is reduced by taking the two electrons, which causes the current to flow as long as iodine is present. The current produced is directly proportional to the amount of iodine generated by consuming the water. When all the water is consumed, no iodine is produced further and the current suddenly falls to zero, and the amount of water is determined.

The main reactions involved are given below:

$ROH + SO_2 + R_1N \rightarrow [R_1NH]^+ SO_3R^-$ (3.4)

$H_2O + I_2 + [R_1NH]^+ SO_3R^- + 2 R_1N \rightarrow [R_1NH]^+ SO_4R^- + 2[R_1NH]^+ I^-$ (3.5)

In the reactions above, $R= CH_3$, $R1= C_5H_5$ (3.6)

Many substances release the water very slowly, or high temperature is needed, which makes it unsuitable for direct Karl fisher titration. Some samples are not soluble in alcohol which also makes the determination hard. To avoid these problems the sample is heated in an oven so called Karl fisher oven. The water is detached from the sample at 110 ^{0}C and measured unconnectedly from it. The water evaporated is carried with a dry gas to a titration cell, where it is determined by coulometeric method. As the sample does not interact with the reagent, only the water enters the cell, which assists to avoid unwanted side reaction to make any byproducts [20].

3.4 Part second-Aging of fuels in presence of polymer

In the second part, the fuels are aged in the presence of polymer POM (polyoxymethylene), using same conditions of time and temperature (100 hours and 85 ^{0}C). Blend B20 is chosen with both types of RME (1.6 and 9 hr stability), and using both open and close (inert) system. In this way four different schemes are made, given in the Table 3.2. The stability of the system is increasing from scheme 1 to 4, i.e. the scheme 1 is the worst and scheme 4 is the best system on stability wise.

Table 3.2 Schemes for fuel aging with polymer

	Scheme 1	**Scheme 2**	**Scheme 3**	**Scheme 4**
stability	1.6 hr	9 hr	1.6 hr	9 hr
system	Open system	Open system	N_2 system	N_2 system

The fuel is analyzed by using the same methods as in the first part. The aged fuel in the presence of polymer is compared with the fuel-lacking polymer.

Aging of the diesel and biodiesel blended fuels produce high molecular weight products which precipitate down the vessel. These products stick with the polymer surface make a glue layer on it, which can be seen with naked eye. As a result, the concentration of heavy entity decreases in the fuel, which possibly decrease the oxidized and acidic constituents.

3.5 Aging of copolymer (POM)

The copolymer (polyoxymethylene) is aged for 10 weeks (1600 hours) by changing the fuel every week. The polymer samples are taken after every 400 hours and the analysis are made both before and after washing. The polymer is washed with ethanol using ultrasonic bath.

3.6 Analysis of the polymer

The properties measured for the polymer are:

1. IR spectroscopy
2. SEM and light microscope
3. Immersion tests
4. Change in weight
5. Penetration of fuel inside polymer
6. Analysis of deposits on polymer surface
7. Pendulum impact test

3.6.1 IR spectroscopy

IR spectroscope is used to study the chemistry of polymer to observe any changes occur with aging. The polymer sample is positioned in the path of IR radiation to collect spectra from the functional group involved; each species (functional groups) in the sample absorbs different IR frequencies. The change in absorption spectra with ageing the polymer gives fairly enough information about polymer damage. Fourier transform infrared (FTIR) instrument is used for this analysis using 32 scans per sample.

3.6.2 SEM and Light microscope

The microscopic study is required for envision the polymer surface to see any cracks or fractures on the surface. The light microscope can provide plenty of information about the surface damage or formation of some sort of materials on the surface. It works on the principal of illuminating the polymer sample with light using glass lenses, the images are then viewed with computer at different magnifications. The polymer first analyzed with light microscope, the SEM (scanning electron microscope) then used for more profound study.

3.6.3 Immersion tests

The material, POM is more chemically resistant to petrol, diesel and even with 15 to 20 % mix of methanol in petrol. It is observed that 2 % absorption can take place when immersed in fuel (petrol/methanol, 85/15 % mix) at room temperature [19]. However the absorption of biodiesel blended fuel is unknown, which is examined in this work. The absorption of the fuel can certainly swell the polymer, which will change the volume of the polymer. The material swelling is established by measuring the change in volume at different immersion time.

Mettler Toledo AX 204 balance is used for this analysis. It uses the Archimedes principle, first measuring the weight of sample in air and afterward in ethanol. Before analyzing the weight and volume, the specimen is washed with ethanol in ultrasonic bath and dried at ambient temperature.

3.6.4 Penetration of fuel inside polymer

The copolymer (POM) absorbs certain fuels as mentioned earlier for petrol/methanol mix. Absorption of biodiesel blended fuel is studied in this work which can either take in from corner or main surface of the polymer. The fuel penetrates inside the polymer material up to certain level which is analyzed by cutting the sample in to thin slices of 45 µm thickness. The thin layers (slices) are made with a cutting machine adjusting the blades to go down by 45 µm in depth. The thin segments are analyzed using IR spectroscope for fuel existence inside the polymer.

3.6.5 Analysis of deposits on polymer surface

Oxidation of the biodiesel fuel produces hydro peroxides which in turn decompose and produce low molecular weight substances. Heavy entities are furthermore produced by polymerizing the small units. These decomposition and polymerization processes develop a thin layer of residue on polymer surface. The layer developed is too thin and hardly detached from the surface, but a soluble solvent dissolve the layer which can easily analyzed after separating the solvent. Ethanol and toluene are individually used for different samples, no obvious difference found amongst but the residues are fairly soluble in both. The residues are separated by vaporizing the solvent 30^{o}C below its boiling point to avoid any residue-escaping. IR spectroscope then used to analyze the chemical nature of residue.

3.6.6 Pendulum impact test

This mechanical testing is performed as a culmination result of the whole work to perceive how much strength the polymer lost. The impact test is made here to determine the fragility of the specimen after aging in fuel (Biodiesel blend, B20). Nevertheless the polymer absorbs fuel as mentioned earlier and furthermore the polymer also gets in contact with acidic constituents obtained from the fuel oxidation, which might change the strength of polymer sample. A charpy impact test machine CEAST 6545/000 is used. The tests are conducted by breaking the polymer and measuring the energy absorbed by the polymer (work done on the sample). The work done gauges in joule are then compared for different aged specimen with the reference polymer. The analysis is made at ambient temperature and the sample preparation (standard specimen size and notching) is made according to the standard given in appendix 6.6.

4 Results and discussions

4.1 Part first- Aging of fuel without polymer

4.1.1 Acid number

Sample B-20 (1.6 and 9 hour stability)

The sample B20 with 1.6 hour stability is more prone to oxidation, the sample acidity increases with the aging time as shown in the Figure 4.1. This increase is due to acidic constituents produced from hydroperoxides decomposition. After 68 hours of aging time in open system at 85 ^{0}C the acid number increases from ASTM requirements i.e. the maximum allowed acid value is 0.8 mg of KOH/g. On the other hand the sample with 9 hour stability is more stable; the value didn't get to 0.1 at entire aging time as the temperature kept blow the stable temperature which is 110 ^{0}C for this sample. The same trend then appeared for sample B10 with 1.6 and 9 hour stability, see appendix 6.1.

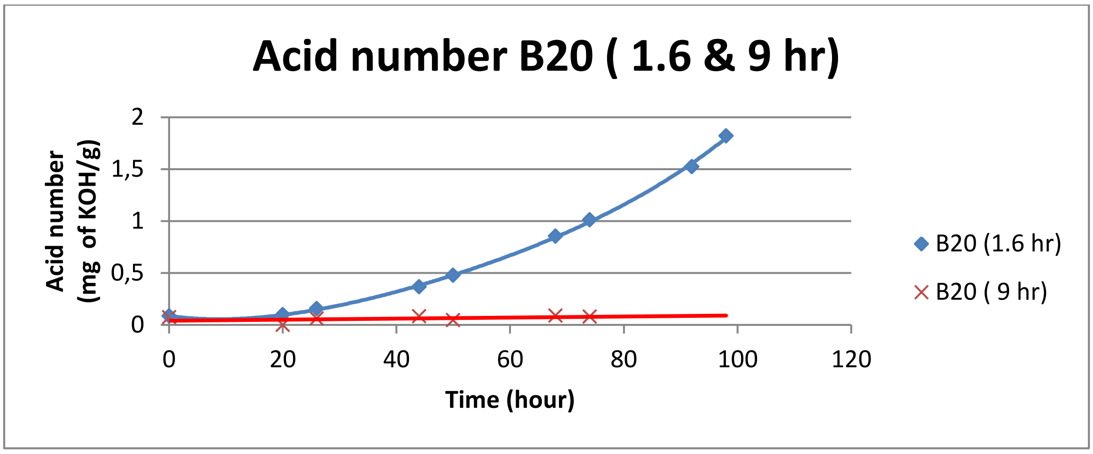


Figure 4.1 Acid number B20 (1.6 & 9 hr)

Table 4.1 Acid number B20 (1.6 and 9)

Sample B-20	**Acid number [mg of KOH/g]**	
Time [hours]	1.6 hr stable	9 hr stable
0	0.085	0.073
20	0.096	0
26	0.157	0.06
44	0.364	0.081
50	0.425	0.046
68	0.851	0.089
74	1.010	0.078
92	1.522	
100	1.819	

Sample B10, B20, B30 (1.6 hour stability)

The Figure 4.2 shows the acidity of three samples B10, B20 and B30 with 1.6 hour stability. B20 and B30 are more oxidized, the acidic constituents is increasing more as the aging time increases. After 64 hour of contact with air these samples does not follow the ASTM standard for acid value (0.8 mg of KOH/ g). Sample B10 is more stable as compared with the rest; the value is slightly increasing in the beginning up to 74 hours, then decreasing at the end of aging time. The value at all the time is far below the ASTM standard.

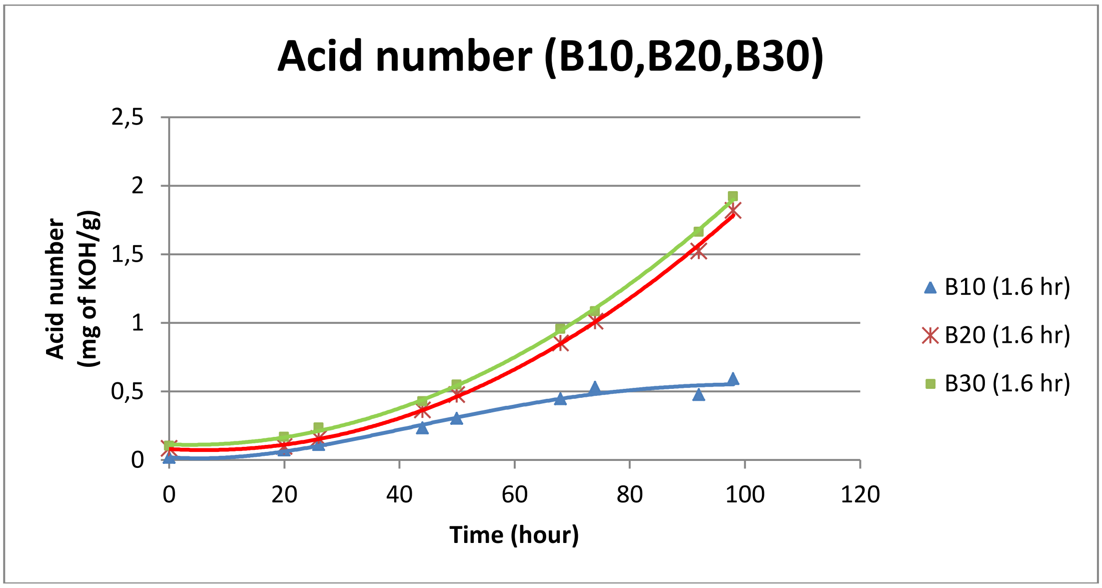


Figure 4.2 Acid number B10, B20, and B30 (1.6 hour stability)

Table 4.2 Acid number B10, B20 and B30 (1.6 hr)

Time [hour]	Acid number [mg of KOH/g]		
	B-10	B-20	B-30
0	0,0175	0,085	0,1036
20	0,0712	0,0967	0,1672
26	0,1124	0,1571	0,2354
44	0, 2341	0, 3649	0,4277
50	0, 3030	0, 4756	0,5491
68	0, 4456	0, 8516	0,955
74	0, 5305	0,010	1,0836
92	0, 4753	1,522	1,663
100	0, 5919	1, 8196	1,922

4.1.2 Unstable behavior of Sample B20

Sample B20 (9 hour - open system)

The Figure 4.3 shows the instability behavior of sample B20 with 9 hour stability. This sample is stable at 110 ^{0}C as explained earlier. From time t=0 to 74 hours the aging temperature is 85 ^{0}C. The graph shows stable acid value until time, t = 74 hours. Unintentionally the temperature was raised after 74 hour to 130 ^{0}C which is far-off from stability temperature (110 ^{0}C); the acid value is abruptly increased as shown by the steep line in the graph. The same behavior showed for hydroperoxide number and water contents; see the graphs in appendix 6.2 and 6.3.

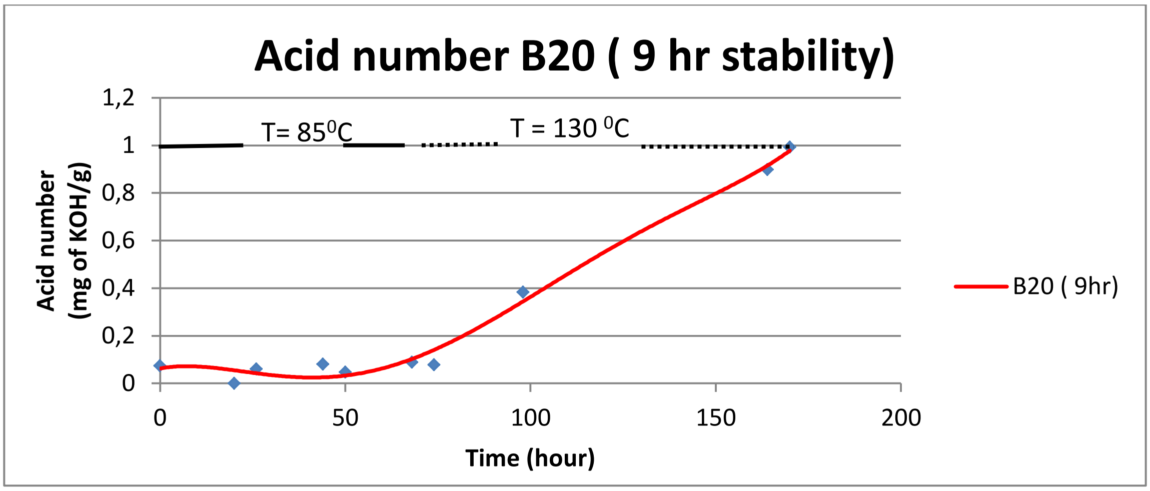


Figure 4.3 Acid number B20-9 hr-O.S

Sample B20 (9 hour – N2 system)

The same experimental setup then made with inert system (oxygen-free environment) by using N2 gas to prevent the flow of air. There is a little increase in the beginning after 74 hours, but the values again drop to original value after 100 hours of aging, see Figure 4.4. It means that the fuel works above the stability temperature as long as the system remains free of air.

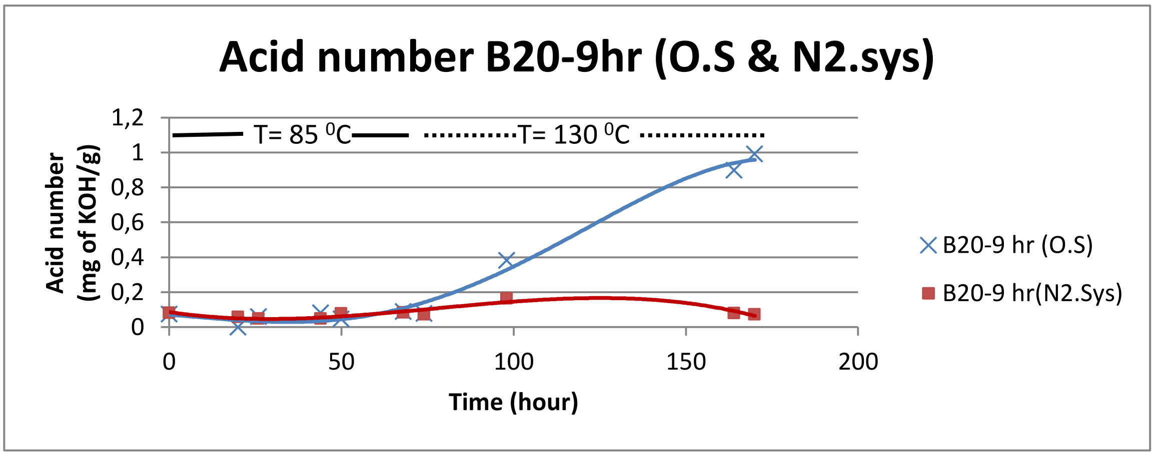


Figure 4.4 Acid number B20-9hr- O.S & N2.S

4.1.3 Hydroperoxide number

Sample B-20 (1.6 and 9 hour stability)

As the alkyl ester oxidizes, the hydroperoxide number increases. The readily oxidized 1.6 hour stable sample has high peroxide number. The number is rising as the aging time increases. The same blend with 9 hour stability is more locked i.e. no increase in peroxide value with the time as long as the temperature kept below its stability temperature (110 ^{0}C). The clear difference in peroxides number for both the samples is shown in the Figure 4.5.

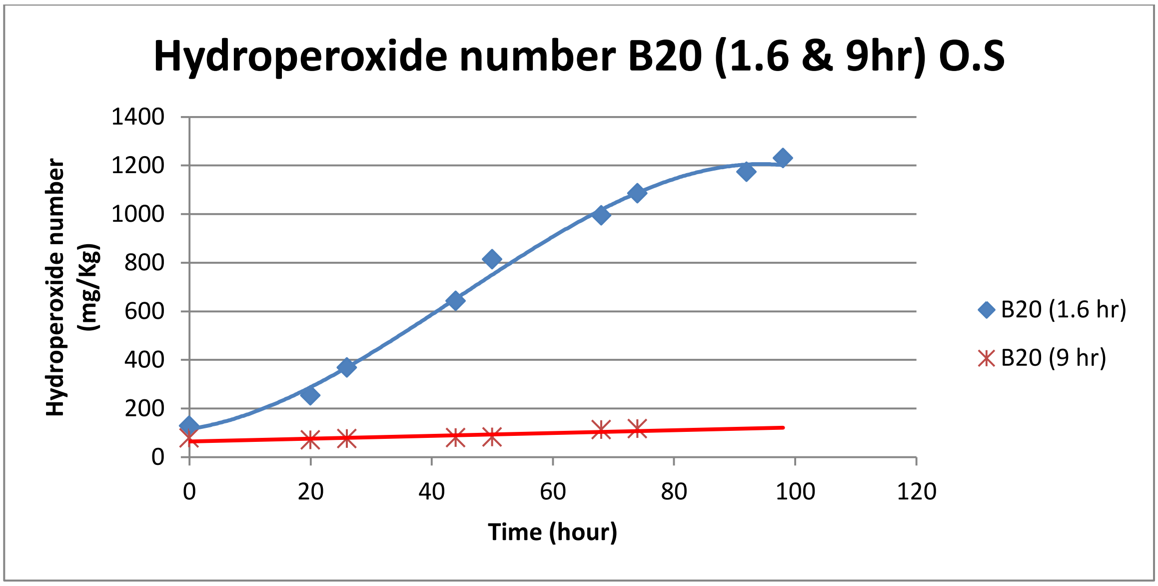


Figure 4.5 Hydro peroxide number B20 (1.6 & 9 hr)

Table 4.3 Hydro peroxide number B20 (1.6 & 9 hr)

Sample B20	**Hydroperoxide number [mg/kg]**	
Time [hour]	1.6 hour stability	9 hour stability
0	128	78,53
20	254,18	70,62
26	368,21	76,07
44	642,8	80,14
50	813,22	82,11
68	993,78	111,96
74	1084,68	116,77
92	1172,92	
100	1229,79	

Sample B10, B20, B30 (1.6 hour stability)

Figure 4.6 is for hydroperoxide number of the three samples B10, B20 and B30 with 1.6 hour stability. The peroxide number is increasing as the time approaching the total aged time of 100 hours. At the start of aging, the three samples shows distinct behavior, later on the sample B20 and B30 curves touches each other. The B30 sample is more aggressive than B10 and looks similar with B20 after 70 hours of aging time.

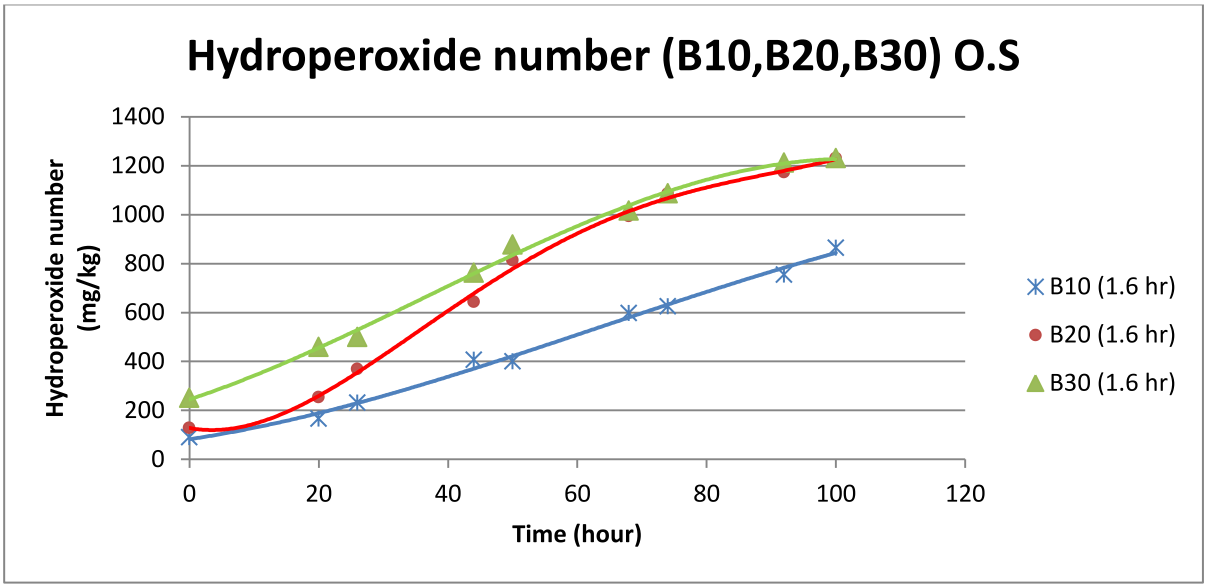


Figure 4.6 Hydro peroxide number B10, B20 and B30 (1.6 hr)

Table 4.4 Hydro peroxide number B10, B20 and B30 (1.6 hr)

Sample B10, B20, B30	Hydroperoxide number (mg/kg)		
Time (hour)	B-10	B-20	B-30
0	90,08	128	250,421
20	165,378	254,18	459,327
26	231,034	368,21	499,746
44	406,993	642,8	762,253
50	400,21	813,22	877,052
68	597,057	993,78	1016,098
74	625,148	1084,68	1086,273
92	754,859	1172,924	1212,0371
100	863,476	1229,79	1230,619

4.1.4 Water contents

Sample B-20 (1.6 and 9 hour stability)

The Figure 4.7 represents the water contents of sample B20 with 1.6 and 9 hour stability. The high acid constituent sample (B20-1.6 hr) has more water contents and increasing with the aging time. The ASTM standard for water contents is 500 ppm, though the sample B20 (1.6 hr stable) is significantly oxidized but still the water contents is less than ASTM requirements. The 9 hour stable sample has low water contents i.e. far away from ASTM standard and more stable. The line is plateau throughout the aging time. The obvious explanation for water production is given in the literature part, two causes are explained. First the water is produced if the initiator is hydroxyl ion ($OH^{\cdot}$) in the initiation step of oxidation or if methanol is present in the fuel, which reacts with free fatty acids to produce water and ester; more detail is given in the literature part.

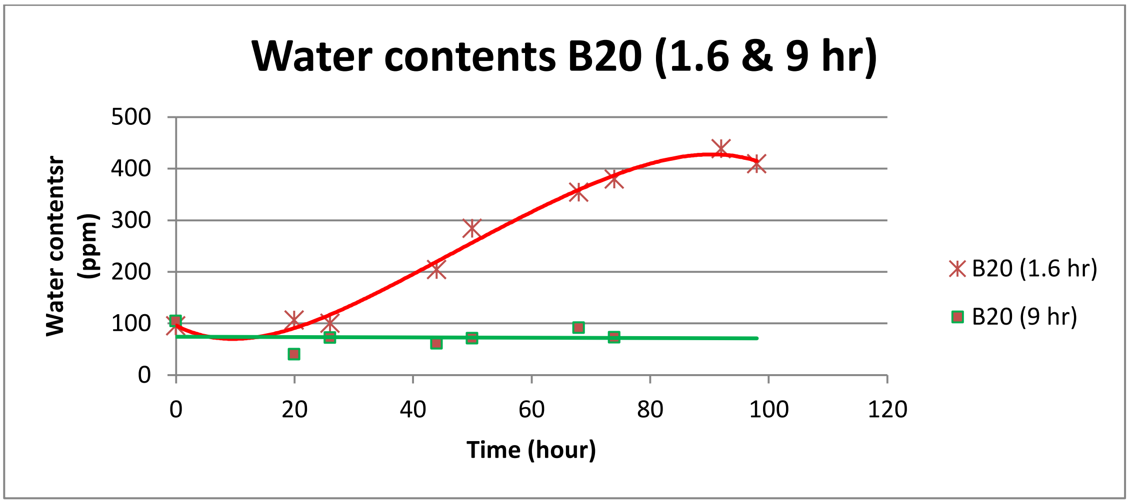


Figure 4.7 water contents B20 (1.6 & 9 hr)

Table 4.5 water contents B20 (1.6 & 9 hr)

Sample B20 (1.6 & 9hr)	**Water contents [ppm]**	
Time (hour)	1.6 hour stability	9 hour stability
0	95	104
20	106	40
26	100	72
44	204	61
50	284	71
68	354	91
74	379	73
92	438	
100	409	

Sample B10, B20, B30

The Figure 4.8 illustrates the water contents of the three samples with 1.6 hour stability. The water contents increase with the aging time for sample B20 and B30. In the beginning the water contents of B20 are similar with B10 afterward increases from B30. The water contents of B10 are slightly increases in start then become constant after 44 hours. In all the three samples the amount of water is increasing, i.e. the water contents after aging are more than the initial contents.

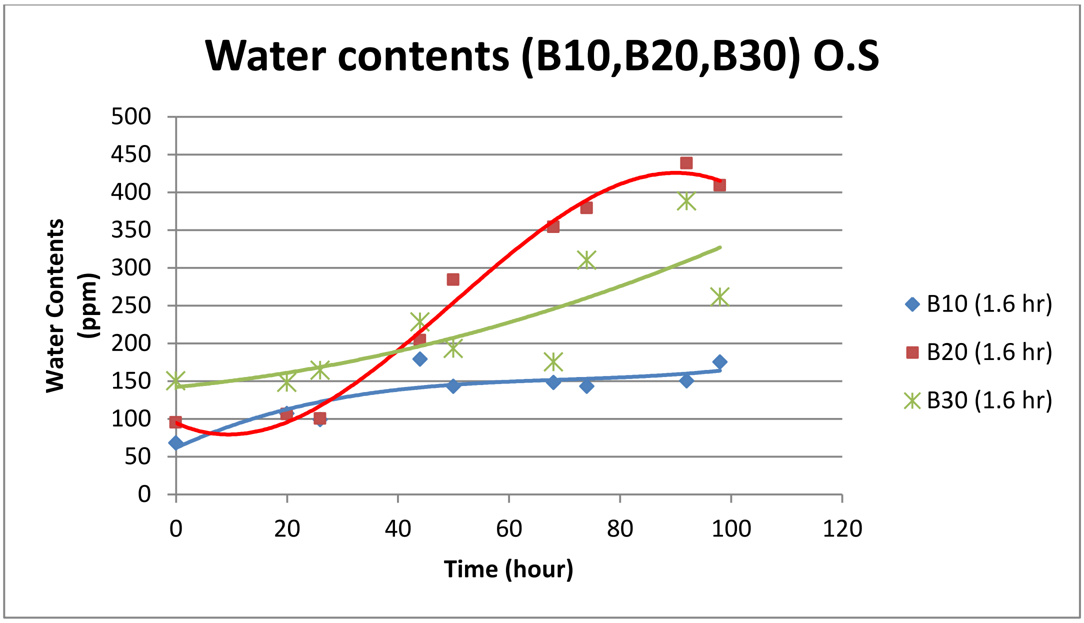


Figure 4.8 water contents B10, B20 and B30 (1.6 hr)

Table 4.6 Water contents B10, B20 and B30 (1.6 hr)

Sample B10, B20,B30	**Water contents [ppm]**		
Time (hour)	B-10	B-20	B-30
0	68	95	150
20	107	106	148
26	99	100	164
44	179	204	228
50	143	284	199
68	148	354	275
74	143	379	310
92	150	438	388
100	175	409	261

4.2 Part second- Aging of fuels in presence of polymer

4.2.1 Acid number

Sample B20-9hr - O.S (with & without polymer)

The acid number of sample B20 with and without polymer is shown in the Figure 4.9, using open system with 9 hour stable fuel. The cross line shows the acid number without polymer while the other line (dotted) shows the same fuel in presence of polymer. There is no significant difference found during entire aging time while using the more stable fuel (9 hour stability).

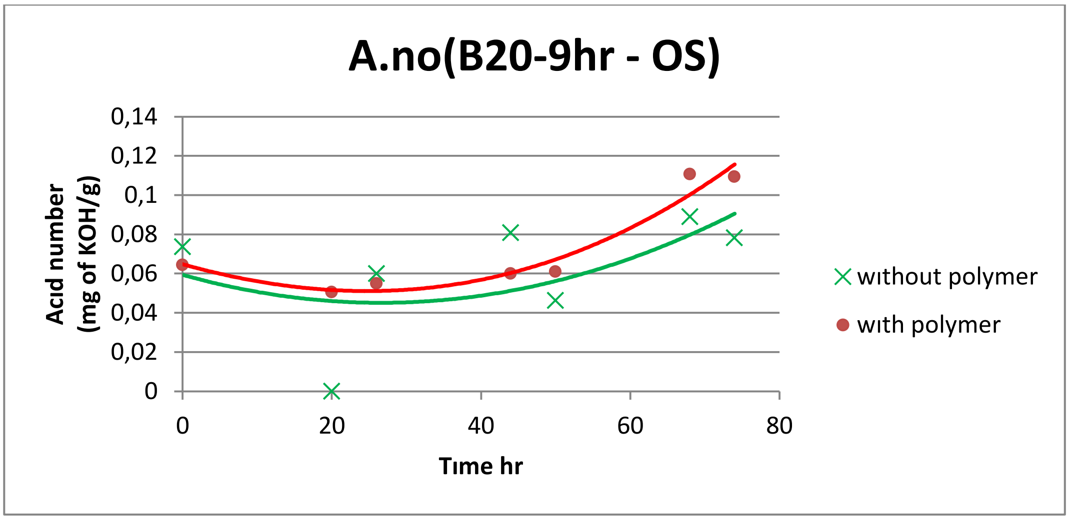


Figure 4.9 Acid number B20-9hr-O.S (with & without polymer)

Sample B20-9hr – N2.Sys (with & without polymer)

Analyzing the acid number for more stable system using 9 hour stable fuel with N2 system, again no changes found, all the values are exactly same except in last two points, see Figure 4.10.

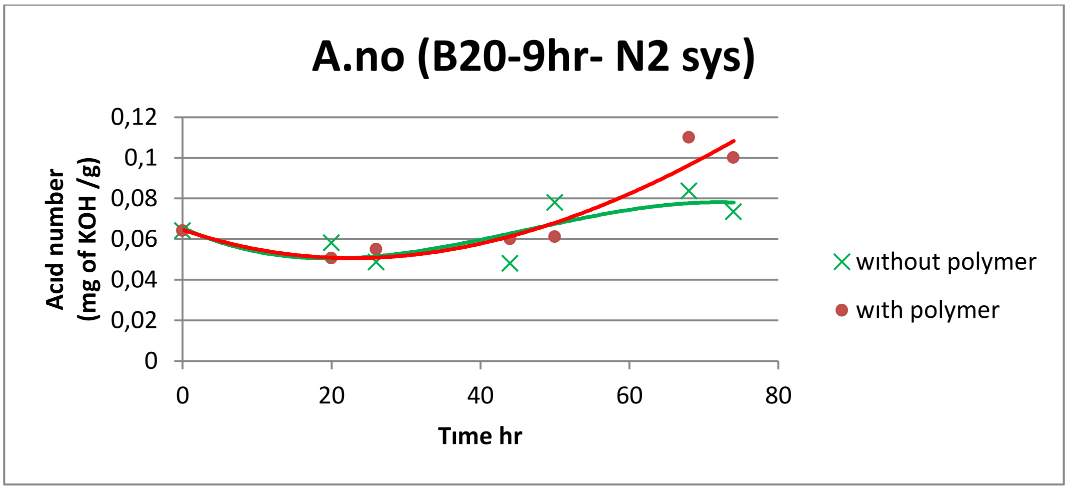


Figure 4.10 Acid number B20-9hr-N2.S (with &without polymer)

Sample B20-1.6hr - O.S (with & without polymer)

The worst case is using the less stable fuel (1.6 hour stability) in open system. This fuel is highly oxidized by aging for 100 hours; the values go beyond the ASTM standards after 70 hours of aging. After analyzing the same fuel in presence of polymer, very less value are observed as shown in the Figure 4.11. In both cases (with & without polymer) the fuel are oxidized by same amount but less value for the polymer part is because of attaching the acid constituents with the polymer surface instead of dissolving in fuel. As the hydro peroxide decompose, it form acidic entities which precipitate down the vessel and stick with the polymer surface and develop a thin layer of residue which can be seen with naked eyes.

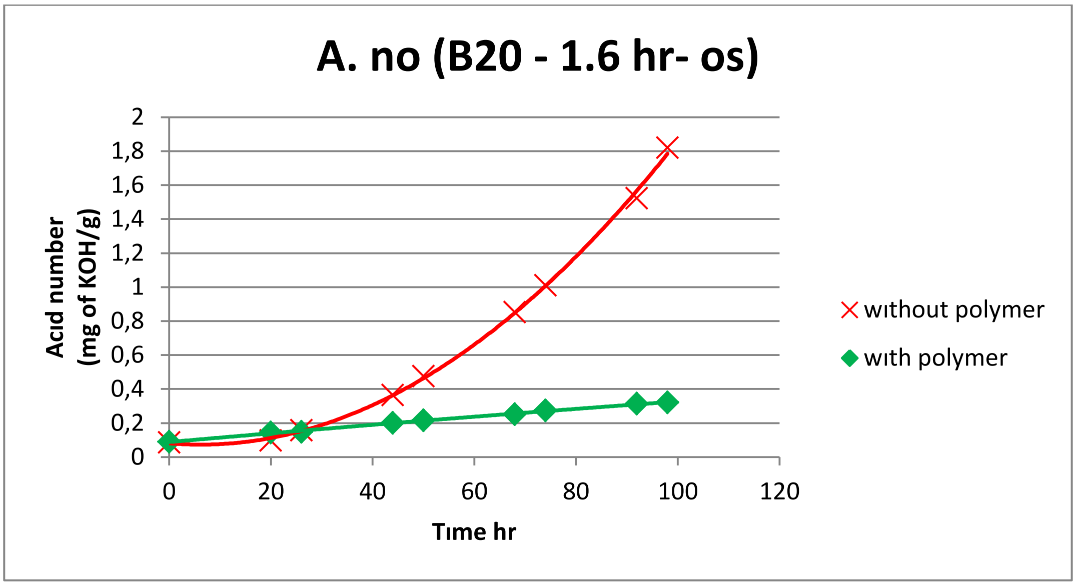


Figure 4.11-Acid number B20-1.6 hr-O.S (with &without polymer)

4.2.2 Hydro peroxide number and water contents

Following the analysis of hydro peroxide number and water contents, similar values are observed for more stable system (9 hr fuel or using N2 system). The same behavior then showed for less stable system i.e. clear difference in both hydro peroxide and water contents for with & without polymer pieces as using 1.6 hr fuel in open system. These graphs are shown in appendix 6.4.

4.3 Polyoxymethylene (POM)

4.3.1 IR spectroscopy

The IR spectroscopy is used to observe the changes occur with ageing the polymer. Initial analysis is made with reference sample to understand the fundamental peaks of unaged polymer. Before going in detail to each spectrum, it's important to enlighten the major influenced-ageing peaks. The most important peaks are located at 1700 cm^{-1} (carbonyl group, C=O), 3000-2850 (alkenes, C-H) and 3400 (hydroxyl group, O-H) [21]. The presence of carbonyl peak is clear indication for fuel existence, an obvious group of alkyl ester. If the hydroxyl peak is present along with the carbonyl group, then the chemical specie is most probably carboxylic acid.

The bottom spectra in the Figure 4.12 represents the reference sample, hold no sign of carbonyl (1700 cm-1) and hydroxyl group (3400 cm^{-1}). The first two spectra at top illustrate the polymer sample aged for 400 and 800 hours in open system using 1.6 hour stable fuel. The peak increases with the ageing time at 1700, 2850 and 3400 cm^{-1}, possibly shows the presence of fuel on polymer surface. The second spectrum from bottom is for same sample (400 hours aged) after washing to wipe out all the fuels, it seems quite similar with reference spectra except a small peak at wave number of 1700 cm^{-1}). This small peak is a sign of fuel inside the polymer which is investigated further with other method (fuel penetration inside the polymer).

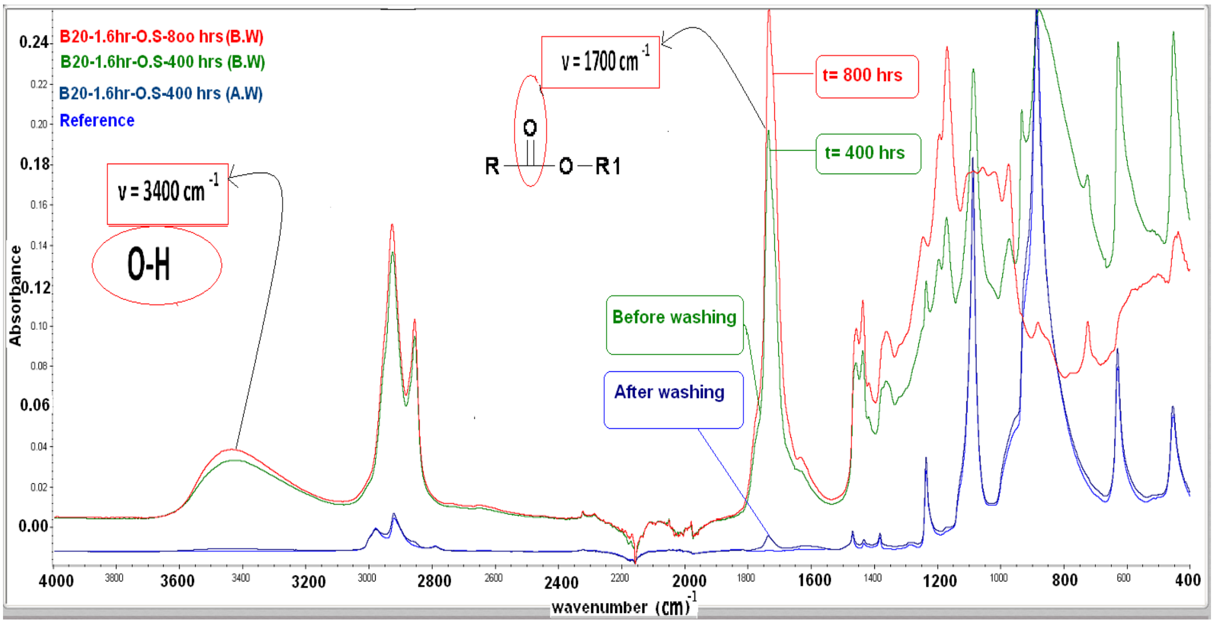


Figure 4.12 IR Spectroscopy

IR spectroscopy (Open and N2 system)

The Figure 4.13 is for aging the polymer in open and N2 system. The presence of oxygen in the open system undoubtedly oxidizes the biodiesel fuel produce unwanted remains like hydro peroxide and acidic constituents. The spectrum in the figure is for total ageing time of 1600 hour after washing and drying the sample before analysis. The spectra obtain in oxygen-free environment (N_2 system) appear analogous to reference sample apart from the peak at 1700 cm^{-1}. There is gradual increase in peak with the ageing time which shows the increase amount of fuel inside the polymer. On the other hand-ageing the polymer in open system, the first two spectra (400 and 800 hours ageing) are similar with N2 system differing only in peak height. But as the ageing time gets larger from 800 hours, the corresponding peak is (at 1700 cm^{-1}) drastically enlarged as shown in the figure. In addition to carbonyl group, the 1200 and 1600 hours sample shows the presence hydroxyl group as well, which indicates the availability of acidic components. The last two spectra (1200 & 1600 hours sample) completely showed dissimilar behavior with reference polymer.

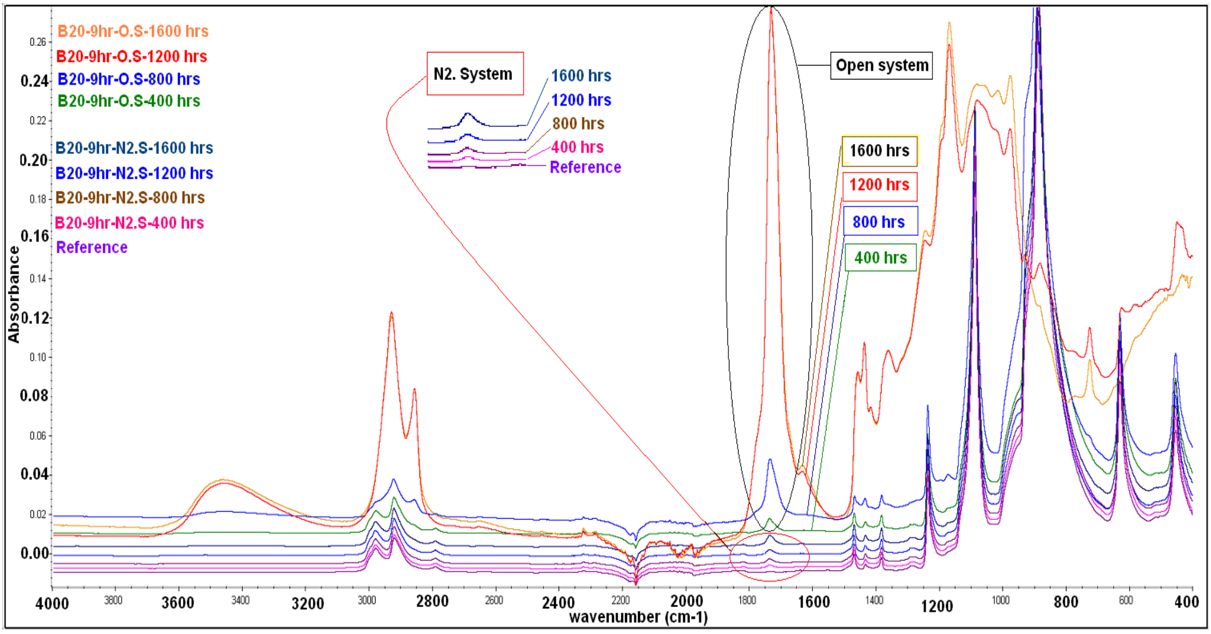


Figure 4.13 IR Spectroscopy (O.S & N2.S)

4.3.2 Light microscope

The Figure 4.14 to 4.30 shows the polymer sample analyzed with light microscope using magnification of 3.2 X. The amount of residue is visible on the surface which increases with ageing time, furthermore the amount of deposits appear more in open system. The effect of less stable (1.6 hours) fuel is also clears in the pictures, for the reason it is more volunteer to oxidation and turn out more residue. The 9 hour (more stable) fuel contains fewer residues however less increase occurs with ageing.

When the polymer aged for 1200 and 1600 hours in open system, enormous amount of residue appeared on its surface which looks like a polymerized product, see Figure 4.25 and 4.26. These samples are then analyzed with SEM for more profound study.

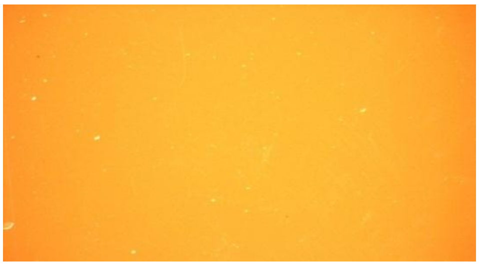


Figure 4.14 Reference (POM)

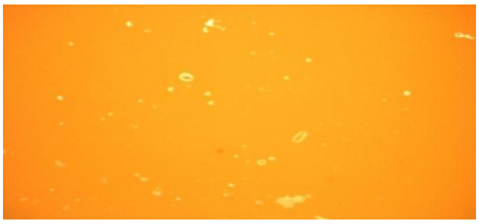


Figure 4.15 B20-9hr-N2.sys-400hrs

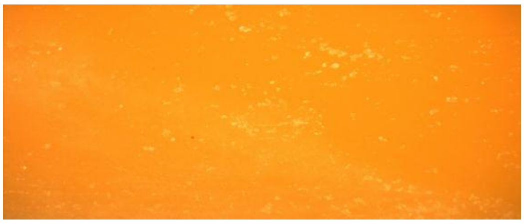


Figure 4.16 B20-9hr-N2.sys-800hrs

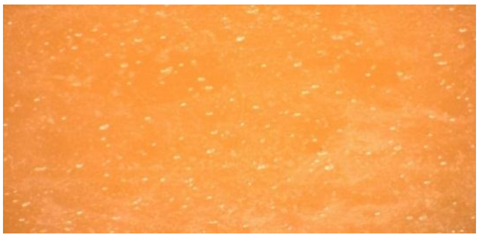


Figure 4.17 B20-9hr-N2.sys-1200hrs

Figure 4.18 B20-9hr-N2.sys-1600hrs

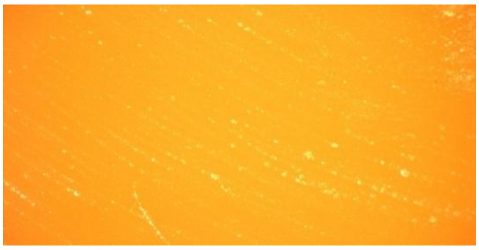


Figure 4.19 B20-1.6hr-N2.sys-400hrs

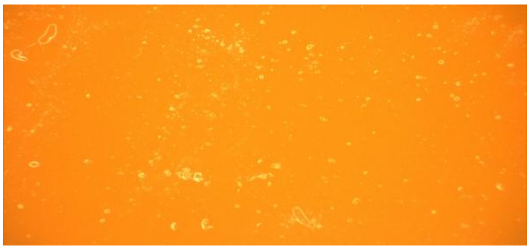


Figure 4.20 B20-1.6hr-N2.sys-800hrs

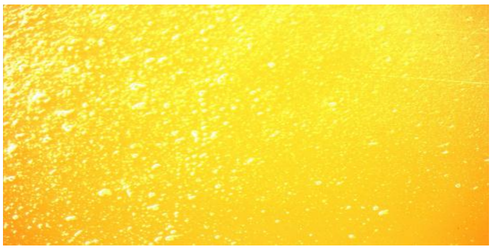


Figure 4.21 B20-9hr-N2.sys-1200hrs

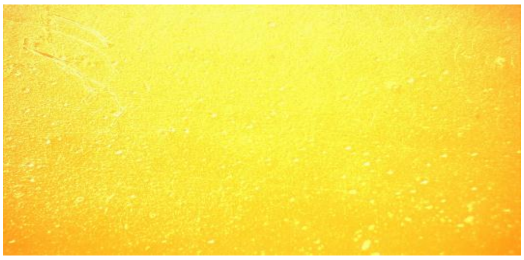


Figure 4.22 B20-9hr-N2.sys-1600hrs

Figure 4.23 B20-9hr-O.S-400hrs

Figure 4.24 B20-9hr-O.S-800hrs

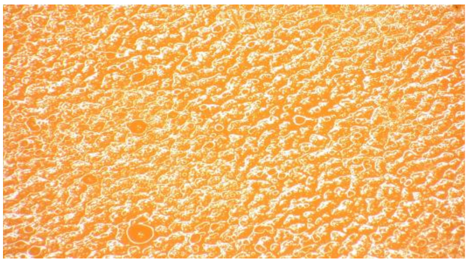


Figure 4.25 B20-9hr-O.S-1200hrs

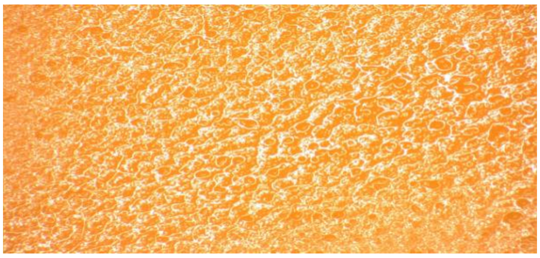


Figure 4.26 B20-9hr-O.S-1600hrs

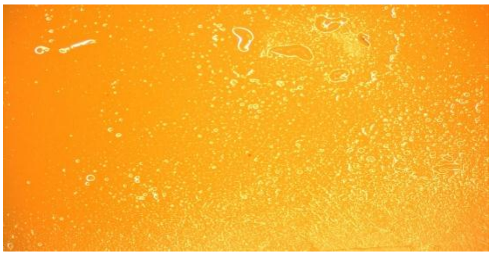


Figure 4.27 B20-1.6hr-O.S-400hrs

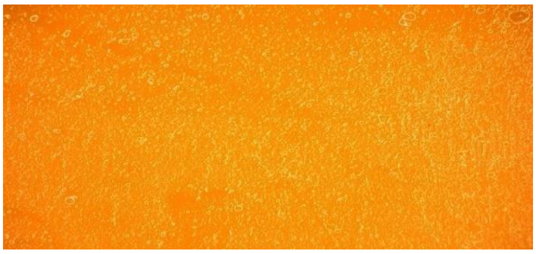


Figure 4.28 B20-1.6hr-O.S-800hrs

Figure 4.29 B20-1.6hr-O.S-1200hrs

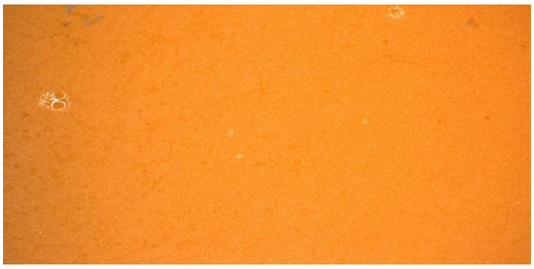


Figure 4.30 B20-1.6hr-O.S-1600hrs

4.3.3 Scanning electron microscope

B20-9hr-open system-1200 hours aging

The analysis made with light microscope are only limited for residue monitoring as no sign of cracks or fracture are observed. The polymer as aged for 1200 and 1600 hours in open system shows a lot of white spots on its surface which are likewise visible with naked eyes. SEM is then used for the deeper observation of those samples. Figure 4.31 is for reference sample, obviously shows no sign of defects on its surface. After 1200 hours of aging the residues are polymerized on the polymer surface, nevertheless the sample still contain clean surface which are focused for close observation, it is found that certain cracks/damaged parts are appeared below the residue layer as shown in the Figure 4.33.

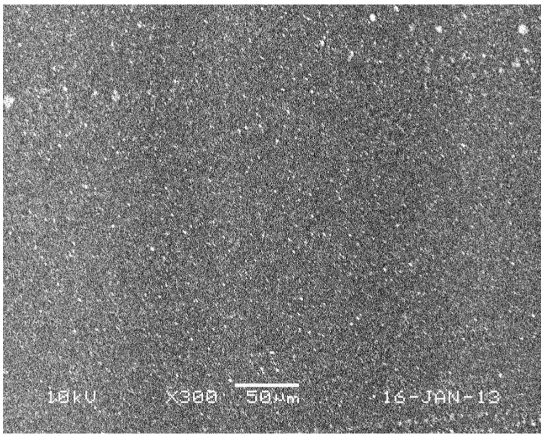


Figure 4.31 Reference (POM)

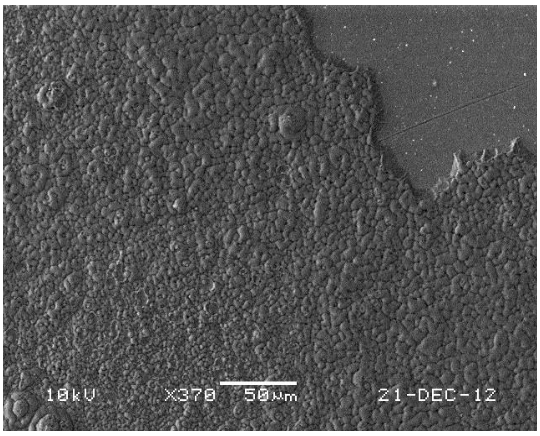


Figure 4.32 B20-9hr-O.S-1200hrs

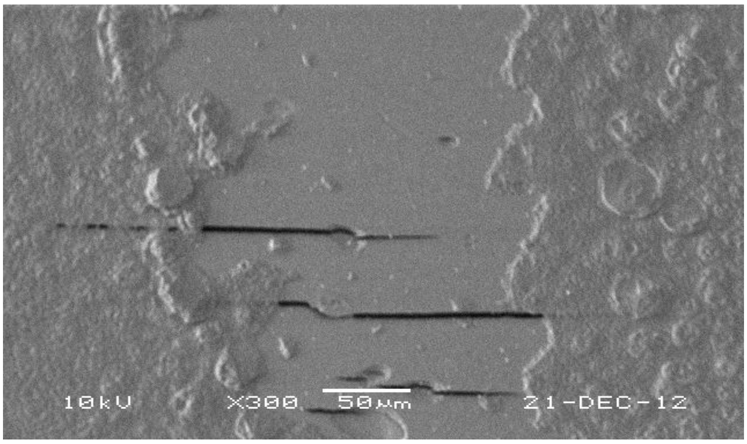


Figure 4.33 B20-9hr-O.S-1200hrs

B20-9hr-open system-1600 hours aging

Figure 4.34 and 4.35 shows 1600 hours aged sample in open system. It can be seen from the Figure 4.34 that the fuel deposits are completely polymerized on entire surface of the polymer. The fractures are not visible due high residue polymerization; however as focused on small clean part, the cracks are quite deep and larger than 1200 hours aged sample, see Figure 4.35. The appearance of cracks on these samples severely affects its strength, which is investigated with impact pendulum testing.

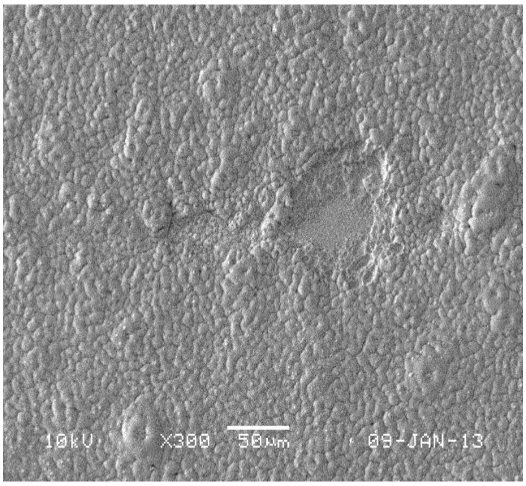


Figure 4.34 B20-9hr-O.S- 1600hrs

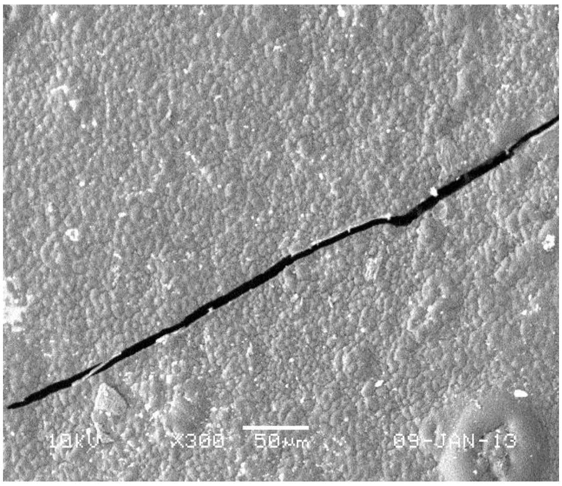


Figure 4.35 B20-9hr-O.S-1600hrs

4.3.4 Immersion tests

Change in volume- Open system

The polymer swelling is determined by measuring the change in volume at different aging time. The Figure 4.36 shows swelling of polymer in open system with 1.6 and 9 hour fuel. The change in volume increases with ageing time, which indicates that the fuel absorb inside the polymer at entire period of ageing. It is also clear from the graph that the polymer material swell more in 1.6 hour fuel as it reaches 3.2 % swelling, the maximum swelling observed for 9 hour fuel is 2%.

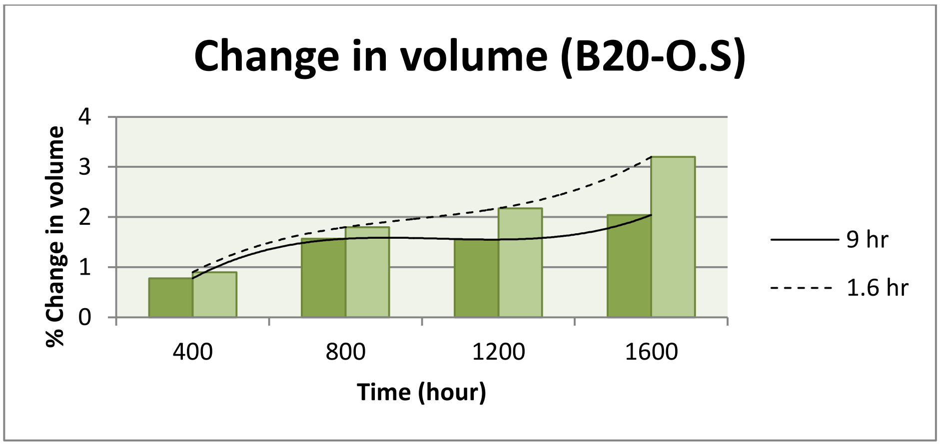


Figure 4.36 Change in volume (B20- O.S)

Percentage Change in weight- open system

The same behavior is then showed for percentage change in weight i.e. increases the weight with ageing time and more % change in weight using 1.6 hour fuel, see the Figure 4.37.

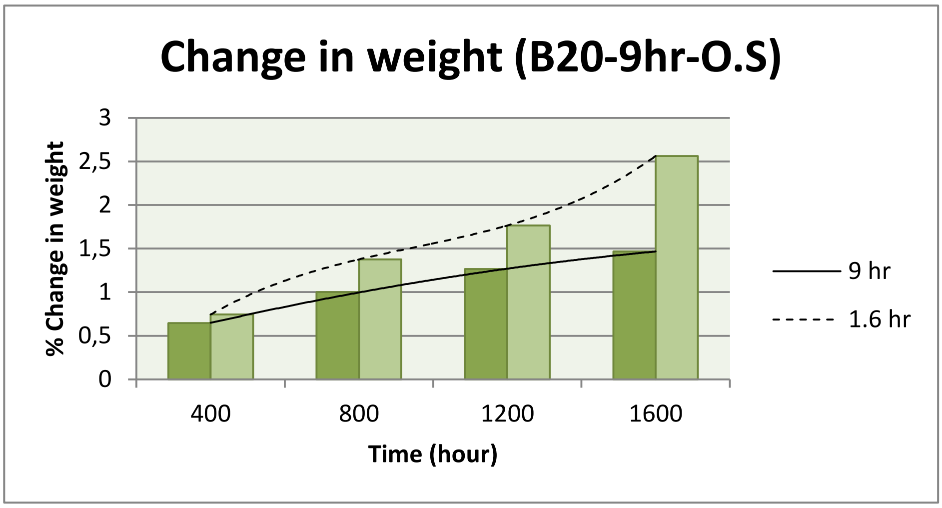


Figure 4.37 Change in weight (B20-O.S)

Change in volume- N2 system

The same measurement is then made in oxygen-free environment (inert system); the change in volume (swelling) of the polymer is shown in the Figure 4.38. The maximum swelling is 1 % at 800 hours which increase from 0.4 % at 400 hour of ageing. The first two ageing period (400 and 800 hours) causes the polymer to swell due to fuel pick up inside the polymer material. The polymer starts to de-swell after 800 hours of ageing because of leaching out the fuel as the saturation attain inside. The material again starts to swell after 1200 hours; this swelling is either because of the fuel penetrates again or the residue on the polymer surface is polymerized due to longer stay (1600 hours ageing) and high concentration.

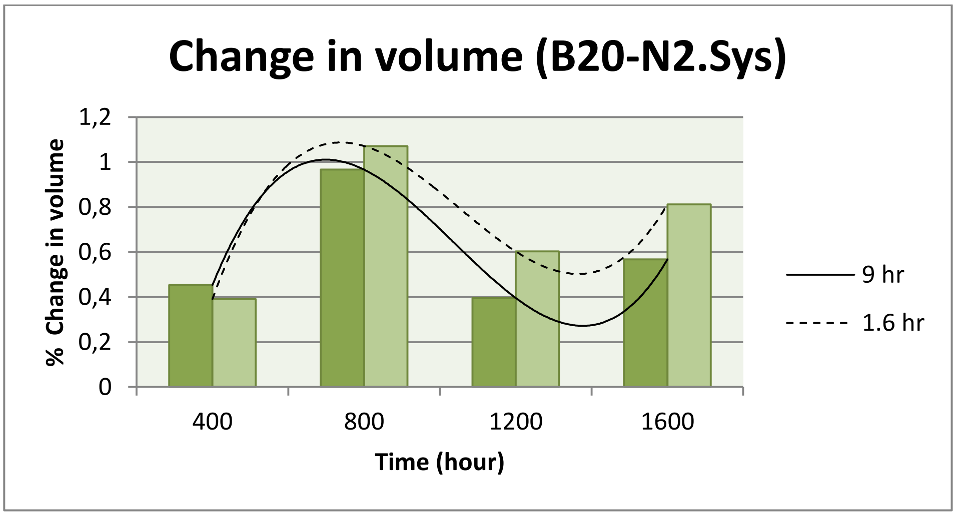


Figure 4.38 Change in volume (B20-N2.S)

Percentage Change in weight- N2 system

The same decrease in the percentage weight change occurs at 1200 hours then increases at 1600 hours of ageing. The difference for the 1.6 and 9 hour fuel is shown in the Figure 4.39.

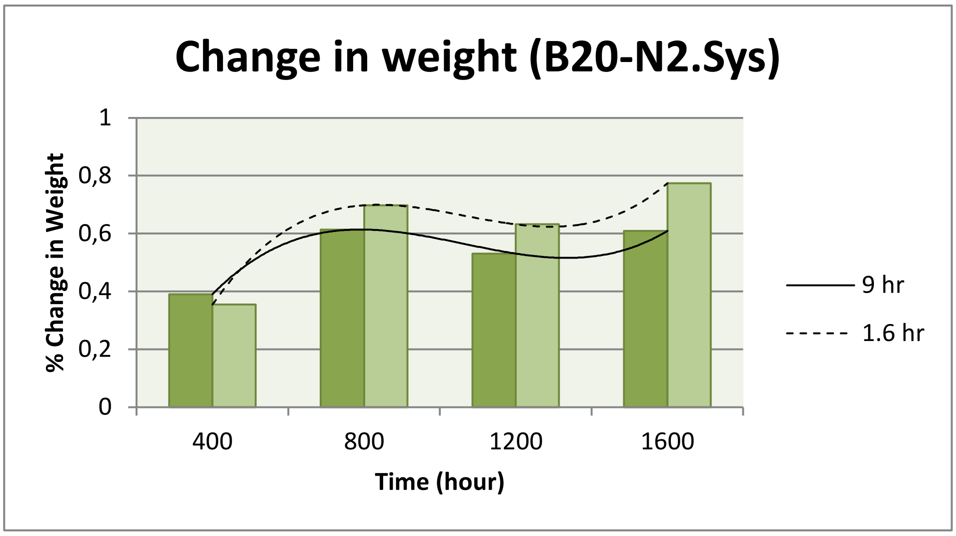


Figure 4.39 Change in weight (B20-N2.S)

4.3.5 Penetration of fuel inside polymer

The penetration of fuel inside the polymer is carried out by conceiving a practically new method which gives quite accurate indication of fuel inside the polymer. Analysis of the thin layer (45 µm in thickness) not only gives information about the fuel existence but in addition examine the ageing of inner surface of the polymer.

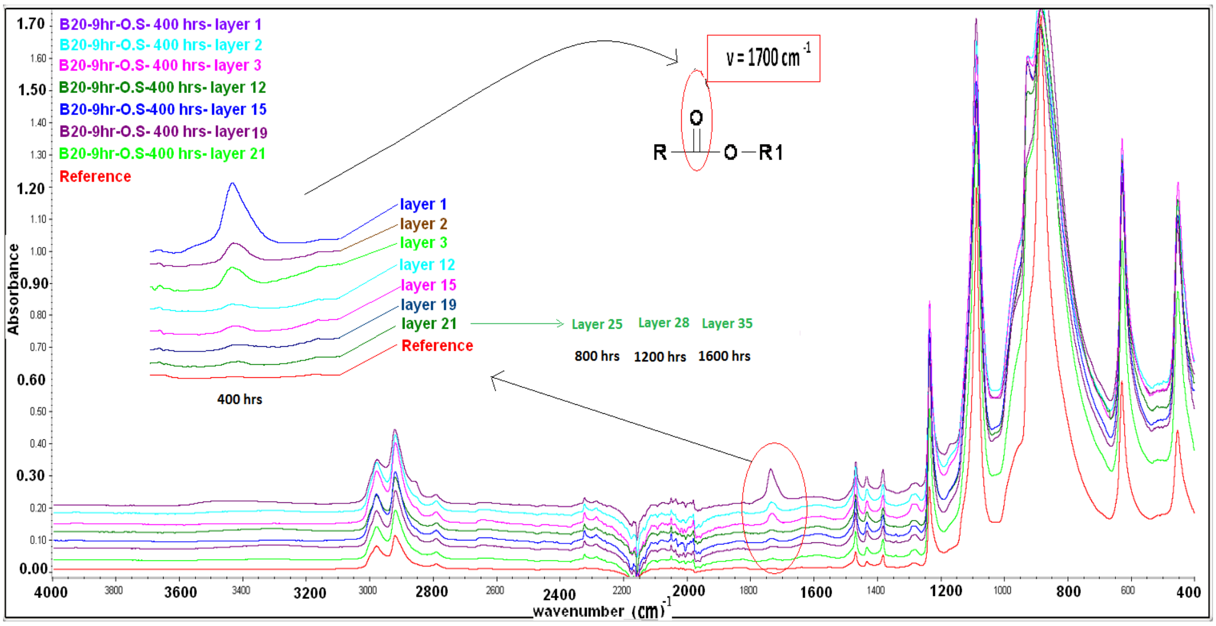


Figure 4.40 Penetration of fuel inside polymer

The spectrum in the Figure 4.40 is for different layers of the polymer after 400 hour of ageing in open system. The top spectrum is for layer 1 and then follows down up to 21 from top to bottom as shown in the figure. The base line is the reference (fresh sample) spectra for comparison of internal ageing and fuel existence. There are no major differences observed in each peak which show any changes in the interior part except the peak at 1700 cm^{-1}, which possibly shows the existence of fuel as explained earlier. The height of the peak decreases from top to bottom layer, the layer 21 closely match with the reference spectra indicate no fuel existence.

With increase in ageing time, the fuel progressively goes down and consequently the number of peaks increases. For 800, 1200 and 1600 hours ageing, the matching spectra with the reference polymer is layer 25, 28 and 35 consecutively, see appendix 6.5.

4.3.6 Analysis of deposits on polymer surface

The amount of residues after sorting out from the solvent are found more in open system. For the N2 system, it is not so large in extent but fairly enough for analysis. Figure 4.41 shows the spectrum for open and N2 system at entire aging period using the 9 hour fuel. The spectrum getting after each analysis is searched in library which contains spectra for almost every chemical substance. For the inert system (using N_2) the spectrum matches 96 % with methyl linoleate which is an alkyl ester of fatty acid also called biodiesel. Thus it's the biodiesel which precipitate down and making a layer on polymer surface, furthermore a larger peak at 3400 cm^{-1} is observed for open system. This peak represent hydroxyl group (OH) and its presence with carbonyl group characterizes the residue as a short chain of carboxylic acid.

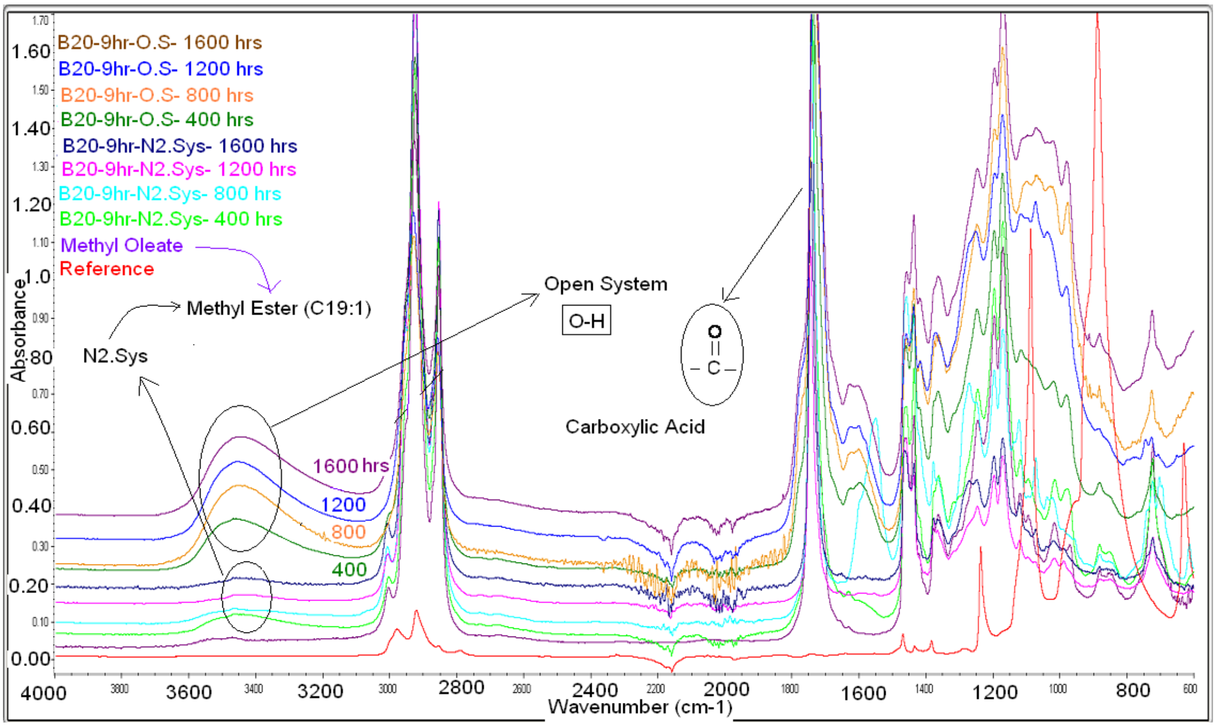


Figure 4.41 Penetration of fuel inside polymer (Open &Nitrogen system)

4.3.7 Impact pendulum test

Figure 4.42 shows the impact resistance, gauges in kJ/m^2, of the specimens at different aging time. The analyses are made by aging the polymer in 9 hour fuel using open and N_2 (inert) system. For the N_2 system, the energy required/absorbed to break the sample is almost same at each period of aging. No changes in strength are observed as preventing the flow of air inside (creating inert system). For the open system the impact resistance increases after 400 hours of aging, this increase is because of the fuel or oxidized entities of the fuel absorbs inside the polymer. The resistance again drops to reference value after 800 hours and decreases further after 1200 and 1600 hours of aging. The total loss in strength is almost 35 % after aging the sample in open system.

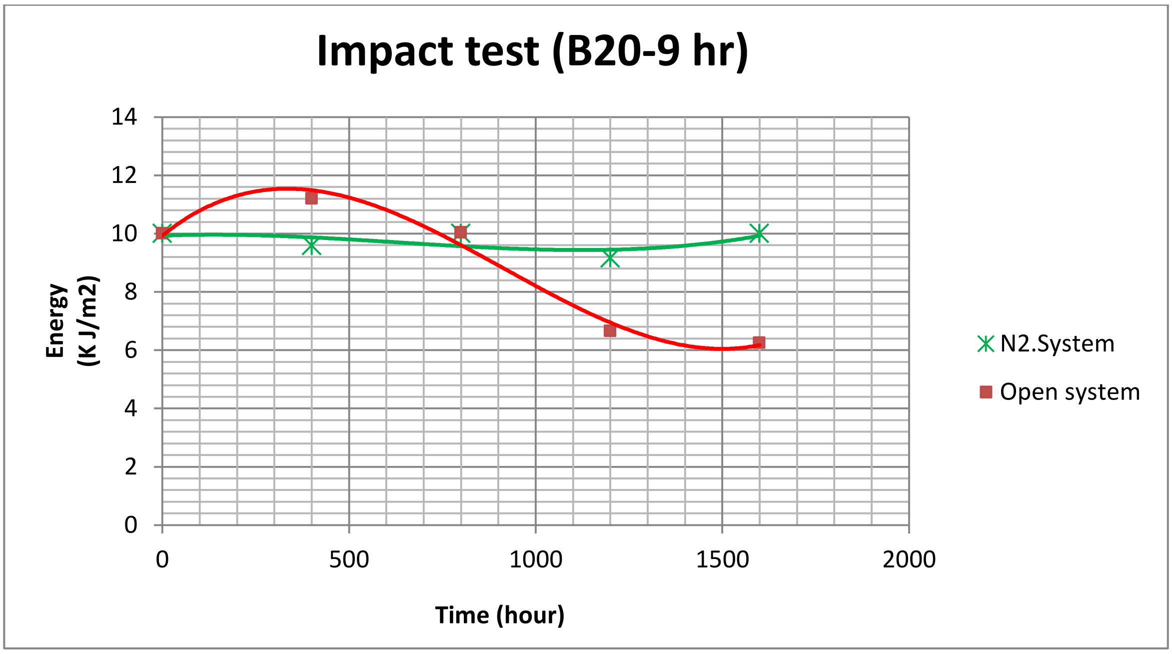


Figure 4.42 Impact pendulum testing

Table 4.7 Impact resistance

		Impact resistance [kJ/m^2]			
Time [hour]	0	400	800	1200	1600
Nitrogen system	10	9,583	10	9,16	10
Open system	10	11,2	10,04	6,66	6,25

5 CONCLUSIONS

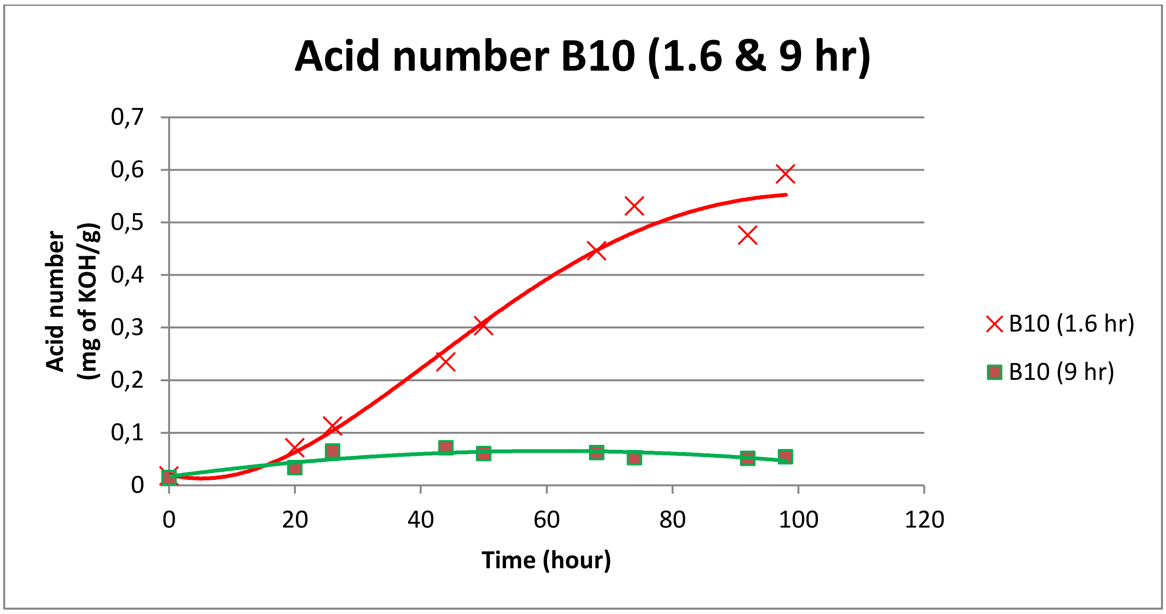
Biodiesel is the best alternative fuel to conventional diesel and can be used in car engines with slight alteration prior to cause any operational problems. The big problem with biodiesel is of readily oxidation and creating high peroxide and acidic constituents. This property of biodiesel diminishes the gain to fully substitute the non-renewable petro diesel fuel. One way of reducing this problem is to prevent the flow of air by creating inert system as made in this work by using N_2 gas. No changes in acid value, peroxide number and water contents are observed as using the oxygen-free environment. The more convenient way for the oxidation control is to use antioxidants in order to increase the stability of fuel. The 9 hour fuel contains additional antioxidants and performed better than the 1.6 hour fuel. The other approach of overcoming this intimidation is to make a blend with petro-diesel, but the higher blends B20 and B30 does not follow the ASTM specifications in term of acid value as long as the fuel does not contain antioxidants or an inert system is created. The completely unstable behavior showed by one of the blend clarifies that the fuel needs to be handled below the stability temperature. The fuel B10 works with the desired specifications without adding antioxidants or inert system. Moreover the behavior of B20 found more analogous with B30 and distantly from the B10 blend. As a result the use of B30 is preferred in the sense to substitute more of the non-renewable fuel, provided to make use of the antioxidants.

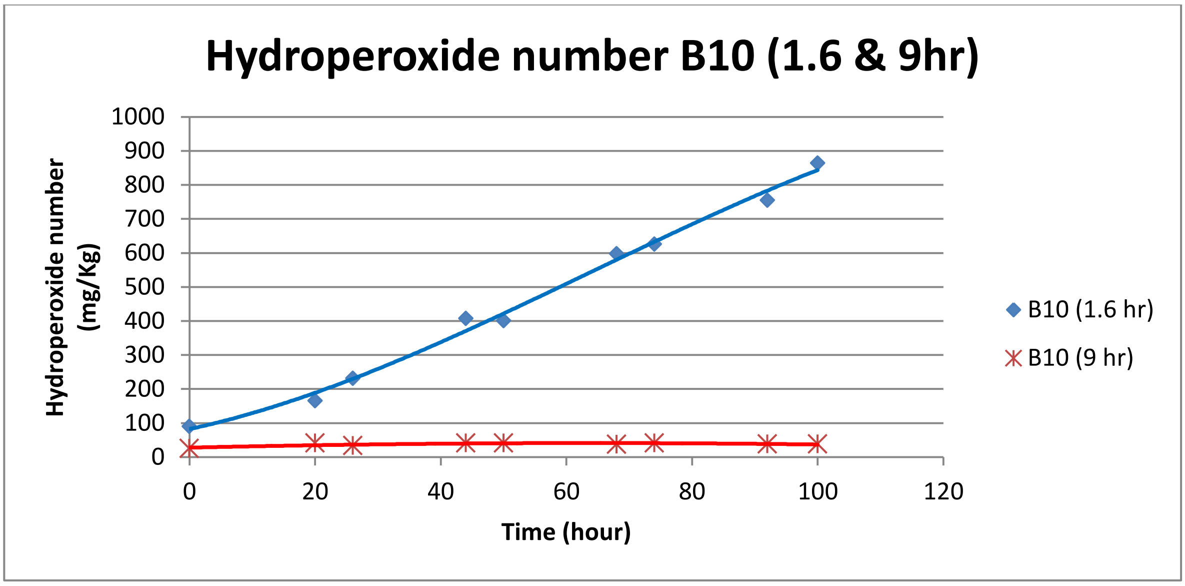
The characterization products (acid, peroxide and water contents) of the fuel aged in the presence of polymer has similar values with the fuel-lacking polymer. For the inert system, there is no change in the polymer structure; the strength of the sample remains same and saturation reached after 1 % of fuel absorption. For the system having access to air, highly oxidizes the fuel creating larger amount of residues which precipitate down the vessel and stick with the polymer surface. These deposits are then polymerized after 1200 hours and 1600 hours of aging and might have greater impact on car parts after long exposure, i.e. plugging fuel filter and damaging the fuel tank. The polymerized products and various cracks on the surface of the polymer completely showed dissimilar behavior with reference polymer whilst analyze with IR spectroscope and scanning electron microscope. The maximum swelling of the polymer is 3 % and the fuel absorbed more in less stable fuel (1.6 hour) as compared with the stable fuel (9 hour stability). The fuel penetration analyzed for open system increases with the aging time. The last analysis (impact test) made as a culmination result of entire work which shows 35 % loss in strength as compared with original (unaged) polymer.

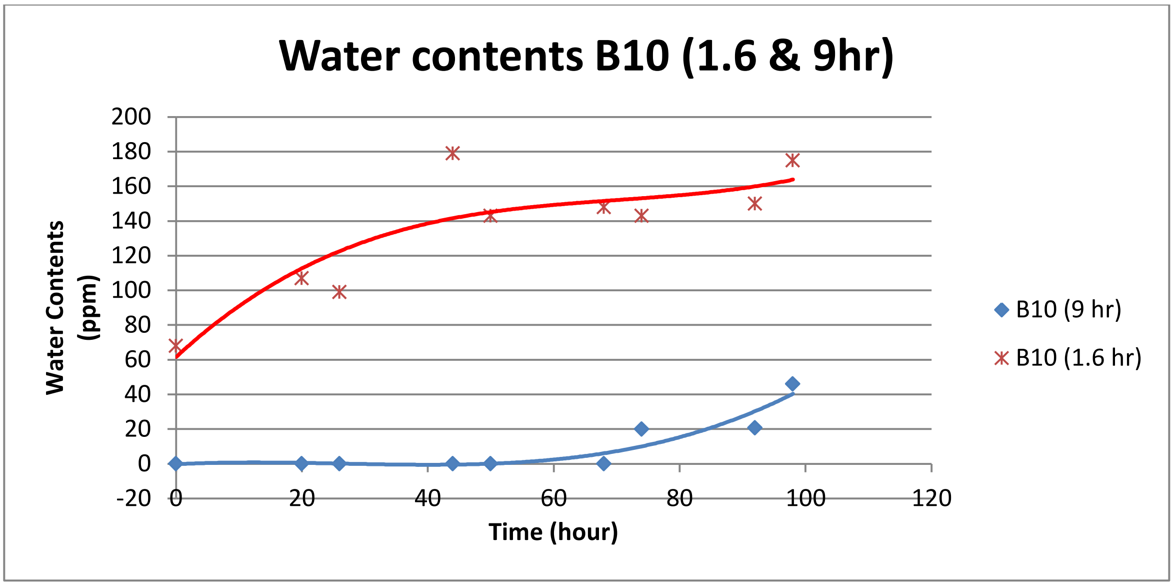
Thus the high acid value of the fuel precludes the use of car components (polymer in this work) because of less compatibility with high acid constituents and can be limited by preventing/ reducing the access of oxygen or using more antioxidants.

6 APPENDICES

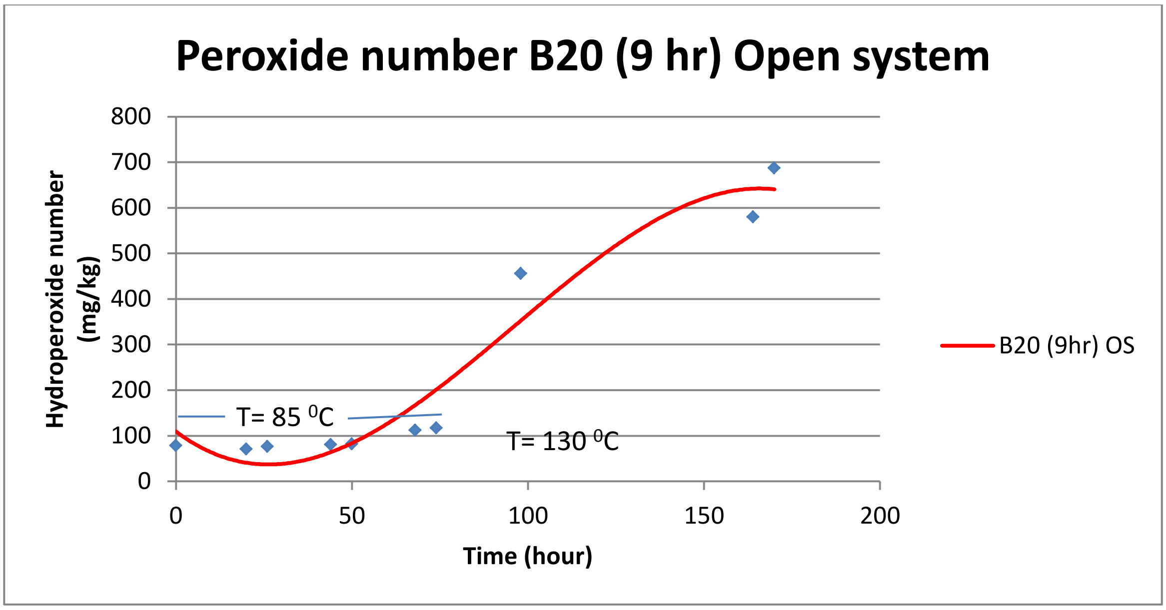
6.1 Part first-Sample B-10 (1.6 and 9 hour stability)



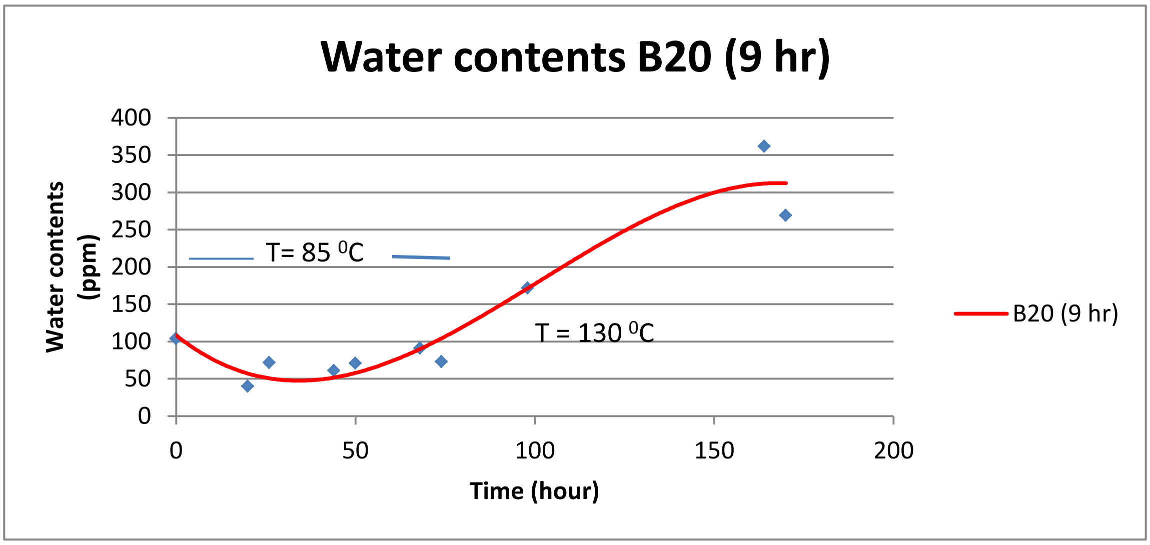




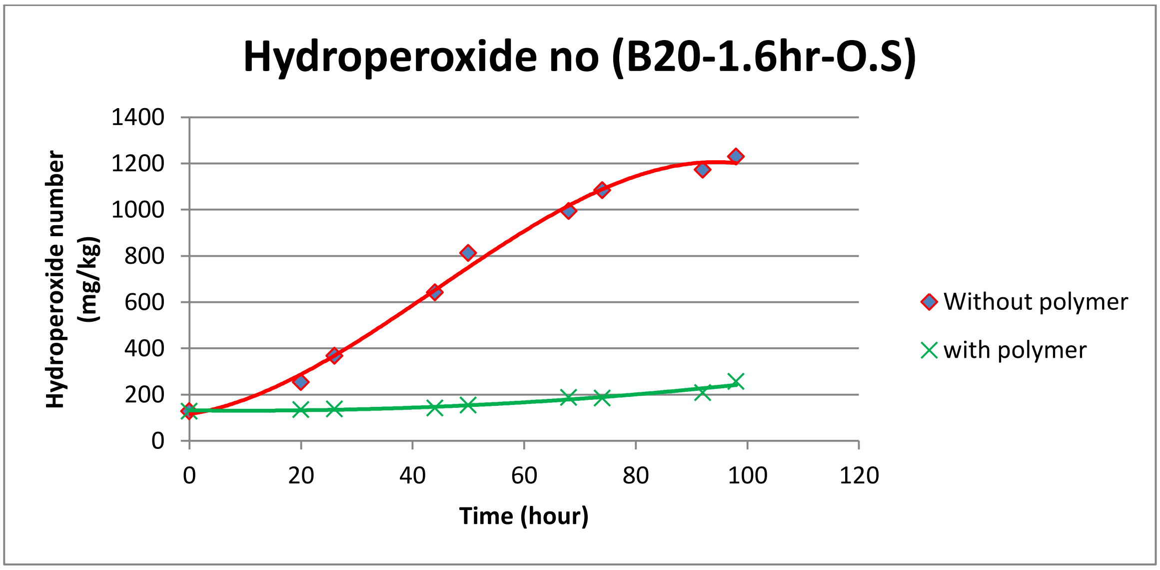
6.2 Instability of fuel (Sample B20 -9 hour stability)

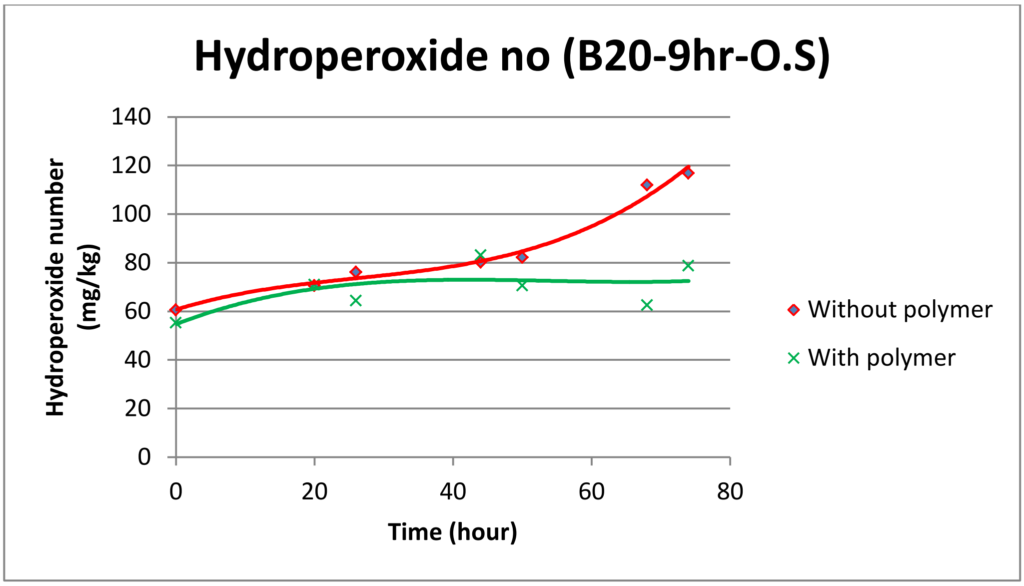


6.3 Sample B20 (9 hour stability)

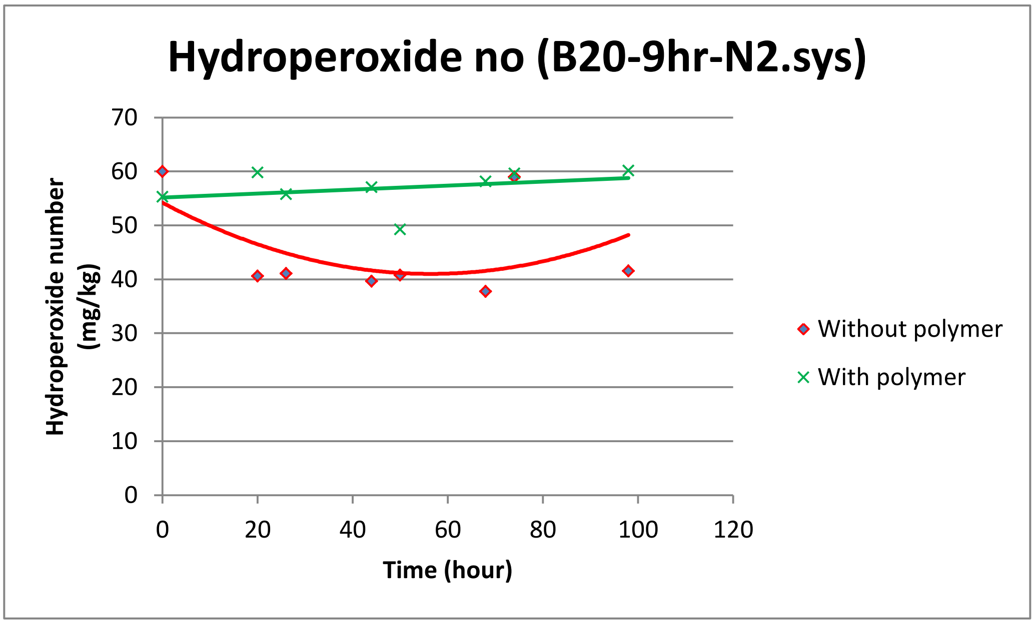


6.4 Part second (Sample B20- with & without polymer)

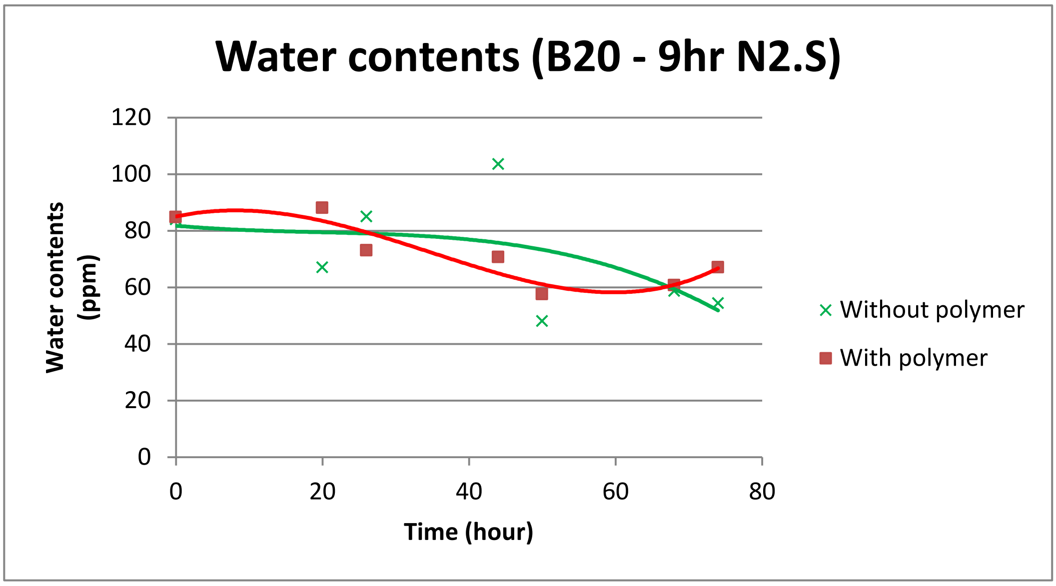


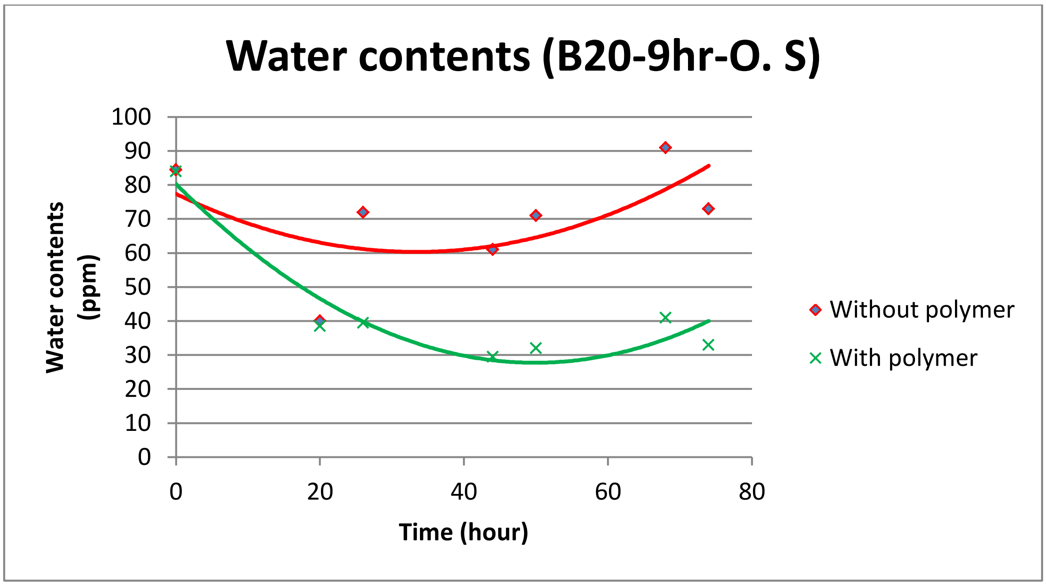


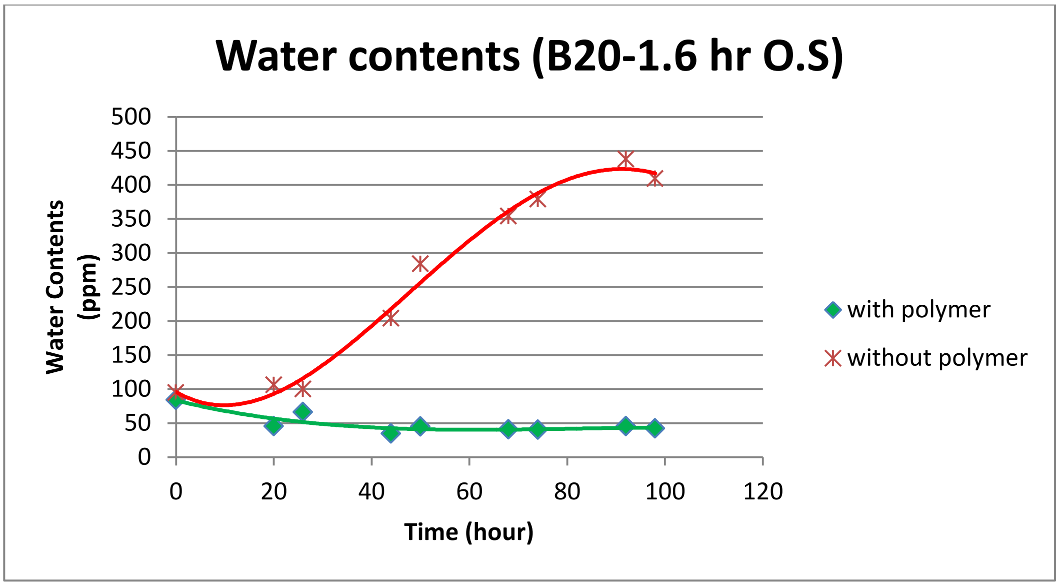
Hydroperoxide no (B20-9hr-O.S)
Hydroperoxide number (mg/kg)
140
120
100
80
60
40
20
0
0
20
40
60
80
Time (hour)
Without polymer
With polymer



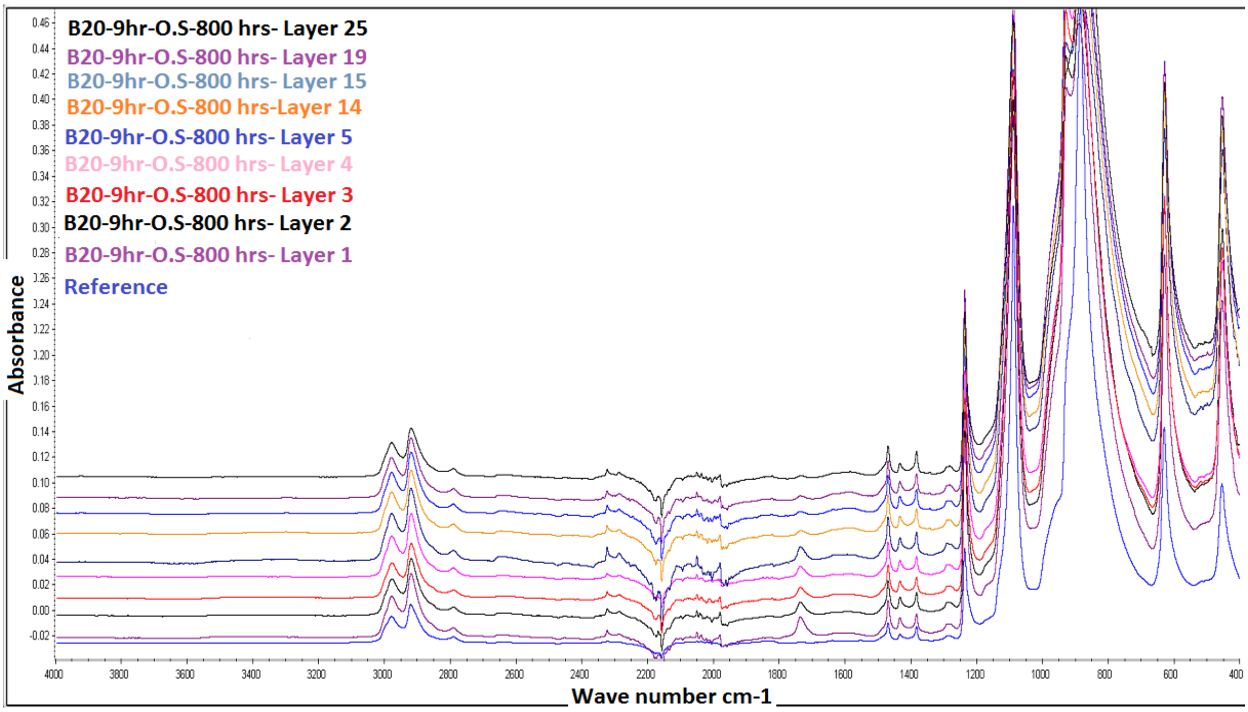
Hydroperoxide no (B20-9hr-N2.sys)
Hydroperoxide number (mg/kg)
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Time (hour)
Without polymer
With polymer

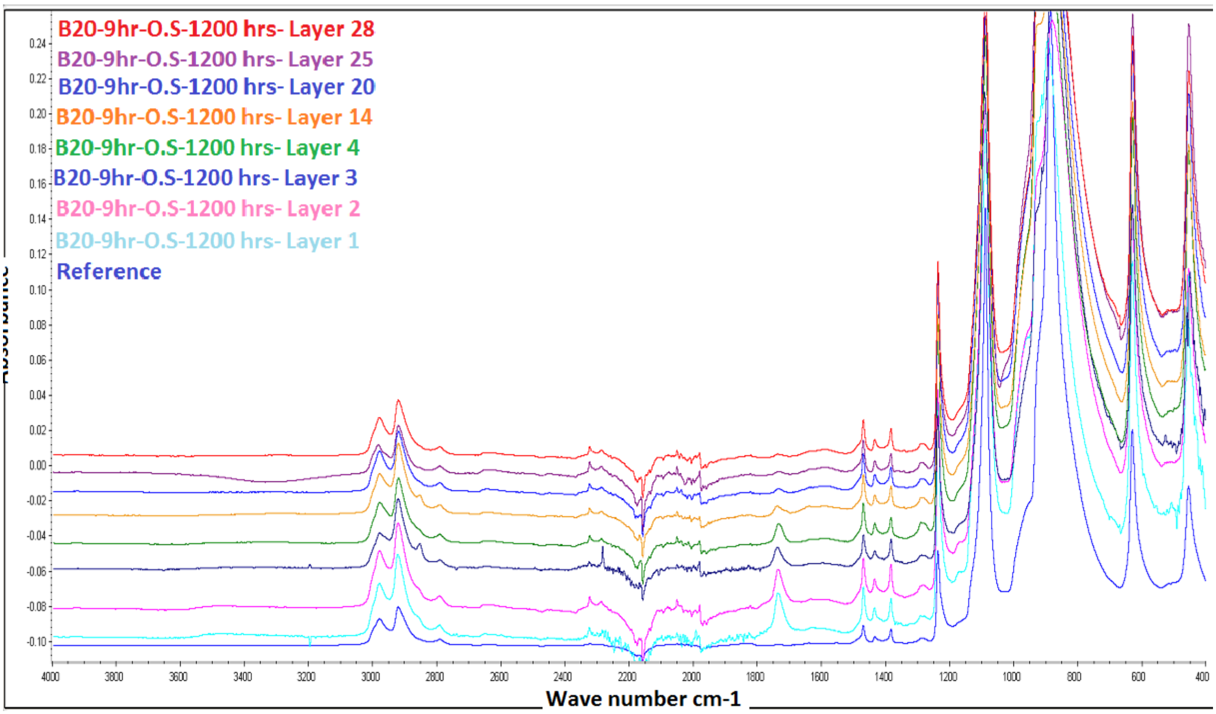

Water contents (B20 - 9hr N2.S)
Water contents (ppm)
120
100
80
60
40
20
0
0
20
40
60
80
Time (hour)
× Without polymer
■ With polymer

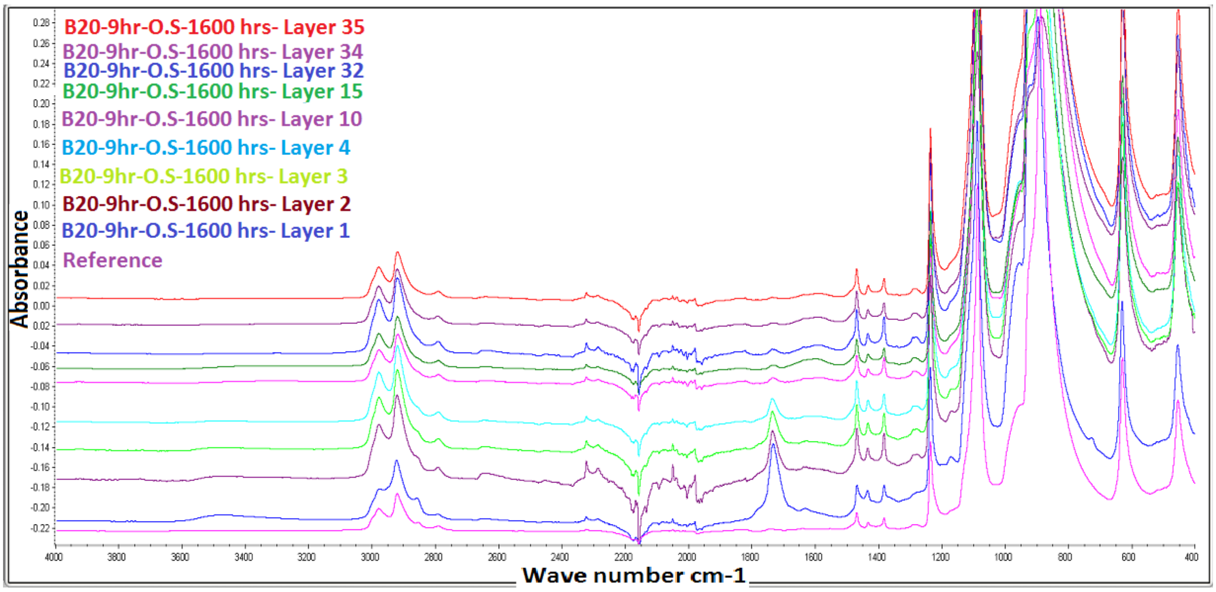

Water contents (B20-9hr-O. S)
Water contents (ppm)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
Time (hour)
◆ Without polymer
× With polymer



6.5 Penetration of fuel inside polymer




B20-9hr-O.S-1200 hrs- Layer 28
B20-9hr-O.S-1200 hrs- Layer 25
B20-9hr-O.S-1200 hrs- Layer 20
B20-9hr-O.S-1200 hrs- Layer 14
B20-9hr-O.S-1200 hrs- Layer 4
B20-9hr-O.S-1200 hrs- Layer 3
B20-9hr-O.S-1200 hrs- Layer 2
B20-9hr-O.S-1200 hrs- Layer 1
Reference
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wave number cm-1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0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
-0.20
-0.22
4000
3800
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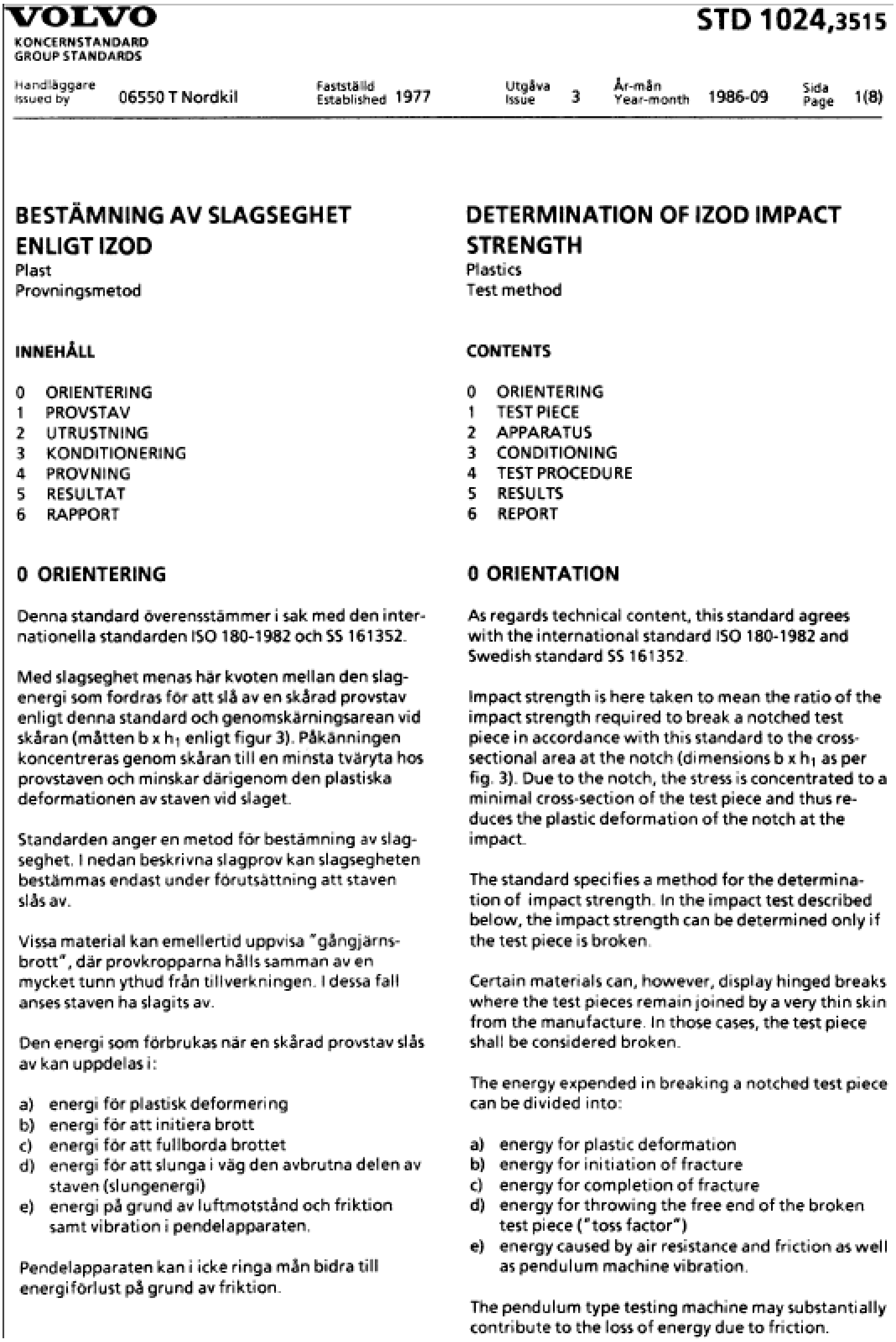
6.6 Standard method for impact test



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Handläggare Issued by	06550 T Nordkil	Fastställd Established	1977	Utgåva Issue	3	År-mån Year-month	1986-09	Sida Page	1(8)

BESTÄMNING AV SLAGSEGHET ENLIGT IZOD

Plast
Provningsmetod

INNEHÅLL

0 ORIENTERING

Denna standard överensstämmer i sak med den internationella standarden ISO 180-1982 och SS 161352.

Med slagseghet menas här kvoten mellan den slagenergi som fordras för att slå av en skårad provstav enligt denna standard och genomskärningsarean vid skåran (måtten b x h_1 enligt figur 3). Påkänningen koncentreras genom skåran till en minsta tväryta hos provstaven och minskar därigenom den plastiska deformationen av staven vid slaget.

Standarden anger en metod för bestämning av slagseghet. I nedan beskrivna slagprov kan slagsegheten bestämmas endast under förutsättning att staven slås av.

Vissa material kan emellertid uppvisa "gångjärnsbrott", där provkropparna hålls samman av en mycket tunn ythud från tillverkningen. I dessa fall anses staven ha slagits av.

Den energi som förbrukas när en skårad provstav slås av kan uppdelas i:

a) energi för plastisk deformering
b) energi för att initiera brott
c) energi för att fullborda brottet
d) energi för att slunga i väg den avbrutna delen av staven (slungenergi)
e) energi på grund av luftmotstånd och friktion samt vibration i pendelapparaten.

Pendelapparaten kan i icke ringa mån bidra till energiförlust på grund av friktion.

DETERMINATION OF IZOD IMPACT STRENGTH

Plastics
Test method

CONTENTS

0 ORIENTATION

As regards technical content, this standard agrees with the international standard ISO 180-1982 and Swedish standard SS 161352.

Impact strength is here taken to mean the ratio of the impact strength required to break a notched test piece in accordance with this standard to the cross-sectional area at the notch (dimensions b x h_1 as per fig. 3). Due to the notch, the stress is concentrated to a minimal cross-section of the test piece and thus reduces the plastic deformation of the notch at the impact.

The standard specifies a method for the determination of impact strength. In the impact test described below, the impact strength can be determined only if the test piece is broken.

Certain materials can, however, display hinged breaks where the test pieces remain joined by a very thin skin from the manufacture. In those cases, the test piece shall be considered broken.

The energy expended in breaking a notched test piece can be divided into:

a) energy for plastic deformation
b) energy for initiation of fracture
c) energy for completion of fracture
d) energy for throwing the free end of the broken test piece ("toss factor")
e) energy caused by air resistance and friction as well as pendulum machine vibration.

The pendulum type testing machine may substantially contribute to the loss of energy due to friction.

Vid provning av plast anses vanligen energiförluster på grund av luftmotstånd och vibration vara försumbara men den senare kan dock vara ansenlig om pendelapparaten inte har tillräckligt stor massa i förhållande till pendelns slagenergi eller inte är tillräckligt stel.

Tillåten energiförlust pga friktion framgår av tabell 1, sid 8.

För att resultat enligt denna standard skall få jämföras måste provstavarna ha samma utformning och storlek samt vara tillverkade på samma sätt och provade med pendel med samma anslagshastighet.

When testing plastics, loss of energy due to air resistance and vibration is usually considered negligable, but the latter may, however, become considerable if the pendulum type testing machine does not have a great enough mass in relation to the pendulum's impact energy, or if it is not rigid enough.

Permitted energy loss due to friction can be seen from table 1, page 8.

Results based on this standard may be compared only if the test pieces conform in shape, size and make, and are tested by means of a pendulum swinging at the same speed during all tests.

1 PROVSTAV

Normalprovstav enligt figur 1 tillverkas först utan skåra och förses därefter med skåra.

1 TEST PIECE

A standard test piece such as in figure 1 is made unnotched, and then given a notch.

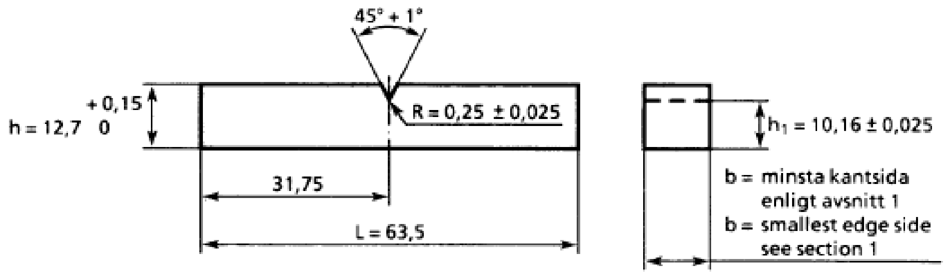

Fig. 1

Formtillverkad normalprovstav skall ha rektangulärt tvärsnitt med två motsatta sidor (h) = 12,7 mm och de två andra (b) mellan 3,2 och 12,7 mm. Måttet (b) bör väljas så att stavens tväryta är representativ för den tväryta som plastmaterialet vanligen har i praktiken.

För att få överensstämmande resultat bör berörda parter komma överens om såväl formverktyg som tillverkningsförfarande för stavarna.

Formtillverkad normalprovstav förses med skåra i den ena sidan med måttet (b).

För en del plastmaterial varierar slagsegheten med skårans längd varför formtillverkade provstavar med bestämt tvärsnitt skall användas vid jämförande provning.

Moulded standard test pieces shall have a rectangular cross-section with two opposite sides holding the dimension (h) = 12.7 mm, and the two others holding (b) between 3.2 and 12.7 mm. Dimension (b) should be chosen so that the cross-section of the test piece represents the cross-section normally found when using this particular plastic.

To obtain uniform results, all parties concerned should agree on moulding tools as well as on how the test pieces shall be made.

Moulded standard test pieces shall be given a notch in one of the edge sides measuring (b).

In some plastics, the impact resistance varies with the length of the notch. This is why moulded test pieces must have a fixed cross-sectional dimension at comparative tests.

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Formpressad normalprovstav skall förses med skåra i en sida som är parallell med pressriktningen vid tillverkningen.

Slagsegheten kan vara olika om skåran görs i en sida som är vinkelrät mot i stället för parallell med pressriktningen vid tillverkningen.

Modifierad normalprovstav tas ut ur skivor i två riktningar parallella med skivans kantytor, såvida inte annat anges.

Följande termer och definitioner används för att beskriva hur stavar tas ut och hur slagpåkänningen appliceras på stavar ur laminatskivor:

Flatsida: Slagpåkänningen appliceras på den ursprungliga skivans flatsida.

Kantsida: Slagpåkänningen appliceras på den ursprungliga skivans kantyta.

Längdriktning: Den ursprungliga skivans längdriktning.

Tvärriktning: Den ursprungliga skivans tvärriktning. Om den ursprungliga skivan är kvadratisk skall den ena riktningen godtyckligt väljas som längdriktning och den däremot vinkelräta riktningen som tvärriktning.

Den modifierade provstavens ena tvärsnittsmått skall vara lika med skivans tjocklek men får inte överskrida 12,7 mm.

Om skivan är tjockare än 12,7 mm skall den bearbetas till nämnda tjocklek. På stav tagen ur sådan skiva får slagpåkänningen anbringas på flatsidan eller på kantsidan. Om staven slås på flatsidan skall skåran göras i den bearbetade sidan av skivan (om denna endast är bearbetad från en sida). Om staven tagits ut ur en tjock skiva skall det anges från vilken del av skivan som staven tagits ut, t ex från mitten (om skivan bearbetats från båda sidor), från översidan eller från undersidan (om skivan bearbetats från en sida).

Om skivan är tunnare än 12,7 mm får man ta ut ett antal delstavar med en sammanlagd tjocklek mellan 3,2 och 12,7 mm. Delstavarna provas tillsammans - som ett parallellepipediskt paket - på kantsidan. Om de är tunnare än 1,6 mm skall de för att buckling eller vridning vid slaget skall förhindras, limmas samman till en hel stav. Eventuellt lösningsmedel i limmet skall ha avdunstat före provning.

Moulded standard test pieces shall be given a notch in a side, which is parallel to the direction of application of moulding pressure.

The impact strength may differ if the notch is made in a side which is perpendicular, instead of parallel to the direction of moulding.

Modified standard test pieces shall be taken from sheet material, in two directions parallel to the sheet edges unless otherwise specified.

The following terms and definitions are used to describe how test pieces shall be taken, and how stress shall be applied to test pieces of laminated sheet at impact:

Flatwise: Load applied to the flat side of the original sheet.

Edgewise: Load applied to the edge of the original sheet.

Lengthwise: In the longitudinal direction of the original sheet.

Crosswise: Across the length of the original sheet. If the original sheet was square, then one direction should be arbitrarily selected as the length, and the direction perpendicular to this is described as being crosswise.

The cross-sectional dimension at one end of the modified test piece shall be equal to the sheet thickness, but must not exceed 12.7 mm.

If the sheet is thicker than 12.7 mm, it should be machined down to this size. On test pieces taken from such sheets, the load must either be applied flatwise or edgewise. If the test piece is struck on the flat side, the notch should be made on the machined side of the sheet (if machined on one side only). If the piece has been taken out off a thick sheet, it should be stated from which part of the sheet the piece was taken, for example from the centre (if the sheet was machined on both sides), or from the top or the bottom (if the sheet was machined on one side only).

If the sheet is less than 12.7 mm thick, a number of individual pieces should be taken with a total thickness ranging from 3.2 to 12.7 mm. These individual pieces are then aligned with each other - as a sort of a parallelepipedic package- and then tested edgewise. Pieces less than 1.6 mm in thickness shall be laminated together into a single test piece with suitable adhesive to prevent buckling or twisting during the impact. Any existing solvent in the adhesive should have evaporated before testing.

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Limmet får inte påverka provningsresultatet. Det har konstaterats att närvaro av lösningsmedel i sammansatta stavar av vissa plastmaterial (bl a cellulosaplaster) påverkar provningsresultatet.

Ej sammansatt provstav tagen ur skiva tunnare än 12,7 mm får användas under förutsättning att den är bred nog att säkert kunna spännas fast under provningen och att slagsegheten är tillräckligt hög för att noggrant kunna bestämmas med tillgänglig pendelapparat.

Skåran skall göras i fräsmaskin eller svarv försedd med fräs. Enskärs- eller tvåskärsfräs får användas, men enskärsfräsen rekommenderas eftersom den är lättare att slipa till önskad profil. Fräsens skär skall vara jämnt och slätt utan hack och andra defekter samt vara omsorgsfullt skärpt (eggslipat och henat). Skär utan avbackning med en eggvinkel av 15-20° har visat sig vara användbara. Fräsprofilen skall vara sådan att den i staven - i rät vinkel mot stavens längdaxel - åstadkommer en skåra med profil och djup enligt figur 1.

På en enskärsfräs kan skärets profil kontrolleras i stället för skårans om det kan visas att de båda överensstämmer eller att det för det plastmaterial som skårats finns ett bestämt förhållande mellan de båda. Undersökningar har visat att skåror i olika plastmaterial kan ha olika profil trots att de gjorts med samma fräs.

För vissa plastmaterial t ex polystyren kan toleransområdet 0,225-0,275 mm för rundningsradien hos skårans botten vara för stor för att ge tillförlitliga provningsreultat. I sådana fall skall toleransområdet minskas till 0,2375-0,2625 mm.

Skårans bisektrisplan skall vara 90 ± 2° mot stavens skårade sida.

En hastighet av 1,5-3,2 m/s hos fräsens skär och en matningshastighet av 0,2-2,1 mm/s har visat sig vara lämpliga för de flesta plastmaterial.

Även om ovan angivna hastigheter har visat sig vara användbara vid skårning av de flesta plastmaterial kan det vara nödvändigt att undersöka hastighetens inverkan om nya eller mindre bekanta plastmaterial skall skåras.

Efter 500 skåror - eller tidigare om kraftigt nötande plastmaterial skårats - skall skåran i en stav undersökas beträffande skårvinkeln, skårans rundning samt beträffande hack och andra defekter.

The adhesive must not be allowed to influence the test result. It is known that the presence of solvents in laminated test pieces of certain plastics (including cellulose plastics) does affect the test result.

Non-laminated test pieces taken out of a sheet with a thickness of less than 12.7 mm, may be used only if they are wide enough to be securely clamped during the tests, and if their impact resistance is of such a magnitude that an accurate reading may be obtained by means of the machine in use.

The notching should be done on a milling machine, or on a lathe fitted with a milling cutter. Either a single- or a double-tooth cutter may be used, but the single-tooth cutter is preferred because it is more readily ground to the desired contour. The cutting edge shall be even and smooth, free from nicks or other defects, and carefully sharpened (ground and honed). Tools with no rake, and a work-relief angle of 15-20° have been found to be satisfactory. The formcutter should be such as to produce in the test piece at right angles to the longitudinal axis of the test piece, a notch of the contour and depth shown in figure 1.

With a single-tooth cutter, the contour of the tip of the cutting tool may be checked and adjusted instead of that of the notch, if it can be shown that the two correspond or if a definite relationship exists between them for the specific type of material being nothed. There is some evidence that notches cut by the same cutter in different plastics may differ in contour.

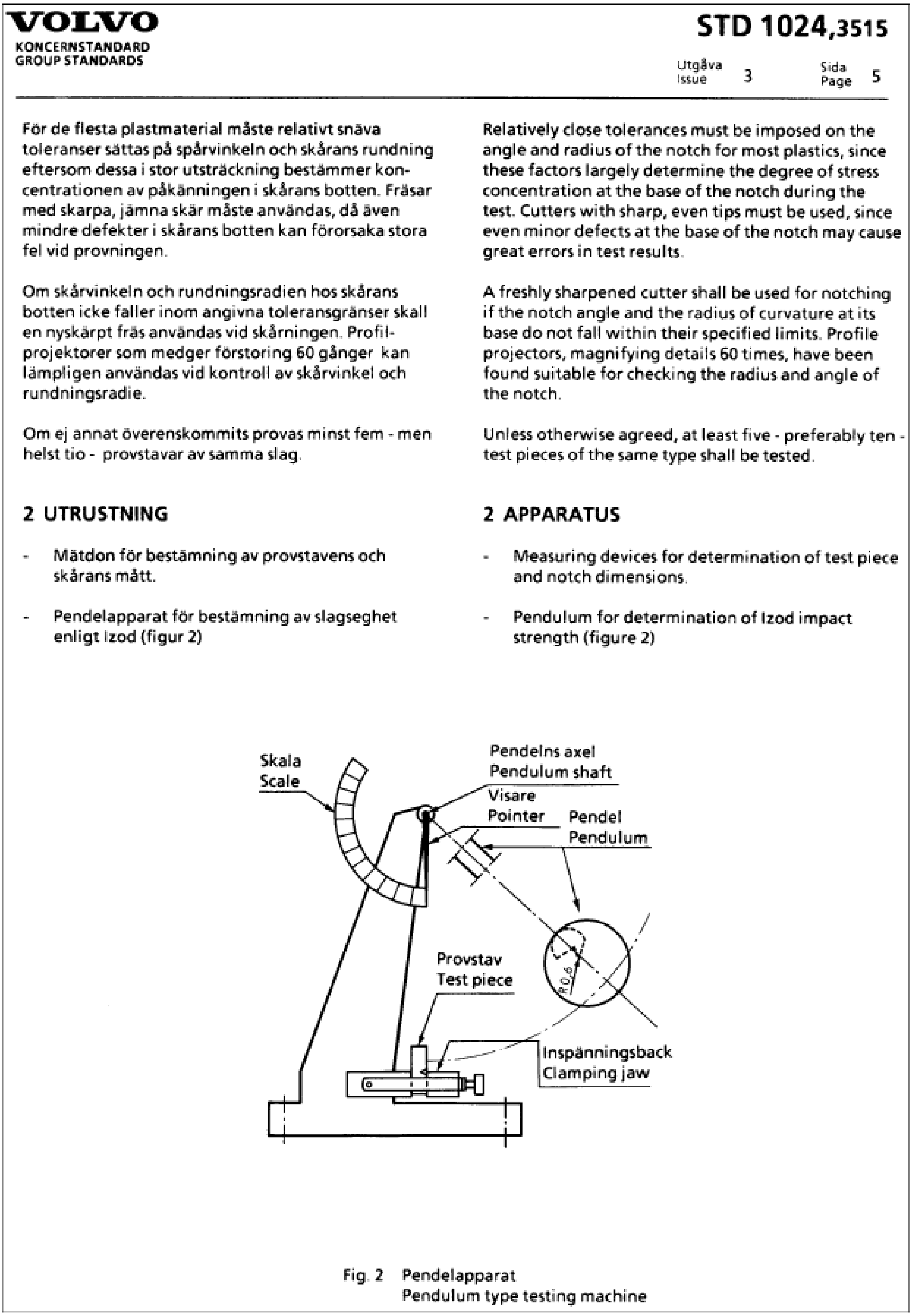
For certain plastics, for example polystyrene, a tolerance zone of 0.225-0.275 mm for the curvature radius may be too wide to yield reliable results. In such cases, the tolerance zone shall be reduced to 0.2375-0.2625 mm.

The plane bisecting the notch shall be at an angle of 90 ± 2° to the notched side of the test piece.

A speed of the tip of the cutting tool of 1.5-3.1 m/s and a feed rate of 0.2-2.1 mm/s have been found to be satisfactory for most plastics.

While the speeds indicated above have been proven suitable when notching most plastics, it may be necessary to test what effect speed has on new, or less familiar plastics.

After 500 notches, or earlier if hard abrasive plastics are being notched, the notch in a test piece shall be checked as to the notch angle, notch base curvature, and for nicks and other defects.



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För de flesta plastmaterial måste relativt snäva toleranser sättas på spårvinkeln och skårans rundning eftersom dessa i stor utsträckning bestämmer koncentrationen av påkänningen i skårans botten. Fräsar med skarpa, jämna skär måste användas, då även mindre defekter i skårans botten kan förorsaka stora fel vid provningen.

Om skårvinkeln och rundningsradien hos skårans botten icke faller inom angivna toleransgränser skall en nyskärpt fräs användas vid skårningen. Profilprojektorer som medger förstoring 60 gånger kan lämpligen användas vid kontroll av skårvinkel och rundningsradie.

Om ej annat överenskommits provas minst fem - men helst tio - provstavar av samma slag.

2 UTRUSTNING

- Mätdon för bestämning av provstavens och skårans mått.
- Pendelapparat för bestämning av slagseghet enligt Izod (figur 2)

Relatively close tolerances must be imposed on the angle and radius of the notch for most plastics, since these factors largely determine the degree of stress concentration at the base of the notch during the test. Cutters with sharp, even tips must be used, since even minor defects at the base of the notch may cause great errors in test results.

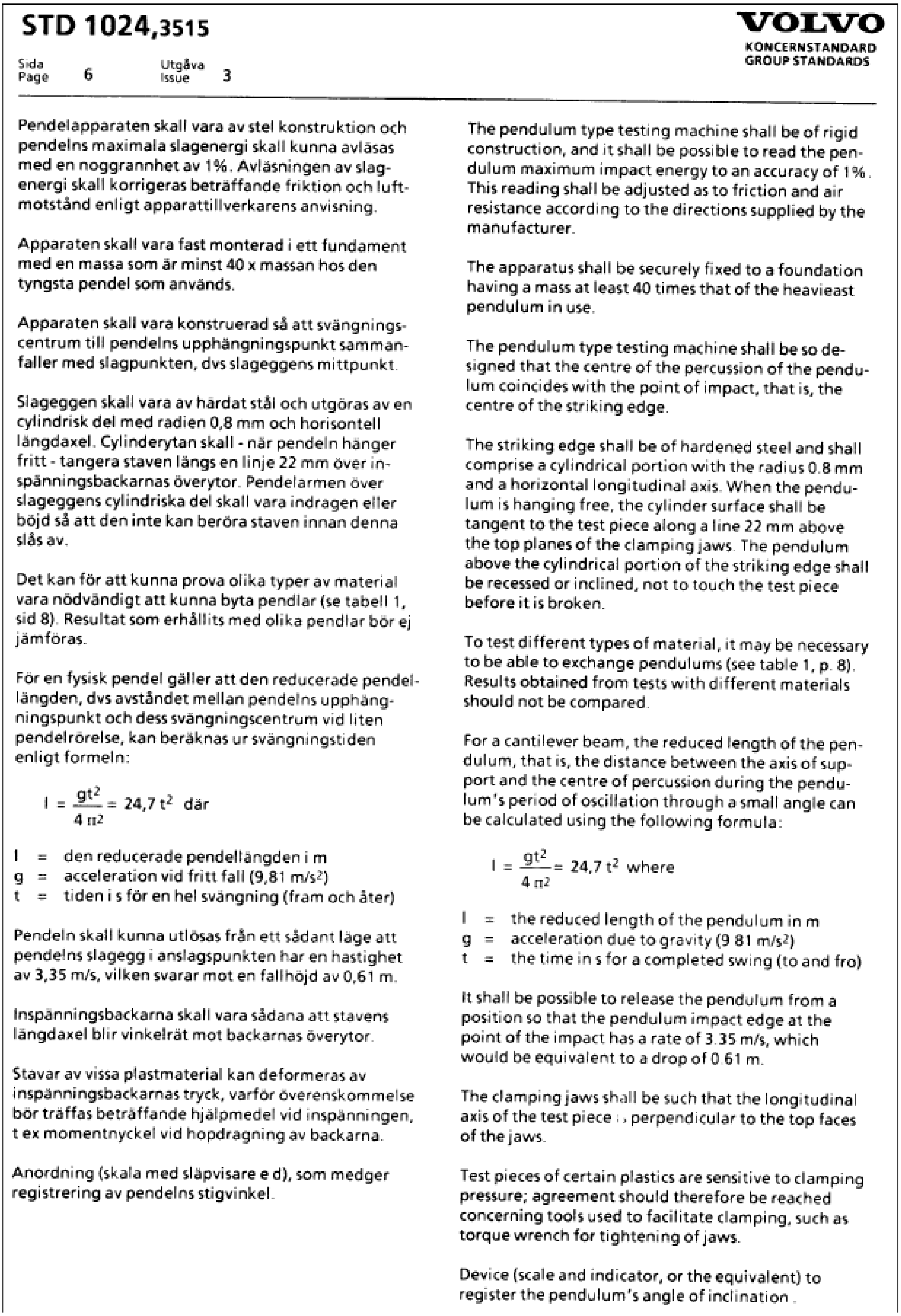
A freshly sharpened cutter shall be used for notching if the notch angle and the radius of curvature at its base do not fall within their specified limits. Profile projectors, magnifying details 60 times, have been found suitable for checking the radius and angle of the notch.

Unless otherwise agreed, at least five - preferably ten - test pieces of the same type shall be tested.

2 APPARATUS

- Measuring devices for determination of test piece and notch dimensions.
- Pendulum for determination of Izod impact strength (figure 2)

Fig. 2 Pendelapparat
Pendulum type testing machine



Pendelapparaten skall vara av stel konstruktion och pendelns maximala slagenergi skall kunna avläsas med en noggrannhet av 1%. Avläsningen av slagenergi skall korrigeras beträffande friktion och luftmotstånd enligt apparattillverkarens anvisning.

Apparaten skall vara fast monterad i ett fundament med en massa som är minst 40 x massan hos den tyngsta pendel som används.

Apparaten skall vara konstruerad så att svängningscentrum till pendelns upphängningspunkt sammanfaller med slagpunkten, dvs slageggens mittpunkt.

Slageggen skall vara av härdat stål och utgöras av en cylindrisk del med radien 0,8 mm och horisontell längdaxel. Cylinderytan skall - när pendeln hänger fritt - tangera staven längs en linje 22 mm över inspänningsbackarnas överytor. Pendelarmen över slageggens cylindriska del skall vara indragen eller böjd så att den inte kan beröra staven innan denna slås av.

Det kan för att kunna prova olika typer av material vara nödvändigt att kunna byta pendlar (se tabell 1, sid 8). Resultat som erhållits med olika pendlar bör ej jämföras.

För en fysisk pendel gäller att den reducerade pendellängden, dvs avståndet mellan pendelns upphängningspunkt och dess svängningscentrum vid liten pendelrörelse, kan beräknas ur svängningstiden enligt formeln:

$$l = \frac{gt^2}{4\pi^2} = 24,7\,t^2 \quad \text{där}$$

l = den reducerade pendellängden i m
g = acceleration vid fritt fall (9,81 m/s^2)
t = tiden i s för en hel svängning (fram och åter)

Pendeln skall kunna utlösas från ett sådant läge att pendelns slagegg i anslagspunkten har en hastighet av 3,35 m/s, vilken svarar mot en fallhöjd av 0,61 m.

Inspänningsbackarna skall vara sådana att stavens längdaxel blir vinkelrät mot backarnas överytor.

Stavar av vissa plastmaterial kan deformeras av inspänningsbackarnas tryck, varför överenskommelse bör träffas beträffande hjälpmedel vid inspänningen, t ex momentnyckel vid hopdragning av backarna.

Anordning (skala med släpvisare e d), som medger registrering av pendelns stigvinkel.

The pendulum type testing machine shall be of rigid construction, and it shall be possible to read the pendulum maximum impact energy to an accuracy of 1%. This reading shall be adjusted as to friction and air resistance according to the directions supplied by the manufacturer.

The apparatus shall be securely fixed to a foundation having a mass at least 40 times that of the heavieast pendulum in use.

The pendulum type testing machine shall be so designed that the centre of the percussion of the pendulum coincides with the point of impact, that is, the centre of the striking edge.

The striking edge shall be of hardened steel and shall comprise a cylindrical portion with the radius 0.8 mm and a horizontal longitudinal axis. When the pendulum is hanging free, the cylinder surface shall be tangent to the test piece along a line 22 mm above the top planes of the clamping jaws. The pendulum above the cylindrical portion of the striking edge shall be recessed or inclined, not to touch the test piece before it is broken.

To test different types of material, it may be necessary to be able to exchange pendulums (see table 1, p. 8). Results obtained from tests with different materials should not be compared.

For a cantilever beam, the reduced length of the pendulum, that is, the distance between the axis of support and the centre of percussion during the pendulum's period of oscillation through a small angle can be calculated using the following formula:

$$l = \frac{gt^2}{4\pi^2} = 24,7\,t^2 \quad \text{where}$$

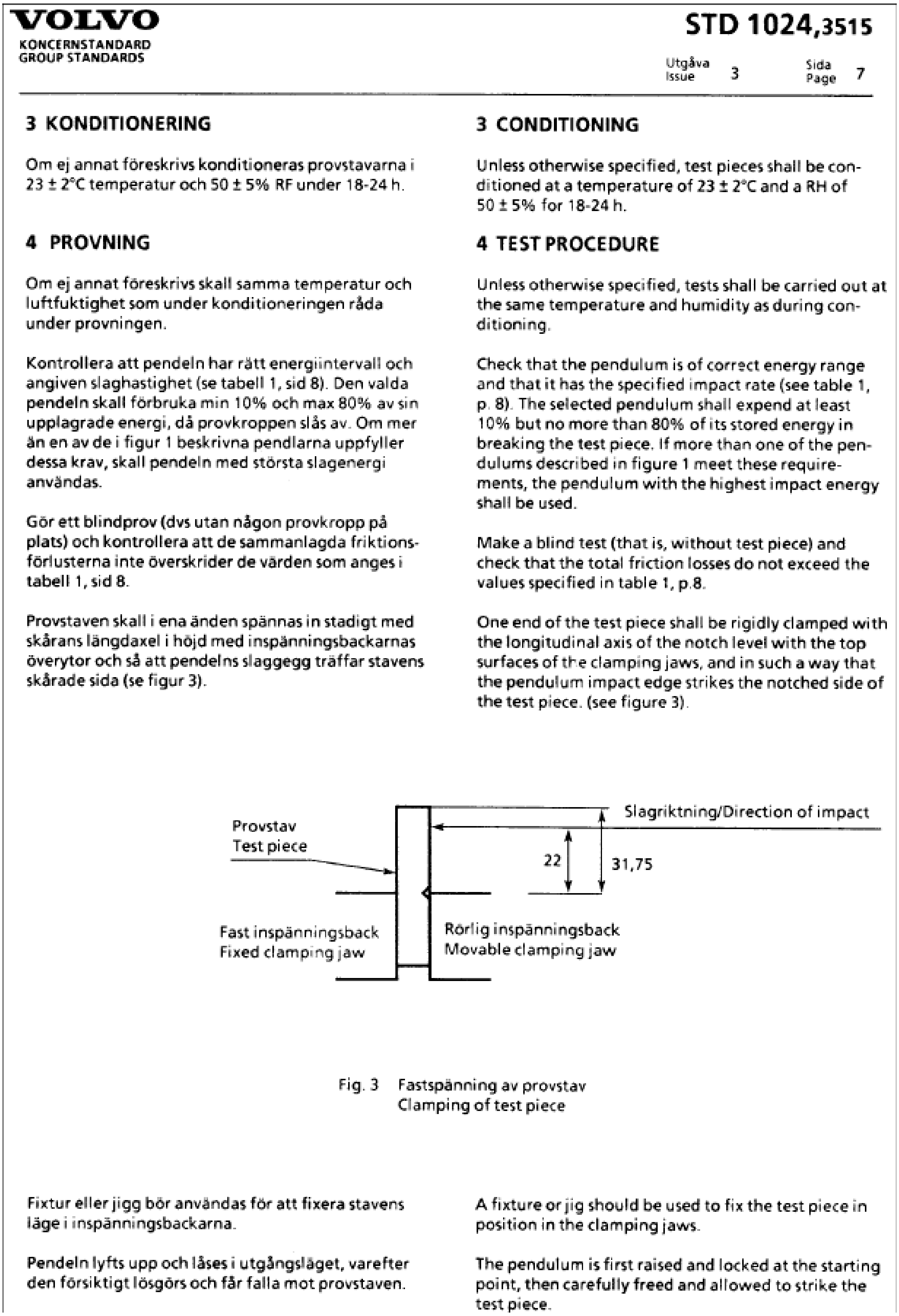
l = the reduced length of the pendulum in m
g = acceleration due to gravity (9 81 m/s^2)
t = the time in s for a completed swing (to and fro)

It shall be possible to release the pendulum from a position so that the pendulum impact edge at the point of the impact has a rate of 3.35 m/s, which would be equivalent to a drop of 0.61 m.

The clamping jaws shall be such that the longitudinal axis of the test piece is perpendicular to the top faces of the jaws.

Test pieces of certain plastics are sensitive to clamping pressure; agreement should therefore be reached concerning tools used to facilitate clamping, such as torque wrench for tightening of jaws.

Device (scale and indicator, or the equivalent) to register the pendulum's angle of inclination.



3 KONDITIONERING

Om ej annat föreskrivs konditioneras provstavarna i 23 ± 2°C temperatur och 50 ± 5% RF under 18-24 h.

4 PROVNING

Om ej annat föreskrivs skall samma temperatur och luftfuktighet som under konditioneringen råda under provningen.

Kontrollera att pendeln har rätt energiintervall och angiven slaghastighet (se tabell 1, sid 8). Den valda pendeln skall förbruka min 10% och max 80% av sin upplagrade energi, då provkroppen slås av. Om mer än en av de i figur 1 beskrivna pendlarna uppfyller dessa krav, skall pendeln med största slagenergi användas.

Gör ett blindprov (dvs utan någon provkropp på plats) och kontrollera att de sammanlagda friktionsförlusterna inte överskrider de värden som anges i tabell 1, sid 8.

Provstaven skall i ena änden spännas in stadigt med skårans längdaxel i höjd med inspänningsbackarnas överytor och så att pendelns slaggegg träffar stavens skårade sida (se figur 3).

3 CONDITIONING

Unless otherwise specified, test pieces shall be conditioned at a temperature of 23 ± 2°C and a RH of 50 ± 5% for 18-24 h.

4 TEST PROCEDURE

Unless otherwise specified, tests shall be carried out at the same temperature and humidity as during conditioning.

Check that the pendulum is of correct energy range and that it has the specified impact rate (see table 1, p. 8). The selected pendulum shall expend at least 10% but no more than 80% of its stored energy in breaking the test piece. If more than one of the pendulums described in figure 1 meet these requirements, the pendulum with the highest impact energy shall be used.

Make a blind test (that is, without test piece) and check that the total friction losses do not exceed the values specified in table 1, p.8.

One end of the test piece shall be rigidly clamped with the longitudinal axis of the notch level with the top surfaces of the clamping jaws, and in such a way that the pendulum impact edge strikes the notched side of the test piece. (see figure 3).

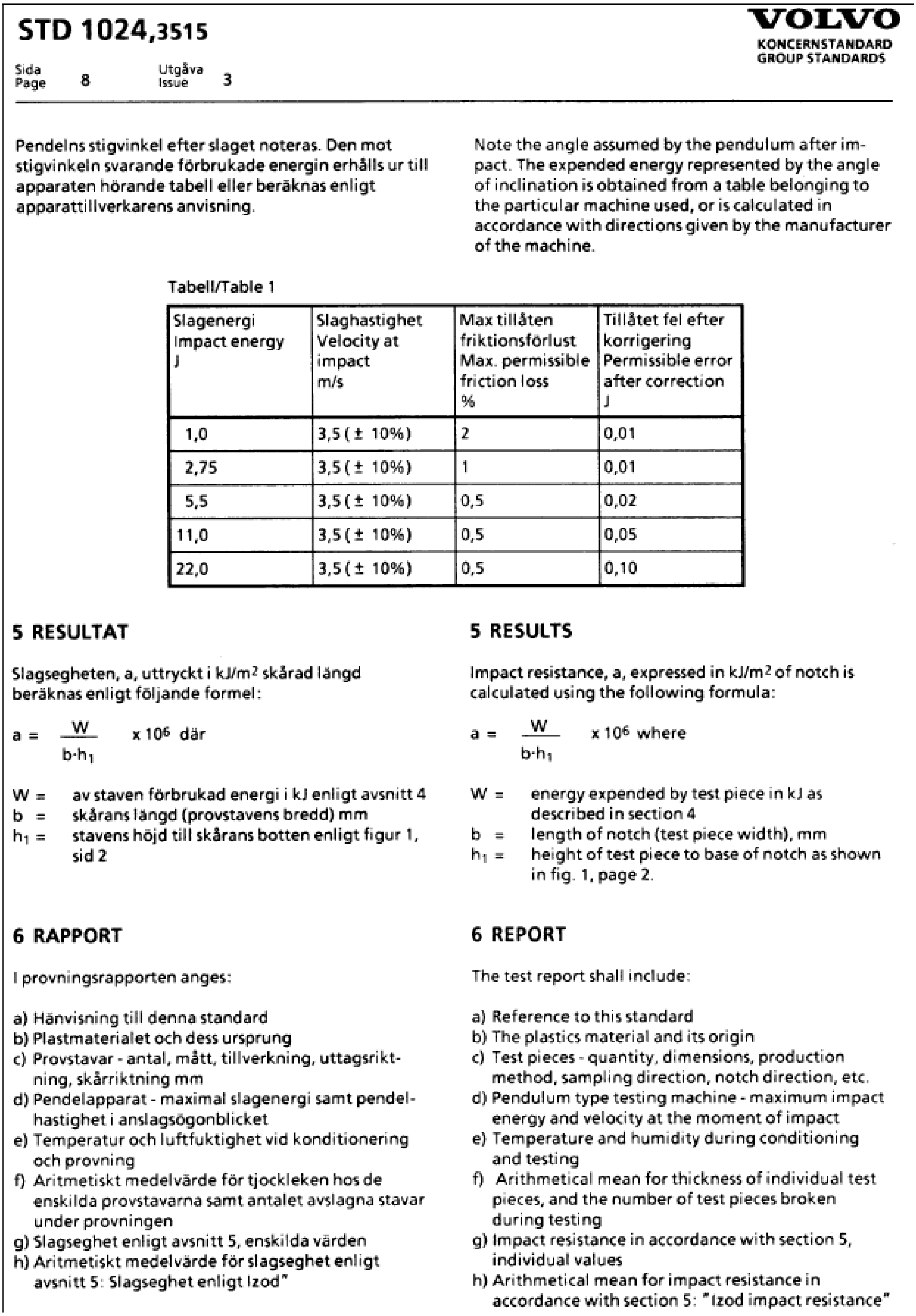
Fig. 3 Fastspänning av provstav
Clamping of test piece

Fixtur eller jigg bör användas för att fixera stavens läge i inspänningsbackarna.

Pendeln lyfts upp och låses i utgångsläget, varefter den försiktigt lösgörs och får falla mot provstaven.

A fixture or jig should be used to fix the test piece in position in the clamping jaws.

The pendulum is first raised and locked at the starting point, then carefully freed and allowed to strike the test piece.



Pendelns stigvinkel efter slaget noteras. Den mot stigvinkeln svarande förbrukade energin erhålls ur till apparaten hörande tabell eller beräknas enligt apparattillverkarens anvisning.

Note the angle assumed by the pendulum after impact. The expended energy represented by the angle of inclination is obtained from a table belonging to the particular machine used, or is calculated in accordance with directions given by the manufacturer of the machine.

Tabell/Table 1

Slagenergi Impact energy J	Slaghastighet Velocity at impact m/s	Max tillåten friktionsförlust Max. permissible friction loss %	Tillåtet fel efter korrigering Permissible error after correction J
1,0	3,5 (± 10%)	2	0,01
2,75	3,5 (± 10%)	1	0,01
5,5	3,5 (± 10%)	0,5	0,02
11,0	3,5 (± 10%)	0,5	0,05
22,0	3,5 (± 10%)	0,5	0,10

5 RESULTAT

Slagsegheten, a, uttryckt i kJ/m² skårad längd beräknas enligt följande formel:

$$a = \frac{W}{b \cdot h_1} \times 10^6 \text{ där}$$

W = av staven förbrukad energi i kJ enligt avsnitt 4
b = skårans längd (provstavens bredd) mm
h_1 = stavens höjd till skårans botten enligt figur 1, sid 2

5 RESULTS

Impact resistance, a, expressed in kJ/m² of notch is calculated using the following formula:

$$a = \frac{W}{b \cdot h_1} \times 10^6 \text{ where}$$

W = energy expended by test piece in kJ as described in section 4
b = length of notch (test piece width), mm
h_1 = height of test piece to base of notch as shown in fig. 1, page 2.

6 RAPPORT

I provningsrapporten anges:

a) Hänvisning till denna standard
b) Plastmaterialet och dess ursprung
c) Provstavar - antal, mått, tillverkning, uttagsriktning, skårriktning mm
d) Pendelapparat - maximal slagenergi samt pendelhastighet i anslagsögonblicket
e) Temperatur och luftfuktighet vid konditionering och provning
f) Aritmetiskt medelvärde för tjockleken hos de enskilda provstavarna samt antalet avslagna stavar under provningen
g) Slagseghet enligt avsnitt 5, enskilda värden
h) Aritmetiskt medelvärde för slagseghet enligt avsnitt 5: Slagseghet enligt Izod"

6 REPORT

The test report shall include:

a) Reference to this standard
b) The plastics material and its origin
c) Test pieces - quantity, dimensions, production method, sampling direction, notch direction, etc.
d) Pendulum type testing machine - maximum impact energy and velocity at the moment of impact
e) Temperature and humidity during conditioning and testing
f) Arithmetical mean for thickness of individual test pieces, and the number of test pieces broken during testing
g) Impact resistance in accordance with section 5, individual values
h) Arithmetical mean for impact resistance in accordance with section 5: "Izod impact resistance"

Volvo Car Corporation

Standard **VCS 1024,35169**

Dept / Issued by 6857 Thomas Andersson Issue 1 Established 2006-02 UM Page 1(2)

The English language version is the original and the reference in case of dispute.

TEST METHOD

Determination of Charpy impact strength of rigid materials

Plastics

Orientation

This VCS standard is based on the previously issued STD 1024,3516, issue 3, which it replaces for Volvo Cars.

This standard refers to ISO 179:-1.

1 Scope and field of application

1.1 This standard specifies a method for the determination of Charpy impact strength of rigid plastics.

Different test parameters are specified according to the type of test specimen and the type of notch. Unless otherwise specified, test specimen of type A (notched rod) or test specimen of type D (unnotched rod) shall be used

1.2 The method is used for investigating the behaviour of specified specimens under specified impact stresses, and for estimating the brittleness or the toughness of specimens within the limitations inherent in the test conditions.

1.3 The method is applicable, e.g, to the following materials:

- rigid thermoplastic moulding and extrusion materials, including filled and reinforced compounds, and rigid thermoplastic sheet;
- rigid thermosetting moulding materials, including filled and reinforced compounds;
- rigid thermosetting sheet, including laminates;

Den engelska språkversionen är originalversion och skall åberopas i händelse av tvist.

PROVNINGSMETOD

Bestämning av slagseghet enligt Charpy hos styva material

Plast

Orientering

Denna VCS-standard baseras på tidigare utgiven STD 1024,3516, utgåva 3, och ersätter denna för Volvo Personvagnar.

Denna standard hänvisar till ISO 179:-1.

1 Omfattning och tillämpning

1.1 Denna standard beskriver en metod för bestämning av slagseghet enligt Charpy hos styva plastmaterial.

Olika provningsparametrar specificeras på basis av den typ av provkropp och skåra som används. Om inget annat anges skall provkropp typ A (skårad stav) eller provkropp typ D (oskårad stav) användas.

1.2 Metoden används för att undersöka hur specificerade provkroppar uppträder då de utsätts för bestämda slagspänningar samt för att uppskatta provkropparnas sprödhet eller seghet inom de gränser som ges av provningsvillkoren.

1.3 Metoden är användbar för bl.a. följande material:

- styva, termoplastiska formsprutnings- och extruderingsmaterial inklusive fyllda och förstärkta blandningar samt styva termoplastiska skivor
- styva, värmehärdande formsprutningsmaterial inklusive fyllda och förstärkta blandningar
- styva, värmehärdande skivor, inklusive laminat

- fibre reinforced materials (composites), incorporating mat, woven fabric, woven rovings, chopped strands, chopped rovings, rovings and milled fibres, including preimpregnated materials (prepregs);
- unidirectional fibre reinforced materials (composites), including pre-impregnated materials (prepregs).

NOTE - The use of notched specimens is unsuitable for some reinforced plastics. The method may not be suitable for foamed materials.

1.4 The method is applied to specimens prepared from moulding materials or to specimens taken from finished and semi-finished products (for example mouldings, laminates, extruded or cast sheets). The method is suitable for production control as well as for the acceptance and rejection of materials according to specifications for moulding materials and products.

1.5 The results obtained by testing specimens of different dimensions and specimens cut from moulded products may not necessarily be the same.

1.6 The method should not be used as a source of data for design calculations on components. Information on the typical behaviour of a material can be obtained by testing different types of test specimens prepared under different conditions, varying the notch radius, and testing at different temperatures.

2 Principle

The test specimen, supported as a horizontal beam, is broken by a single swing of a pendulum, with the line of impact midway between the supports and in the case of notched specimens, directly opposite the notch.

3 Test procedure

Unless otherwise specified, the impact shall be edgewise on test specimen of type 1 with notch of type A in accordance with ISO 179:-1. (Recommendation acc. to ISO 10350 together with test on specimen of type 1 without notch.)

- fiberförstärkta material (kompositer) inklusive matta, vävt tyg, vävd roving, klippta trådar, klippt roving, roving och valkade fibrer, inklusive förimpregnerade material (prepregs);
- material förstärkta med fiber i en riktning (kompositer) inklusive förimpregnerade material (prepregs).

Anm - Användandet av skårade provkroppar är olämpligt för vissa förstärkta plaster. Metoden kan visa sig olämplig för skummade material.

1.4 Metoden används på provkroppar som framställts av pressmaterial eller på provkroppar som tagits ur färdiga eller till hälften bearbetade produkter (t.ex. formartiklar, laminat, strängsprutade eller gjutna skivor). Metoden är lämplig för produktionsstyrning liksom för godkännande eller kassation av material enligt specifikation för formsprutningsmaterial och formsprutade material och produkter

1.5 De resultat som erhålls vid provning av provkroppar med olika dimensioner och provkroppar som tagits ur produkter behöver inte nödvändigtvis ge samma resultat.

1.6 Metoden bör inte användas som en källa för beräkningar av komponenter. Information om det typiska beteendet för ett material kan erhållas genom att prova olika typer av provkroppar som framställts under olika villkor med varierande radie på skåran och med olika provningstemperaturer.

2 Princip

En horisontellt vilande provkropp slås av med ett enda slag från en pendel med slaglinjen mittemellan stöden; vid skårade provkroppar är slaglinjen mitt för skåran.

3 Provning

Provningen skall om inget annat föreskrives utföras i tvärriktningen på provkropp typ 1 med V-skåra typ A enligt ISO 179:-1. (Rekommendation enligt ISO 10350 tillsammans med prov på provkropp typ 1 utan skåra).

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