**ARCADA**

# UV Aging of Epoxy Fiber Composite

Can Gökçe

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Abstract:

This study investigates additives capacity to reduce aging induced by UV light in epoxy. Hypothesis is that additives shield the material from UV light aging. To test this hypothesis 4 different batches of casts were made in moulds. Each batch included 5 pieces. First batch was pure epoxy, second batch was epoxy with cellulose, third batch was epoxy with glass fiber and fourth batch was epoxy with carbon fiber. One piece from each batch was kept as an unexposed sample. Therefore, there were 4 pieces in each batch exposed to UV light: one piece from each batch was exposed to 1 hour of UV light, one was exposed to 5 hours of UV light, one was exposed to 8 hours of UV light and one was exposed to 24 hours of UV light. After that specimens were tested in three-point bending test to collect stress-strain data and then as a last step FTIR scans were made of each sample. FTIR scans planned that scans of each sample`s both directly exposed and unexposed sides and also cross-sectional scans would be conducted.

UV light clearly changes the material`s chemistry after observations in FTIR spectrum. Changes observed after 1 hour of UV light exposure where C-H interactions appear around 2800 until 3200 $cm^{-1}$ and in the region of C-O interactions which is residing around 1050 to 1250 $cm^{-1}$. Absorbance change between 2800 until 3200 $cm^{-1}$ reaches around 20% while it reaches around 40% at wavenumbers between 2800 until 3200 $cm^{-1}$.

UV destroys the cellulose according to findings based on three-point bending tests. Therefore, this study suggests cellulose is not an additive to tackle this challenge. In glass fiber case there is an improvement in modulus as it doubled by compared to no additive casts, however, material becomes brittle. In case of carbon fiber added casts, even though it was expected that carbon fiber additives will increase the modulus significantly, there was a decrease in modulus by compared to pure epoxy, but however carbon fiber showed increase in strain limits. Findings suggest in glass fiber as well as carbon fiber points the need of further observations about how material would react if exposure exceeds 24 hours. FTIR scans points out that material was heated up instead of breaking the bonds which also correlates in getting higher stress levels ($\sigma$) in pure epoxy. Evidently, this study shows that exposure time was not long enough to break bonds to extend that brittleness which was developed.

| Keywords: | Epoxy with additives, carbon fiber as an additive, glass fiber as an additive, cellulose as an additive, FTIR analysis of epoxy |
|---|---|
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## Symbols and Units

| TERM | DEFINITION | UNIT |
| --- | --- | --- |
| $L$ | Length | $mm$ |
| $t$ | Thickness | $mm$ |
| $b$ | Width | $mm$ |
| $A_0$ | Cross sectional area | $mm^2$ |
| $\sigma$ | Stress | $N/mm^2$ |
| $\epsilon$ | Strain | No unit |
| $I$ | Second moment of inertia | $mm^4$ |
| $F$ | Force | $N = kg(m/sec^2)$ |
| $E$ | Yield Strenght | $MPa$ |
| $x$ | displacement | $mm$ |
| $h$ | Planck`s constant | $6{,}626.10^{34} j.sec$ |
| $\nu$ | frequency | $Hz, sec^{-1}$ |
| $FVF$ | Fiber volume fraction | — |
| $V_F$ | Volume of a fiber | $mm^3$ |
| $V_B$ | Volume of a base | $mm^3$ |
| $SDS$ | sodium dodecyl sulfate | — |
| $CB$ | Carbon Black | — |
| $\Delta C$ | Total colour difference | — |
| $D$ | Ligthness | — |
| $i$ | red–green colour coordinate | — |
| $n$ | yellow–blue colour coordinate | — |

# FOREWORD

This thesis the final work of my Bachelor`s Degree in Arcada University of Applied Sciences. The basis of this work is that I find myself motivated to develop better products to use for our needs.

For his help, I would like to take this opportunity to thank Mr. Rene Herrmann for helping me out when I need to ask for any help during my thesis time. In truth, I would not be able to create this thesis in this short time without his strong support.

Finally, I would like to thank my wife Elisa Laukkarinen-Gökçe for handling my times that I spent at front of the computer to write my assignments, exams and finally this thesis.

# 1 INTRODUCTION

This thesis is about UV aging of epoxy and the prevention of epoxy aging by means of additive. Aging process is the UV induced breakage of bonds. Preventing it therefore is shielding of radiation from the part of the incident ray that does not reflect nor transmit. The part of the radiation that is absorbed can have two different effects on the material. If the radiation has higher energy than the bonds in the material it will break the bond. If the energy is lower, it will cause heating. Preventing the aging of epoxy was planned to be done by adding additives into epoxy adhesive. Their performances would be tracked physically as well as chemically after 1, 5, 8 and 24 hours of artificial sunlight exposure to simulate adhesive aging.

*Table 1 Casted 20 specimens in different UV light exposures*

| Planned Casts | Uv Light Exposure by time | | | | |
|---|---|---|---|---|---|
| | No exposure | 1 Hour | 5 Hour | 8 Hour | 24 Hour |
| Pure Epoxy | ✓ | ✓ | ✓ | ✓ | ✓ |
| Epoxy+Glass Fiber | ✓ | ✓ | ✓ | ✓ | ✓ |
| Epoxy+Cellulose | ✓ | ✓ | ✓ | ✓ | ✓ |
| Epoxy+Carbon Fiber | ✓ | ✓ | ✓ | ✓ | ✓ |

Adhesives are being used in many industries and adhesive performances are directly connected to the success of many devices and applications which we use in daily life routines. Material science field is developing all the time and the aim of material science is to develop materials that are lighter, easier to manufacture and extend the lifespan of the product.

Products are being exposed to factors such as force over the material, heating etc. during their usage. These factors change the product from micro to macro level. These factors determine the lifespan of that product. However, engineers can affect that lifespan and the effect of factors that the product faces. This study was conducted to increase epoxy product`s modulus of elasticity by using additives and observe whether these additives can reduce the UV light`s eradicating effects on adhesives. There are effects of UV light which affect material`s mechanical properties in bending modulus [1]. Hypothesis of this thesis is that as batches of adhesives with different additives will be created, these adhesives with additives will result adhesive joints which can have longer lifespan in terms of UV aging and can also withstand higher forces.

Biltema laminating epoxy was used as an adhesive in this study. It is known that this particular product can withstand certain tensile stress, compression, shear and so on as it was engineered while quality checked accordingly [2] .
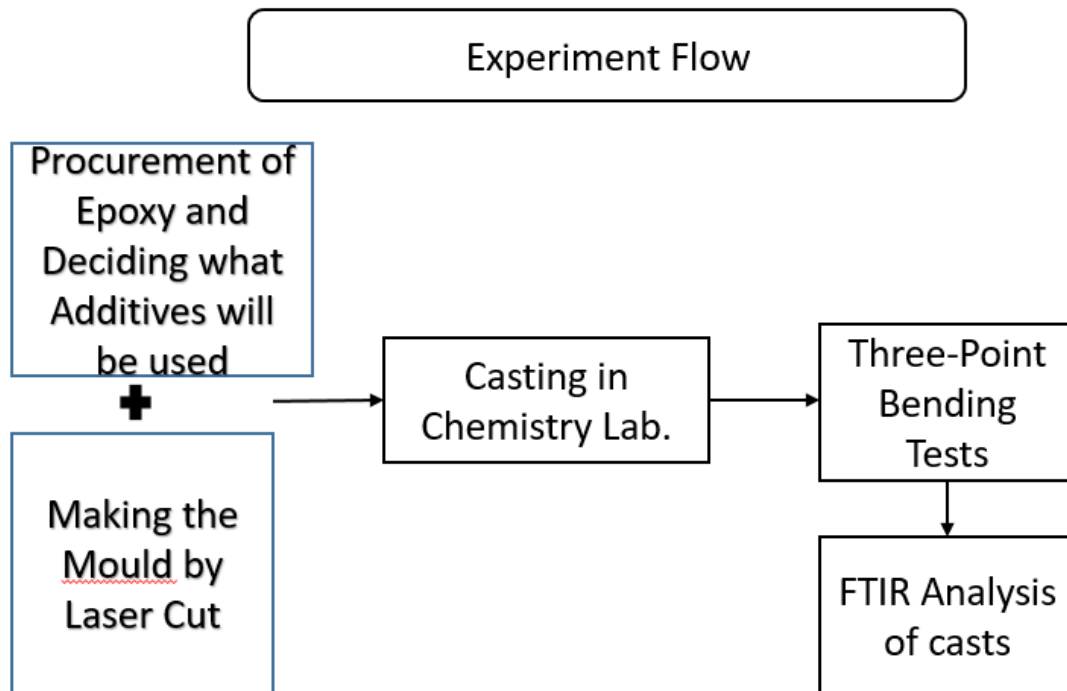


*Figure 1 The flow of experiments in this thesis*

It was decided that instead of having great numbers of different additives which would result of having many outcomes to collect data out of, additives were set to be maximum 3. Epoxy is a well-known adhesive and that is why it was chosen to be used in this study. After cutting the mould, specimens were casted in chemistry laboratory. For fastening the mould, screws and nuts were necessary and those were purchased from K-Rauta Oulunkylä. The right size of the screws and nuts was checked in the store by trying them into the mould.

Casts of four different batches which were glass fiber, pure, cellulose and carbon fiber added epoxies were moulded respectively. The casts which were planned to be exposed to UV light were placed at front of the UV light source and the one cast from each batches were not exposed. These unexposed casts from each batches would give base information to compare with exposed specimens.

After UV light exposures, three-point bending tests was the following phase of the thesis. After stress and strain curve was taken out from these tests, FTIR analysis was conducted on the casts. FTIR analyses was set so that scans will be performed from each sample and

from five different points from directly UV light exposed side, while five different points from indirectly exposed side. It was also planned that, after cutting the casts from the middle, also section scans were set to be made.

## 1.1 Adhesives

Adhesive is any substance that is capable of holding materials together in a functional manner by surface attachment that resists separation. "Adhesive" as a general term includes cement, mucilage, glue, and paste—terms that are often used interchangeably for any organic material that forms an adhesive bond [3]. The use of adhesives offers many advantages over binding techniques such as sewing, mechanical fastening, thermal bonding, etc. These include the ability to bind different materials together, to distribute stress more efficiently across the joint, the cost effectiveness of an easily mechanized process, an improvement in aesthetic design, and increased design flexibility. Disadvantages of adhesive use include decreased stability at high temperatures, relative weakness in bonding large objects with a small bonding surface area, and greater difficulty in separating objects during testing [4].

Epoxy as an adhesive hardens by mixing two or more components which react chemically. This reaction causes polymers to cross-link into epoxies [4].

Nowadays thanks to material science advancements, adhesives are gaining their positions in aeronautical production in which high performance is necessity. Adhesives are common to use in airplanes [5]. Adhesives have low density by compared to metal products that are used as screws and nuts, they offer low weight and equal strength distribution. Uneven force distribution may bring failures too soon to joints while it can be prevented when distribution is unified. Adhesives can distribute the force evenly. In the end, adhesives are main players in this thesis because as mentioned adhesives are being used in many industry areas, it is a worthwhile material to focus and study.

## 1.2 Additives

Additives in adhesives are mostly being used in industry as reinforcing and redirecting the force that was applied. They are well searched and proved their role in adhesive joints. Additives, as they are mostly light materials, are to be benefitted from lowering the weight

of the joints while also giving a reinforcement,  However, there are many other additives in the market to make adhesive to gain new features such as defoaming and radiation curings [6]. This thesis was focused in whether the additives which will be implemented into epoxy resin will inhibit the effects of radiation on adhesive. For giving solid examples, some organic additives in industry such as benzophenones are being used to prevent ultraviolet (UV) light from damaging scents and colors in products such as perfumes and soaps. It can also be added to plastic packaging as a UV blocker to prevent photo-degradation of the packaging polymers [7]. Therefore, by properties of some additives can seal the material to slow down the aging effect of sunlight.

In adhesive usage along with additives it should be clarified which additive and what adhesive on which surface should be used. However, this study did not focus on adhesive and substrate bonding in during the presence of additives due to narrowing down the variables to work out on meaningful information. Thus, only additives and certain adhesive was used. The additives which were used in this study were glass fiber, carbon fiber and cellulose respectively.

*Table 2 Additive parameters*

|  | Glass Fiber | Carbon Fiber | Cellulose |
|---|---|---|---|
| Particle Size | 9-14 µm | 6- 8 µm | 200-300 µm |
| Density | 2,53-2,55 g/cm³ | 1,76 g/cm³ | 0,10 g/cm³ |

**Glass fiber as an Additive**

Kevra powder glass fiber was used and according to company information, it has 2,53-2,55 g/cm³ bulk density and particle size is 9-14 µm [8].

**Cellulose as an Additive**

Kevra cellulose micro-fibers was used and according to company information, it has 0,10 g/cm³ bulk density and particle size is 200-300 µm [9]. Company says that it is obtained out of wood pulps and after powdered and bleached. Bleaching the material is because of having colour concerns and therefore to avoid too much change in mixture. Cellulose can be considered as environment friendly material. But mixing with resin would make the cellulose unobtainable out of the mixture after its service time to decompose it.

**Carbon Fiber as an Additive**

In various sources carbon fiber powder`s density is varying around 1,76 g/cm³ and length is around <150 µm and diameter is around 6 to 8 µm. Typically carbon fiber is black

coloured material and also readily reacts on airborne so it should be handled carefully in fume hood. Carbon fiber brings many advantages as an additive in an adhesive in its tensile performances and thermal properties along with electrical conductivity [10].

## 1.3  UV light on Polymers

The sun, the reason of day and light and majority of our energy could be observed positively in studies about how to benefit more out of it but in this study sun is talked about how to avoid it. Sun has different regions on spectra. Ultra violet (UV) lights are in the region above our eye limits to observe it without any other support [11]. UV radiation in Finland is relatively not higher than majority of the world because of its position on globe [12], but having said that, sunlight deviation in seasons is drastically higher in arctic region.

When it comes to epoxy adhesives, despite several excellent properties including low shrinkage, good chemical resistance,
curable at low temperatures and the absence of byproducts or volatiles, epoxy resins are susceptible to ultra violet (UV) damage and their durability is reduced substantially when exposed to outdoor environments [13]. Due to these, UV light is set to use in this thesis as it has an aging effect on polymers. Even though Finland is exposed relatively less to the sun, sun still has aging effects on polymers anyway here and more globally. The energy from sunlight that is destructive to polymers is between 320 and 270 nm. This destructive energy constitutes less than five percent of the total radiation reaching the surface of the planet. The absorption of this UV radiation results in mechanical and chemical degradation of the polymer structures [13]. Achieving of avoidance in any means would result less maintenance costs and less bad impacts on environment.
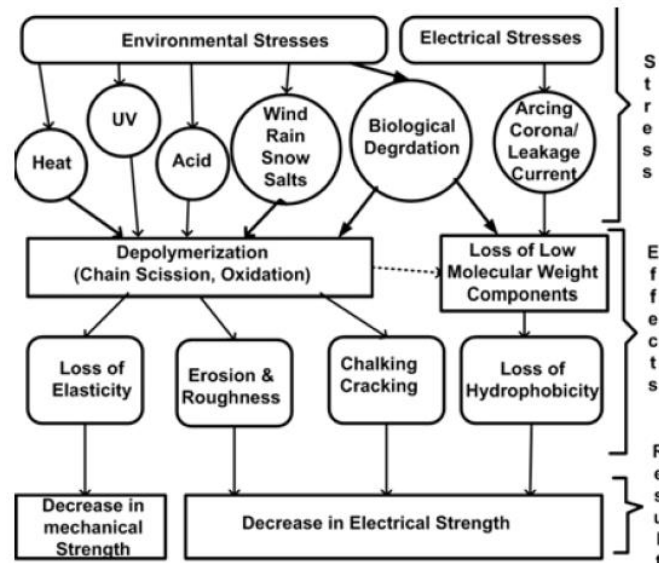
*Figure 2 Factors involved in aging of polymers [13]*

According to Amin (2006) there are two type of stresses: one is environmental and other is electrical stresses. UV light is considered as an environmental stress as it is due to sunlight [13]. UV light will be absorbed by the material and as a result either heats up the material or breaks the chains [14] and electron jumps [15] in the material. These occurrences eventually put toll to material`s functionalities. In this study it was planned to outline the chain scission which is caused by UV light by using FTIR machine in micro level, while following it in three-point bending tests in physical level. In order to clarify, by locating three-point bending results in the Figure 3, results will be allocated the area of "decrease in mechanical strength".

## 2   LITERATURE REVIEW ON UV PROTECTION OF POLYMERS

This chapter was created to offer knowledge which was achieved before this thesis was made. Articles were picked to analyse the hypotheses and methods that they used.  After, their results and conclusions were skimmed to this text. Finally, their findings were discussed in relation to aim of this thesis. It should be stated that in this section all texts mostly cited directly from scientific essays or interpreted again from the findings due to keeping the relevant information in the thesis.

## 2.1 Improving the UV degradation resistance of epoxy coatings using modified carbon black nanoparticles [16]

**Introduction**

This study was conducted because discoloration and chalking of epoxy coating in the presence of UV is the major cause of concern for limiting the use of epoxies for outdoor applications [17]. Kelleher and Gesner have studied the degradation of high molecular weight epoxy polymer of bisphenol A. They found that there was a decrease in intrinsic viscosity as well as gel formation, indicating that chain scission and cross-linking occurred simultaneously [18]. Apart from the epoxy`s deficiencies against UV light, Carbon black (CB) has been introduced as an established light stabilizing additive in polymers for many years [19].

In this study, CB nanoparticles were used in epoxy coatings. The aim was to investigate the effect of CB nanoparticles on improvement of the UV resistance of epoxy based coatings via elimination of a resistant topcoat against UV such as polyurethane in coating system [16].

**Method**

The surfactant used for the dispersion of CB was sodium dodecyl sulfate (SDS; Aldrich; 99.5%). CB nanoparticles were dispersed in Epoxy's solvent. SDS was employed to enhance the dispersion of the CB. First, SDS was added to epoxy's solvent with vigorous stirring at the ambient temperature. Subsequently, an appropriate amount of CB was mixed with a homogeneous SDS suspension in an ultrasonic mixer (750 W) for 2 h (hours) to obtain a homogeneous CB suspension. A solution with the concentration ratio of CB to SDS 1:1, 1:2 and1:3 by weight was obtained. Dispersed mixture of CB to SDS with weight ratio of 1:2 remained stable for more than 2 weeks in glass vial without any precipitation that showed more stability than two other mixtures that selected for preparing nanocoatings [24]. A UIP1000 HD ultrasonic instrument from Hielscher Ultrasound Technology Co. was used for preparation of nanometric CB. A Zeiss Sigma VP Field Emission Scanning Electron Microscope (FESEM) was used to evaluate the preparation of CB nanoparticles into epoxy's solvent.

After all, modified CB nanoparticles were added to the resin and the mixture was stirred for 2 h with 2000 rpm. The mixture was then applied on the panels by air spraying and

cured at room temperature for 10days. the CB concentration of 0.25, 0.75and 2.5 wt%, respectively.

The UV exposure of the specimens was carried out using a Xenotest Beta LM Atlas Accelerated Weathering tester. The test was carried out according to ASTM D 6695 standard [25]. The environmental conditions were set at 18 min UV irradiation and water spray then 102 min only UV irradiation. Temperature and humidity were 63 ± 2 ° C and the 50 ± 5% RH, respectively. The wavelength of radiation was 340 nm that were filtered by borosilicate glass. The surface morphology of the samples was tested by optical microscopy. The changes in surface properties of samples were characterized after 1000h. In order to investigate the degradation mechanism of the epoxy nanocoatings, an ATR-FTIR study of the test samples was conducted before and after 1000 and 2000h UV exposure. An IFS 48 ATR-FTIR instrument from BRUKER was used to investigate the changes occurred to molecular bonding. The transmission mode was used in the wavenumber range of 400–4000 $cm^{-1}$1and at a resolution of 4 $cm^{-1}$.

The gloss, colour attributes (L*, a*, b*) and total colour difference (ΔC*) were measured using a D65/2 ° - Erichsen model 565/45 spectrometer by CIE 1976 formula as follows; where D* is lightness, i* and n* are red–green and yellow–blue colour coordinates, respectively and Δ represents the difference in corresponding parameters before and after exposure.

$$\Delta C *= \sqrt{((\Delta D *)^2 + (\Delta i *)^2 + (\Delta n *)^2}$$

**Results and Conclusions**

By using SDS as a surfactant, nanoparticles of CB were uniformly dispersed in an epoxy matrix. Agglomeration of CB particles can decrease the UV resistance of the coating. Modification of CB particles on the surface effectively prevented agglomeration and improved compatibility between CB particles and resin. The characteristic of CB nanocoating rises by high degree of nanoparticles dispersion in resin which increases resistance of coating against UV irradiation.

Carbon black nanoparticles played an important role in stabilizing the epoxy by acting as an effective antioxidant and free radical scavenger with great effectiveness balanced by a pro-oxidant property under some conditions that can delay the photo-degradation process.

Water can accelerate UV degradation of coatings. The water molecules enhance the photo-oxidative reactions due to the increased $OH^-$ and $H^+$ ions and the water molecules can be located on the free volume sites between polymer molecules, improving the mobility of free radicals within the surface layer, thus accelerating photo-oxidation.

The surface microcracks in degraded areas significantly decreased when 2.5 wt% CB was added to the coating. It seems that high concentrations of CB significantly decrease UV degradation in the nanocoatings.

The colour difference values (ΔC*) for samples containing different wt% of CB nanoparticles showed that with increasing CB nanoparticles the colour difference decreased.

ATR-FTIR analysis showed that the $C - CH_3$ groups were degraded under UV irradiation. Upon exposing the samples under UV radiation, chain scission of the coatings occurred that led to the carbonyl index value increased as a result of increasing carbonyl band.


## 2.2 Evaluation of oil fly ash as a light stabilizer for epoxy composites: Accelerated weathering study [20]

**Introduction**

UV radiation and humidity exposure are amongst the severe cause of degradation of epoxy matrix composites. The chemical degradation of polymer matrices due to UV radiation occurs by activation of polymer macromolecules arising from the absorption of photons. This process generates free radicals in the presence of air or oxygen, and induces dissociation of chemical bonds on the surface as well as inside the material by diffusion Micro-cracking is a major cause of polymer composite failure and it serves as catalysts for further damage including macrocracks, moisture swelling and debonding. Moisture absorption in polymer usually causes plasticization and hydrolytic effects that are either reversible or irreversible. The modulus and glass transition temperature of epoxy polymers are often reduced after moisture absorption.

Particularly, industries are presently using Hostavin®N24 (0.5 wt%) as a commercial light stabilizer in epoxy based industrial pipes for outdoor services.

This study focused on the impact of epoxy matrix using residual oil fly ash (OFA) as filler by accelerated weathering environment exposure and examine the potential use of OFA

as light stabilizer in epoxy based industrial pipes to replace the commercial UV stabilizer either completely or partially.

**Method**

Oil fly ash (OFA) was obtained from Saudi Aramco and used after purifying by water wash and followed by drying at 80 °C for 24 h. Liquid bisphenol-A epoxy resin and iso-phorone diamine were purchased. The diamine was used as a curing agent.

OFA filled epoxy composite was prepared for the purpose of complete replacement of commercial light stabilizer. The 4 wt% OFA, with respect to epoxy resin with curing agent, was first dispersed at 50 °C by ultra-sonication for 1 h and after curing agent was added. The mixture obtained was degassed under vacuum at 30 °C and 0.01 mm Hg for 15 min to remove air bubbles. the mixture was poured into a Teflon® coated iron mould. It was thermally cured at 120 °C for 30 min for pre-curing and increased temperature slowly to 160 °C for 60 min for post-curing. Furthermore, an additive-free (i.e. 0 wt% of filler) and light stabilizer partially filled epoxy system (i.e. epoxy composites comprising a mixture of 0.25 wt% of Hostavin® N24 and 2 wt% of OFA, named as OFA-LS) were also developed by following the same preparation method for comparison. The weight percentage of light stabilizer is calculated with respect to the total weight of the resin and the curing agent.

**Results and Conclusions**

The outdoor service life of OFA(oil fly ash) filled epoxy composites were studied by subjecting to combined exposure of 0.38 $W/m^2$ UV irradiance and 20% humidity with temperature of 50 °C for 0.5, 1.5, 3 and 6 months durations. The effects of exposure were identified from the results of characterizations of morphology, thermal and mechanical properties by comparing before and after exposure. The exposure effects of OFA filled epoxy composites were compared with the epoxy composite comprising commercial light stabilizer i.e. Hostavin® N24 to investigate the possibility of complete or partial replacement of commercial light stabilizer in epoxy pipe formulations. Particularly, by extending the exposure period to 6 months, the 4 wt% OFA filled sample exhibited significantly lower reduction than the control system, which was identified through statistical analysis.

From the overall results, we conclude that the presence of 4 wt% of OFA in epoxy composites has better resistance to long term environmental exposure than the existing commercial light stabilizer i.e. 0.5 wt% of Hostavin® N24.

## 2.3 Relative findings over literature review

UV light`s aging affects on various polymers and tackling these affects by using different approaches were found in this phase. It was clear that UV light degrades polymers by resulting with chalking, decolouration losing functionalities and so on. Polymer chain breakages results to macro level failures.

In both studies additives were used to reduce these affects. In some cases, scientists marked important findings that finding the right balance in additives is important.

Dispersion of the additives is an important point as the additive may not have been designed to disperse in the epoxy. In order to distribute them additional another chemical and additional method for that chemical was used to not let additive to remain as a bulk material. If additives remain as a bulk in the material, it also would carry an air along with the bulk.

Additives apart from using as an improver to the mechanical properties, also offers defensive solutions to the polymers by saving its colours. In Ghasemi-Kahrizsangi, et. al, 2015, it was concluded that colour change in the surface of coatings was stable by incorporation of CB nanoparticles. 2.5 wt% of carbon black pigment with high degree of dispersion caused the colour difference changed negligible.

Most desired offerings of additives proved itself that microcracks on coated surfaces significantly decreased so this is proving finding that reducing material decay will also result back to the material`s mechanical properties at a desired constant and it is good finding for this thesis as well.

Exposure hours to UV light was set to 2000 hours in one study while other was 15 days. Another relevant key was 160 °C for 60 min for post-curing time was set for one study.

# 3 METHOD

## 3.1 Thermoplastic and thermoset polymer

Thermoset polymers are defined as pre-polymers in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing while thermoplastics are reversible polymers [21]. This functionality of thermoplastics offer perfect opportunity to be remolded and designed and used again, in most cases thermoplastics can be recycled as well. Thermosets have functional groups which crosslink to each other and these properties offer heat resistance and so on. Crosslinking is also defined from the same source which is IUPAC that reaction involving sites or groups on existing macromolecules or an interaction between existing macromolecules that results in the formation of a small region in a macromolecule from which at least four chains emanate [22]. Their hardness and structural integrity come from this crosslinking but also it has many downsides like it is not easily remolded or reshaped and also it is hard to get a good surface finish.

### 3.1.1 Epoxy and Epoxy`s Crosslinking Properties

After generic information about thermoset and thermoplastics it is necessary to approach epoxy in a molecular level as it is a necessity to grasp what molecular reactions are expected to happen in the material during the curing process. Epoxies are well wide used adhesives which easily can be found in many stores today. They are thermoset plastics and their cross linking properties are made from monomers containing at least two strained-ring groups called oxiranes. Oxiranes are two carbon atoms and are attached to a large variety of other aliphatic or aromatic organic molecules [23].

When handling epoxies in general, as well as in this thesis in the laboratory sessions, commercially it is offered that first there is a liquid which is chemically generic word called prepolymer and in packages also another substance called curing agent.

Epoxies are formed by the reaction of polyphenolic compounds or other hydrogen molecules. Epoxy adhesives base its reaction function in most cases to a molecule called bisphenol A and epichlorohydrin. Bisphenol A in reaction breaks into its anion and acts as a nucleophile in $S_N2$ reaction with epichlorohydrin. Each epichlorohydrin molecule can

react with two molecules of bisphenol A, once by $S_N2$ displacement of chloride ion and once by nucleophilic opening of the epoxide ring. At the same time, each bisphenol A molecule can react with two epichlorohydrins, leading to a long polymer chain. Each end of a prepolymer chain has an unreacted epoxy group, and each chain has numerous secondary alcohol groups spaced regularly along its midsection.
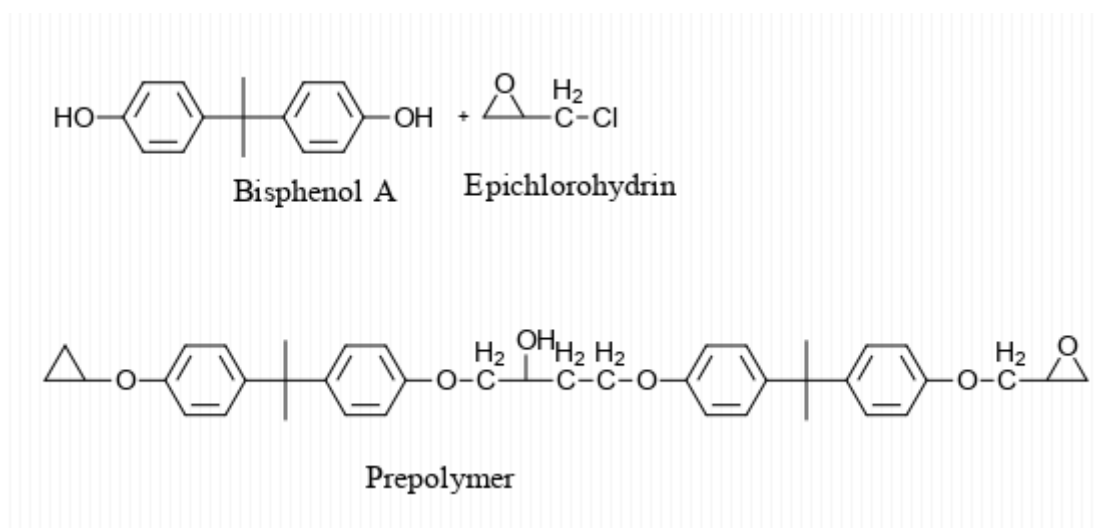


*Figure 3 drawn in Chemdoodle, Bisphenol A Epicholorohydrin reaction [23]*

When the epoxide is to be used, a basic curing agent such as a tertiary amine, $R_3N$, is added to cause the individual prepolymer chains to link together. This "cross-linking" of chains is simply a base-catalyzed epoxide ring-opening of an –OH group in the middle of one chain with an epoxide group on the end of another chain [23].
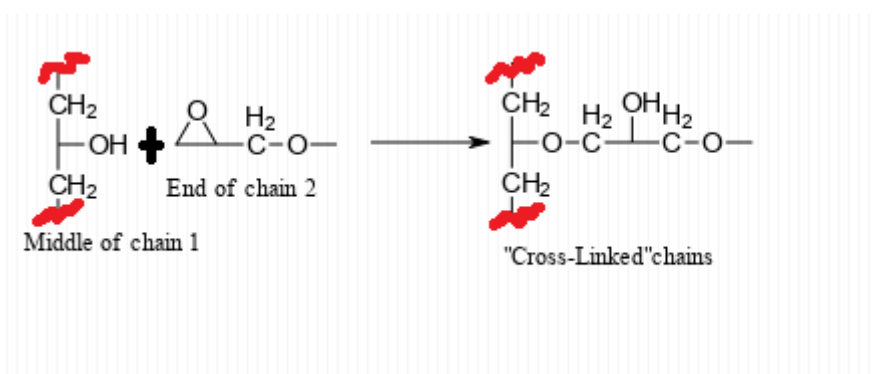


*Figure 4 drawn in Chemdoodle, Crosslinked chains [23]*

The result of such cross-linking is formation of a vast, three dimensional tangle that has enormous strength and chemical resistance [23].

In terms of behavior, cross-linked polymers also bring contrast to other thermoset polymers. In cross-linked systems, the mechanical behavior is also best reflected by the plot of the shear modulus versus temperature. Figure X compares the shear modulus between highly cross-linked, coarsely cross-linked and uncross-linked polymers [24].
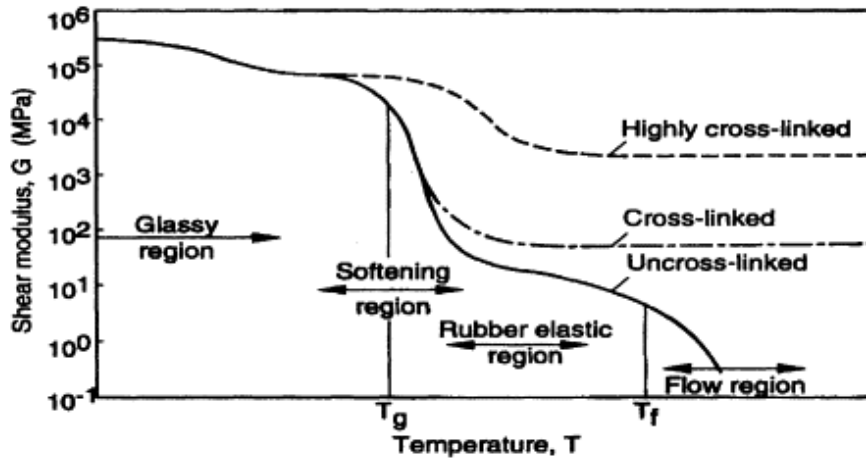


*Figure 5 Cross-linking benefits material by having higher modulus*

## 3.2 RESIN CASTING

As it was planned that every batch would have 0, 1, 5, 8 and 24 hours of UV light exposure, the mould was designed so that it would have 5 cavities for casting. In the outlines, every single batch would have three different additives aside of epoxy resin. Therefore, material that would be a mould of the casts should have been picked so that it would be flexible enough for twisting forces. Thus, the commercially known as acrylic plastic, also known as in chemistry polymethyl methacrylate(PMMA) was chosen to be used as laser cutter manufacturer suggests that as well. PMMA is rigid material in room conditions. After checking the safety sheets of the manufacturer, curing of epoxy was gotten familiar so that it would not lead to any vigorous exothermic reaction. The PMMA`s melting point

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is 160 °C [25] so it was clear that the expected curing reaction will not reach to the temperatures that would possess a risk on the acrylic plastic mould to change its shape. That would make a untraceable change of the young`s modulus of each cast.



*Figure 6 Inkscape software designed mould layers. Left: bottom of the mould. Middle: middle layer of the mould, Right: top layer of the mould.*

Inkscape software is an open source vector graphics editor which Arcada UAS has it in its computer laboratory so Inkscape software was used for casting designing. Having v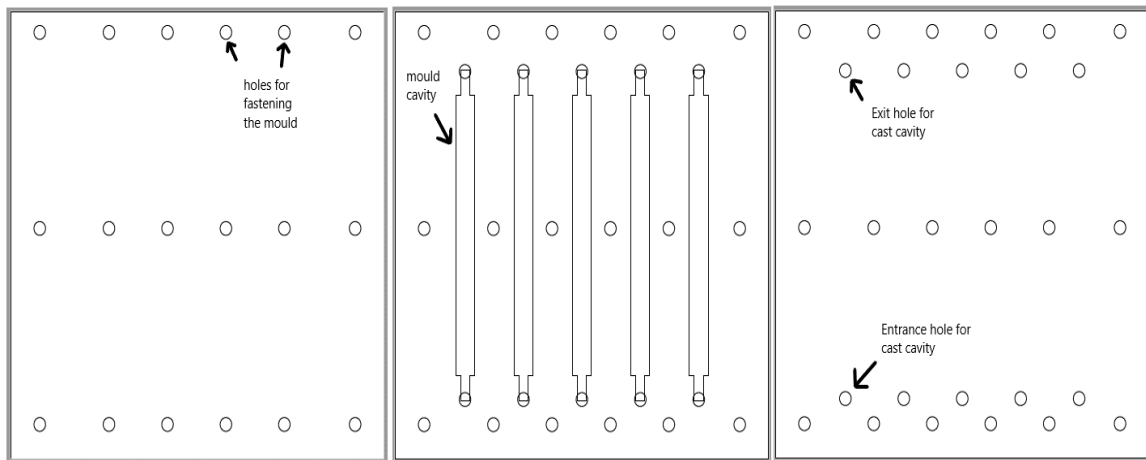ector graphics is the necessity of the mould design because of having image based outcome may bring discrepancies in the cutting phase. After creating the bottom of the mould which is on the left side of the Figure 3, same image was used to create the rest of the mould to avoid nonmatching mould layers as a measures. After creating each layers of the mould, documents were saved as a portable document format (PDF) to save it as a vector graphics.

The thickness of the acrylic plastic that was found to use is 2,94 mm and due to UV light exposure measurement throughout the specimens by time, as well as three-point bending test necessities casts must have been at least 8 mm thick. With these approaches, three middle layers of the mould were planned to cut to make around 8,82 mm thick casts.

For cutting procedures, Iso Omena Public Library`s laser cutting machine, with Epilog Fusion M2 $CO_2$ laser cutter was used. Procedure goes so that after introducing the PDF documents via USB stick to the device, it continues with fixing the travelling speed, power and frequency of the laser software sets itself. After parameters are set, the door must be closed and air ventilation should be switched on due to the fume that will be

created during the operation. All in all the process to get 5 layers in total takes about 5 minutes.

Lasercutting operation also included cutting the holes which were used to fasten the mould by screws, washers and wing nuts. All mould layers had 18 holes to fasten the mould. Fastening parts were purchased from K-Rauta Oulunkylä.
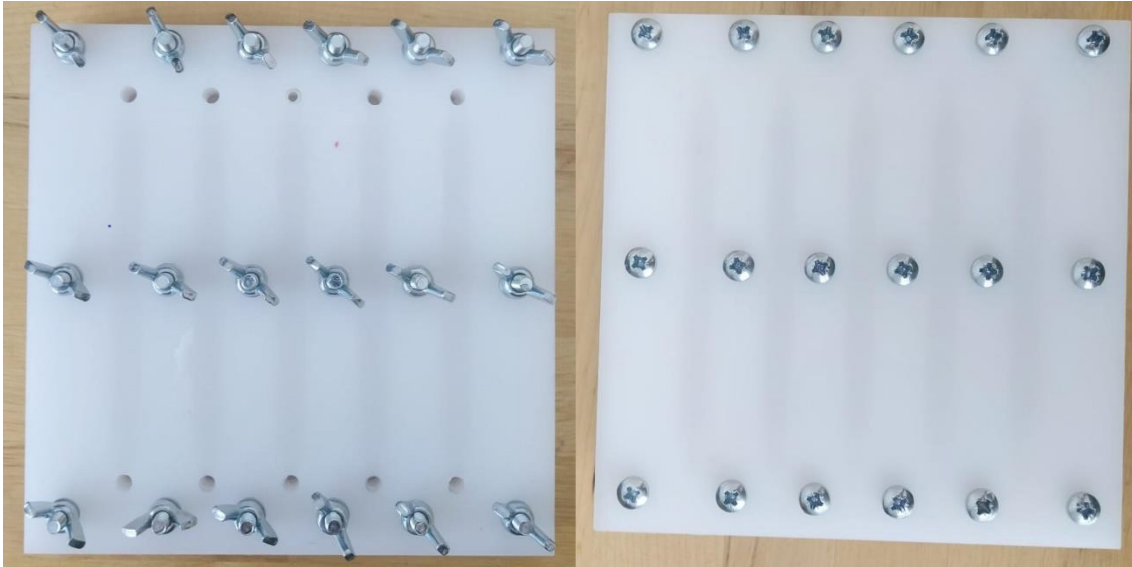


*Figure 7Mould after lasercutting and fastening procedures. Left: top view of the mould where the cast holes are visible. Right: Bottom of the mould.*

After getting cut pieces together, mould cavity thickness was measured to be 1,18 cm. However, due to expected material shrinkage after curing sessions, the measured thicknesses of the casts were less than the actual depth that was provided to the casts.

### 3.2.1  Specimen Manufacturing

Mould should withstand at least five batches series of castings so preserving the mould is a concern for keeping the casting sessions continue for next batches. Due to this, it was necessary to use an agent that would put a non-reacting zone in between the adhesive and the surface of the mould. Chemlease® 75 EZ [26] release agent was one of applicable one which was in the inventory of university laboratory.

According to the data sheet provided by the manufacturer, Chemlease 75 EZ possesses various risks which should be taken into consideration while operating with it. By fulfilling the REACH regulations, manufacturer puts a pictogram that it is labelled as highly flammable, may be fatal if swallowed, skin irritations may appear in case of skin exposure and toxic to aquatic life if accumulated to aqueous habitats.

*Figure 8 Chemlease® 75 EZ pictogram [27]*

Safe operating procedures should be fulfilled during handling the release agent. According to safety data sheet which was obtained from Chem Lease website, the release agent is hazardous and hazard statement the company as mentioned in Figure 9.

| Hazard statements | : | H225 | Highly flammable liquid and vapour. |
|---|---|---|---|
| | | H304 | May be fatal if swallowed and enters airways. |
| | | H315 | Causes skin irritation. |
| | | H336 | May cause drowsiness or dizziness. |
| | | H411 | Toxic to aquatic life with long lasting effects. |

*Figure 9 Chemlease® 75 EZ Hazard Statement [27]*

Safety data sheet suggests that skin irritation can be avoided by using protective gloves, protective clothing, eye protection and face protection [27]. To do so, release agent was handled in the fume hood in chemistry laboratory. Fume hood offers an internally ventilated safe zone which minimizes the exposure of the gas to operator by inhaling. Laboratory uniform, rubber gloves, eye goggles were used during the operations.

Apart from the operator`s safety, using minimum amount of release agent was necessary as it is toxic to the environment. To comply bio-accumulation should be kept minimum, instead of releasing the excessed liquid to the fume hood`s sink, after applying the release agent in the cup, cup was put back to its tank to be used for the next batch. Therefore, there was no any waste regarding the release agent.

All casting operations were held in fume hood. Release agent is highly flammable. Fume hood`s only access to ignitions is that it has a light that it provides. However, fume hoods have electricity provided but their cables are insulated to gases [28].

There were five different batches and release agent played an important role in releasing the casts out of the mould part. Rubbing every five layer of the mould with the release agent before fastening together was necessary. After putting the layers together and fastening the mould, the leftover release agent in the container was syringed into the mould cavity to guarantee the coating of the surface that would directly be in contact with the

26

adhesive mixture. As the screws to fasten the mould are located at the edges of the mould, it is expected that epoxy or epoxy with additives would penetrate into the layers of the mould. Therefore, it was essential to coat each layer of the mould to ease the removal of casts, and to conserve the mould for next rounds.

After release agent phase the mould was fastened by wing nuts and screws. Product prospectus suggests that for 2 base products to 1 hardener ratio in volume. From this point on it should have been measured beforehand how much mixture would be necessary. Cast cavities have 120 mm length, 8,7 mm thickness and 8 mm width and the mould had 5 cavities. Therefore, at every batch 42,5 ml would be needed. But due to possibilities of wasting some of the mixtures in syringing and also leaving some on the surfaces of paper cups mixtures were taken by 20 ml of hardener and 40 ml of base product to meet 1 to 2 ratio. In total, at every batch 60 ml of epoxies consisting of two products was used. It was a key case to calculate all to minimize the waste as epoxy is a plastic which doesn't degrade in nature for years.

In order to achieve good distribution of additives, first hardener and additives are mixed together with magnetic stirrer before adding the base product.

To be able to be removed from the mould all batch of casts required to wait at least one day. After all in casting sessions, casts have remained as they are for at least 10 days before moving to exposure procedures. This time was because of post curing of casts to enhance their cross linkage.

Due to cross linking, curing session of epoxy releases energy to its environment. Biltema epoxy cures at ambient temperature unlike some epoxies which requires to be heated to start curing. Since all handling of mixture was done inside fume hood which has a high air circulation, exothermic reaction did not possess any danger in this case.

## 3.3 Radiation interaction with material

The light on material can be considered as the ones that were reflected (R) from the surface, the ones that transmitted (T) and eventually the ones that are absorbed (A) by the material. Mathematically it can be expressed by using equation:

$$1 = R + T + A$$

Reflection is the process by which electromagnetic radiation is returned either at the boundary between two media (surface reflection) or at the interior of a medium (volume

reflection), whereas transmission is the passage of electromagnetic radiation through a medium. Both processes can be accompanied by diffusion (also called scattering), which is the process of deflecting a unidirectional beam into many directions. In this case, we speak about diffuse reflection and diffuse transmission (see Figure 10)
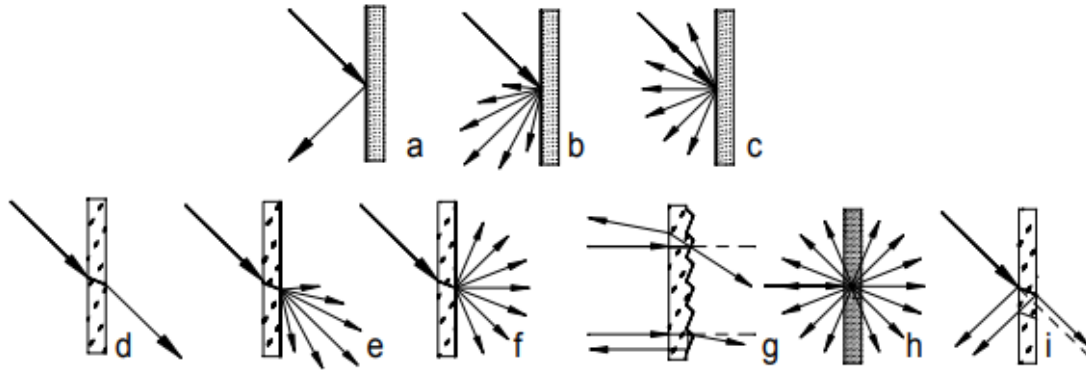


*Figure 10 Scattering reflected or/and transmission lights [29]*

When no diffusion occurs, reflection or transmission of a unidirectional beam results in a unidirectional beam according to the laws of geometrical optics. In this case, we speak about regular reflection (or specular reflection) and regular transmission (or direct transmission). Reflection, transmission and scattering leave the frequency of the radiation unchanged. Absorption is the transformation of radiant power to another type of energy, usually heat, by interaction with matter [29].
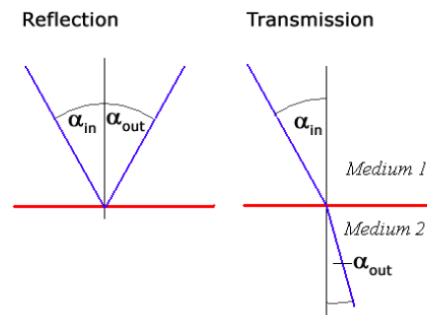


*Figure 11 Reflection and transmission of light [29]*

As the light is also carrying energy, absorbed light interacts with the material by releasing their energy. Carbon atoms establish in between crosslinking but crosslinking bonds are not as easy as typical Carbon-Carbon interaction. As it was mentioned epoxy is thermosetting plastic materials. In most cases, cross-linking is irreversible, and the resulting thermosetting material will degrade or burn if heated without melting [30]. Therefore, totally cured material is expected to have many cross-linked properties. In order to break these

bonds, as the material is tangled up, the energy that must be given should be higher than the standard bond breaking procedure.

Another issue is the intensity of the radiation that is expected to decay by the penetration of depth. This means the bond breakage is expected to be lowered by the depth of the specimen.

$$I = I_0 e^{-kx}$$

*Table 3 Casts' coefficient in terms of UV penetration is 1, 2 and 5 respectively*
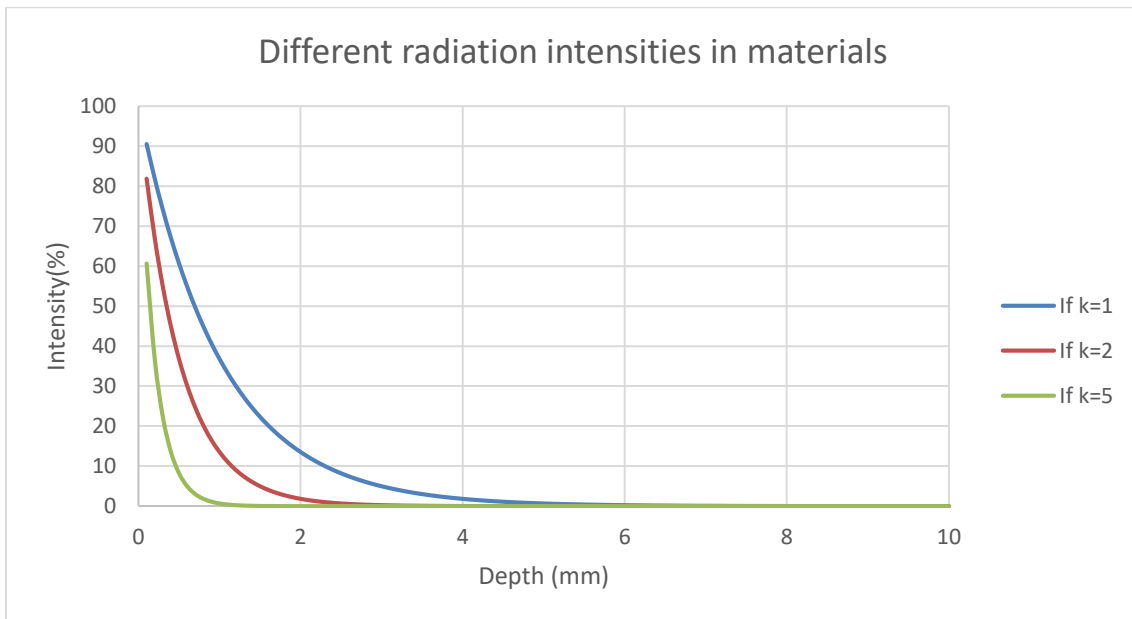


Four different coefficients (k) were used in Table 3 to outline the results how having different coefficients in terms of light penetrability, results back in decay of light in the material. In example when k is set to be 5, by comparing to an example when it is 1 the light penetration drops by more than 5 times in the material by looking at Table 4.

*Table 4 Light penetration by percentage in the material having three different coefficients*

| If k=1 | If k=2 | If k=5 |
|---|---|---|
| 58,88889 | 30 | 11,11111 |

If the additives in the material increases k by sealing the mixture, in another word to say if material becomes harder to be penetrable by UV light, the decay of the UV light in the material will die itself out earlier than in a pure epoxy which has no additives.

The light that will be absorbed have energy that will be released in the specimen. If the energy will not be enough to break the bonds, however it will release that energy to the

specimen which will result heating of the specimen. This is expressed by Planck`s radiation law. Planck explained that radiation will be emitted by a blackbody, a hypothetical body that completely absorbs all radiant energy falling upon it, reaches some equilibrium temperature, and then reemits that energy as quickly as it absorbs it. Planck assumed that the sources of radiation are atoms in a state of oscillation and that the vibrational energy of each oscillator may have any of series of discrete values but never any value between. Planck further assumed that when an oscillator changes from a state of energy $E1$ to a state of lower energy $E2$, the discrete amount of energy $E1 - E2$, or quantum of radiation, is equal to the product of the frequency of the radiation, symbolized by the Greek letter $v$ and a constant $h$, now called Planck's constant, that he determined from blackbody radiation data; i.e.

$$E = hv$$

The value of Planck`s constant is $h = 6.626.10^{-34} Js$ [31]

Radiation penetration will be reduced by the depth. In this thesis additives are expected to reduce also the radiation by increasing the radiation reflection or absorption into their bodies, not the epoxy itself.

In conclusion of radiation interaction, absorbed light (A) is in the area of interest in this thesis more than the others. Absorbed light, also can be expressed as E=hv, should be higher than the bond energy of epoxy adhesive to destroy the bonds. Otherwise, it will create heat in the material which will function as a catalyzer to create more bonds.

Furthermore, intensity $I(x)$ is function of depth $(x)$ and decaying $I(x) = I_0 e^{-kx}$ at $(x) = \frac{1}{k}$ and the intensity is 36,8 % of intrinsic $I(0)$ and at $(x) = \frac{5}{k}$ is 0,67 % of intrinsic intensity. This means that the exposed side of the cast and the unexposed side of the cast will give a different result in FTIR spectrum. More than $\frac{5}{k}$ value is much smaller than thickness of the samples.

The travel decay of the light in the material drops exponentially, while the energy generation from the surface until the light dies out follows the same pattern in the material. Therefore, the decomposition in the specimen due to UV light will be highest on the surface while dropping exponentially during its travel in the material.

## 3.4  Hooke`s Law

Hooke's law is a law of physics that states that the force (F) needed to extend or compress a spring by some distance (x) scales linearly with respect to that distance—that is,

$$F = kx$$

where k is a constant factor characteristic of the spring (i.e., its stiffness), and x is small compared to the total possible deformation of the spring [32]. In this thesis three-point bending tests were conducted in order to collect the bending modulus of the material. Hooke`s law also can be expressed in terms of stress and strain. Stress is the force on unit areas within a material that develops as a result of the externally applied force. Strain is the relative deformation produced by stress. For relatively small stresses, stress is proportional to strain [33].

$$\sigma = \frac{F}{A_0} \left( \frac{N}{mm^2} \right)$$

### 3.4.1  Rule of mixtures

Rule of mixture dictates that additives in mixture increase modulus and strengths of material depending on additive concentration and mechanical material properties. The concentration of the additive by proportion to the whole mixture is a term called fiber volume fraction(FVF) [34].
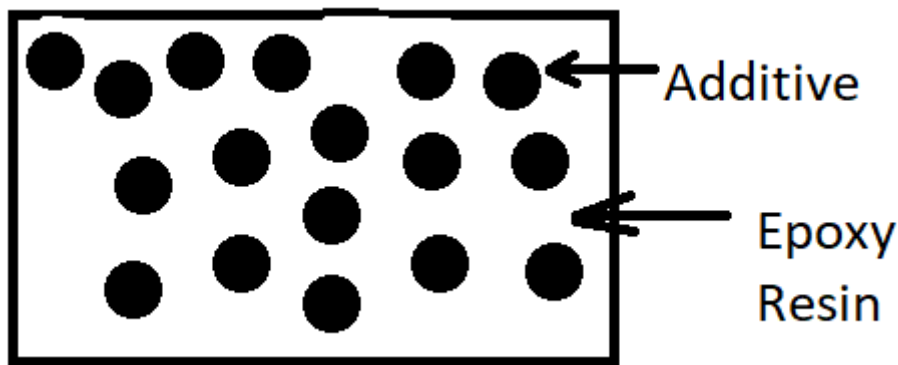


*Figure 12 Powdered additive and epoxy resin in schema predicted as this in micro scale*

$$FVF = \frac{V_F}{V_F + V_B}$$

## 3.5  Using of Fourier Transform Infrared (FTIR) Technology

Plan of analyzing the micro sized elements in scientical searches reside in old times in history of science. The need of seeking for an answer of what humans cannot see by their bare eyes pushed them to seek for better technologies.

Infrared technology today is being used in many scientical disciplines biological sciences, chemistry, engineering and so on, all look for compounds of the substances. Infrared lights differ therefore in technics. It is being researched in three groups.

*Table 5 Type of IR lights and their location in electromagnetic spectrum [4]*

| Electromagnetic Radiation | Spectrophotometer Location |
| --- | --- |
| Near IR | $0.7\ \mu m$ to $2\ \mu m$ or $13300$ to $4000\ cm^{-1}$ |
| Mid IR | $2$ to $25\ \mu m$ or $4000$ to $400\ cm^{-1}$ |
| Far IR | $25$ to $1000\ \mu m$ or $400$ to $20\ cm^{-1}$ |

Fourier transform infrared (FTIR) spectroscopy technology covers in between $13300$ $cm^{-1}$until $20\ cm^{-1}$. In other words, FTIR covers the entire infrared region in general. However, the FTIR machine that Arcada UAS has in its chemistry laboratory is Thermofisher Nicolet IS5 and it is covering only the region in between $4000cm^{-1}$ until $400cm^{-1}$, therefore it is Mid IR.

Working principle of FTIR machine is that infrared beam source creates two different beams: one that reflects through reference remains the validating source of the test, and the other that is first exposed to the specimen so that specimen recombines it before it is reflected through mirrors. After that reciprocal lights move to detectors to create an output as a spectrum.

Mentioned that FTIR machine scans all infrared region. In order to do it in typical FTIR machines there is a metallic component being heated to high temperatures to create infrared laser. As a consequence of a source which being heated to high temperatures, stability of the source must be controlled. In following sections of this thesis it will be mentioned in details that developers of FTIR devices created a system for background test to remove this sides to stop being reflected to result of the tests.

Whole idea of having a spectrum is to prove or to know what material one deals with. In the end of several chemical processes, the outcome must be subjected for a question

whether it is a desired final product. Apart from the material, also the density of the compound is important too. Surely, FTIR machines address these main questions.

What makes this method widely used is that operators enjoy tests of FTIR machine`s non-destructive test environment. Preparing a typical specimen which is planned to be used in scientifical works may take hours to get it to the testing phase. However, having an unexperienced person to use destructive test may lead of losing quite a big time. In this sense, FTIR method also allows the same testing on a same surface that scanning was applied before.

Another virtue of FTIR machine is that operational cost is free and environment friendly. In many cases in chemistry, in order to prove the particular substance exists in the mixture scientist needs to apply chemical tests to precipitate the desired substance with applicable reactant. As chemical reactions create leftovers to be disposed it turns out as a pressure on nature.

After the scanning session the spectra will be provided to the operator. Unless there was no library introduced, machine is unable to inform about spectra analysis of the scanned material but a blank spectra. Although the typical wavenumber ($cm^{-1}$) of for example C-H interactions is well know that it will position around [35], for main cases for operations library should be applicable for referral. Apart from the library of the spectra, for getting scans from a section view in order to analyze bond breakages in the specimen, it should be cut perpendicularly as the laser scans cannot penetrate trough the cast due to weakness of the beam. As the UV light penetration dies out by a function of depth which also was modelled mathematically in section 2.3, it was planned also in this thesis to scan from the section view to model at what hour of exposure UV light can penetrate maximum.

As respect to laser beam, scanning area of the specimen however was applicable for this thesis case, one should also put into a consideration whether the area of the scans would fit into their work.

In this thesis cross-linking of the epoxy, additive behaviors and their relations under UV light and for given radiation exposure was analyzed by FTIR machines.

### 3.5.1 Specifications of Thermo Scientific Nicolet iS5N FT-IR Spectrophotometer.

This study`s FTIR analyses were conducted by using Thermo Scientific brand`s Nicolet iS5N spectrophotometer. Brand offers different sample accessories and in this study ID7 was used. ID7 gauge is a monolithic diamond crystal.

*Figure 13 FTIR machine which was used in this study*



## 3.6 Testometric Machine Three-Point Bending Test

In material sciences the product that was created should be subjected to certain tests to analyze and classify that particular material. Three-point bending test is invented to collect the material`s bending modulus to have a knowledge of that material`s performance under certain stress whether it will fail or handle. It is a lifesaving and fundamental test which is totally deemed important worldwide. There are various derivatives depending on the setup but mainly these mechanical tests were fundamentally implemented by Euler-Bernoulli beam theory. Three-point bending test represents the case of a beam resting on two roller supports and subjected to a concentrated load applied in the middle of the beam [36]. In this thesis the three-point bending setup was planned that the load was applied to the middle of the beam. It is sometimes necessary to distribute the force une-

venly as the beam in real life will face the force unevenly. However, during the calculations in this case the beam length will be divided into two as the force was applied to the middle. Mentioned that three-point bending testing is being used worldwide to determine the standards in between materials, standards apply to the dimensions of the specimens, therefore the force and the beam of the length. ASTM D790 Plastic Flexural 3 Point Bending Test is being used for this respect [37].



*Figure 14 Three-point bending generic picture*

In methodology, Testometric machine has various grips so for specific measurement three-point bending gripe was picked for this test. There is a ruler on the support side of the bending grip and it was set to 8 centimeters, which means, even though casts were longer than 8 centimeters, for this tests only 8 centimeters of length of the casts were subjected to it. After software was set specimens were put to right position and made sure that they are as perpendicular as possible to the grips to not to deviate the measurements in lengths which would result as an unclear outcome.
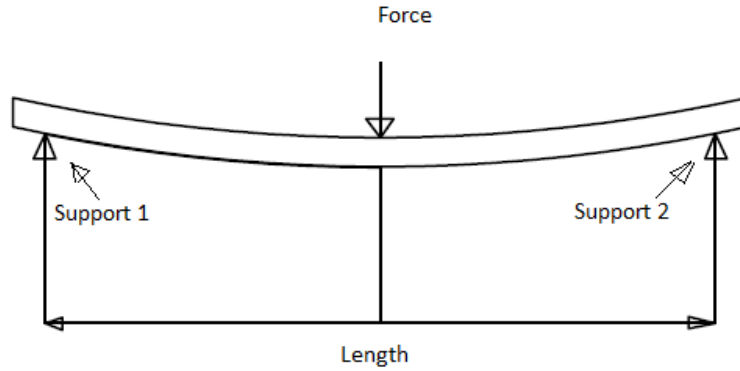
*Figure 15 Three-point bending test schema (was created in AutoCAD 2021)*

$$\sigma = \frac{F}{A_0} \left(\frac{N}{mm^2}\right) \text{ [38]}$$

$$\sigma = \frac{FLc}{4I} = \frac{FLt}{8I} \text{ [39]}$$

$$I = \frac{1}{12} bt^3 (second\ moment\ of\ area) \text{ [40]}$$

In this calculations, second moment of area was used as a rectangular cross-section [2.6.2]. The second moment of area changes depending on the shape of the material which is going to be tested. In this case b is width and t is depth of the material and if the material is hollow the equation would change by subtracting the material by this equation.

$$y = \frac{FL^3}{48EI} \rightarrow E = \frac{FL^3}{48Ix} \text{ [39]}$$

$$\sigma = E\epsilon \rightarrow \epsilon = \frac{\sigma}{E} = \frac{\frac{FLt}{8I}}{\frac{FL^3}{48Ix}} = \frac{FLt48yI}{8IFL^3} = 6\frac{tx}{L^2} \text{ [39]}$$

$$\epsilon = 6\frac{tx}{L^2} \text{ [39]}$$

Testometric machine creates a raw data in force against displacement. However, this raw data could be useful in perfectly unified specimens but specimens in this thesis were not exactly in same dimensions due shrinkage during the curing. For this test, specimens have approximately 8 millimeter thicknesses and the supports of the testometric machine was set to 80 millimeters length, therefore small changes matter.

## 3.7 UV Aging Setup

The UV aging setup should concern several parameters. Firstly, the length between the light beam and the specimens should be set and kept as a constant value. As the UV light also travels in the air, air has a constant value of decaying effect on the UV light. Therefore, UV light in the air decays also by the length. In following, specimen holder should not seal the light or reflect the light. However, there is a loss that holder keeps the specimens from their edges, those parts would anyway not be subjected to the bending tests.
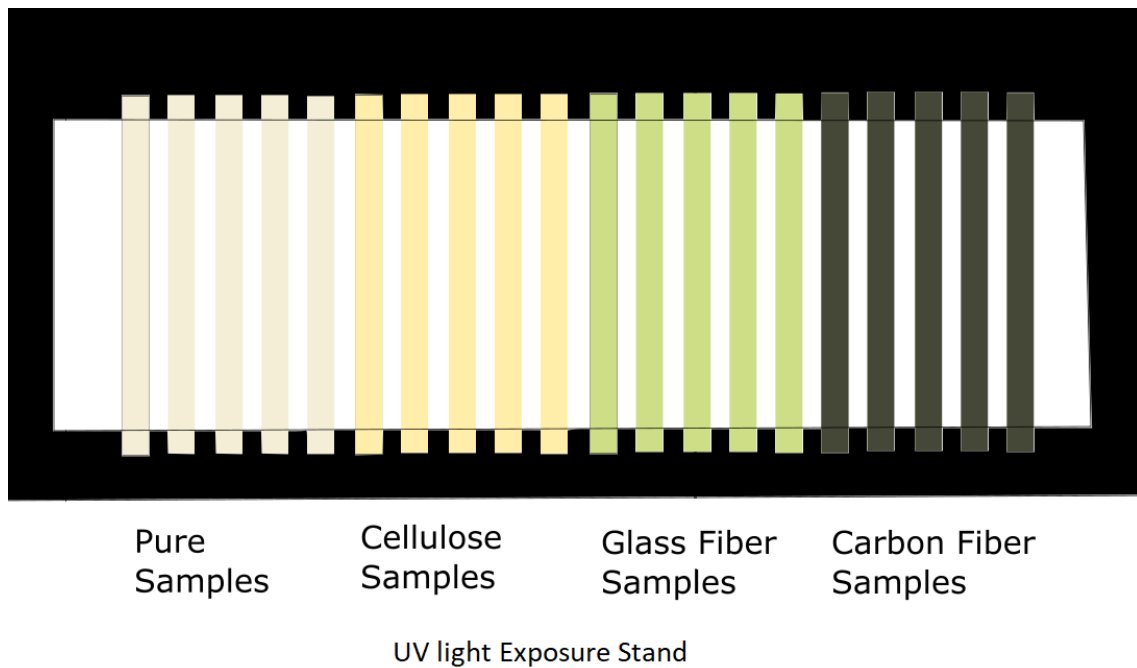


*Figure 16 Steel sheet specimen holder installed and position of samples*

Aging setup was inherit of old theses setups which were done in Arcada UAS. The brand of the UV light is Teleste and the model is SAT 430. The specimen holder was unable to ensure casts position that would stay still unfortunately. It was necessary to put another layer above the casts and aluminium foil was used to fill the gaps. The holder`s position to UV light was direct and opposite. There was 30 centimeter distance ensured by nuts.
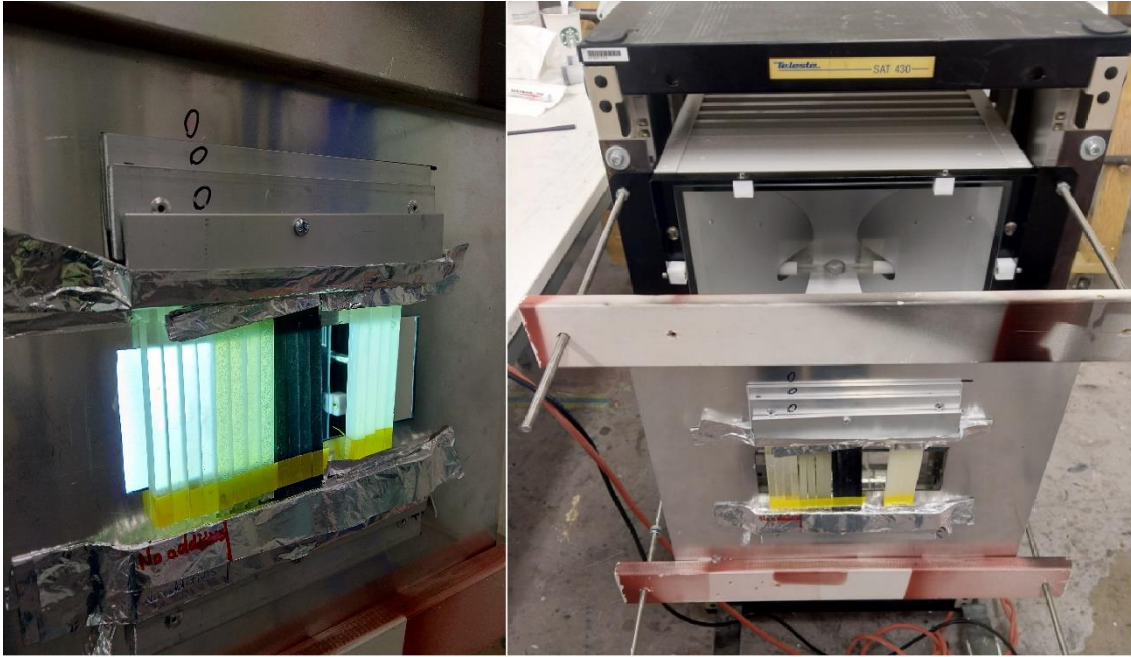
*Figure 17 Left: casts are being exposed to sunlight, Right: Sunlight source and the position of the specimen holder*



*Figure 18 The light elevated specimens to high temperature conditions.*

As also the Figure 18 shows, the heat on the casts reached high levels, up to 75°C. The elevation on the temperatures was expected and this was handled by being present during the procedures.

## 3.8 Sample Observations

In first Glass fiber added epoxies were casted. Glass fiber at this powder form tended to keep itself as a bulk even when picking them up to the spoons. Bulks may lead to bubbles as they carry also air in it. Therefore, it made voids created and those voids expected that decrease the modulus and bring discrepancies in UV light penetration analyzes. Glass fiber powder in the mixture offered greenish colour addition. By holding the material, it gave a stiffness feeling more than any other samples. All glass fiber added casts got broken.

Carbon fiber added casts were almost total black in colour. They were clearly the most flexible casts above all. After three-point bending tests, none of them got broken. It would not be scientical to state as it is just an observation but somewhat carbon fiber casts somewhat inhibited the activation of base product and curing agent reactions. Carbon fiber results do not follow the expectations. It may due to result of bubbles in the casts however casts were so dark coloured that bubbles were not observed clearly.

Cellulose added casts were stiff and all of the casts got broken. Cast colour was orange-yellow and slightly bubbles could be observed.

## 4  RESULTS

## 4.1  Three Point Bending Test Results

After exposures of casts the next step in the thesis was three-point bending procedure. Obtained force over displacement data from the testometric machine was changed to stress over strain graph.

*Table 6 Slope is taken from excel table and number which is in bold are the modulus of the casts*

| slope | 0h | 1h | 5h | 8h | 24h |
|---|---|---|---|---|---|
| No additive | $E_{Bend}$=1941.9 MPa | $E_{Bend}$=1911.2 MPa | $E_{Bend}$=2249.6 MPa | $E_{Bend}$=2159.2 MPa | $E_{Bend}$=2166 MPa |
| Carbon | $E_{Bend}$=1319.5 MPa | $E_{Bend}$=1751.1 MPa | $E_{Bend}$=1969.8 MPa | $E_{Bend}$=1966.9 MPa | $E_{Bend}$=2011.6 MPa |
| Glass fiber | $E_{Bend}$=4327.4 MPa | $E_{Bend}$=4249.6 MPa | $E_{Bend}$=4556.9 MPa | $E_{Bend}$=4642.7 MPa | $E_{Bend}$=4428.5 MPa |
| Cellulose | $E_{Bend}$=1954.6 MPa | $E_{Bend}$=1997.4 MPa | $E_{Bend}$=2223.6 MPa | $E_{Bend}$=2198.3 MPa | $E_{Bend}$=2217.6 MPa |

Table 6 which was obtained from the excel was collected from each of the bending data of the casts. Firstly, linear area in the bending data was focused and rest of the data was neglected in order to get a reliable data.

In case of Glass fiber there is a significant increase in reinforcement and that is according to the rule of mixtures. Glass fiber almost doubled the modulus and appearing to delay the cross linking as relatively as the sigma maximum appears at 8 hours which is later than the others. This concludes that as the cross linking is the key to achieve the best adhesive joint, mixtures that contain glass fiber should be cured more than any others.

For the case of carbon fiber there is a reduction in modulus. However due to all findings which clashes to these results it could be said that the mixture has high amount of bubbles, or cross linking procedure of epoxy was sealed by carbon fiber. It would be recommended that the light penetration should be followed. If carbon fiber slows down the light to penetrate, this could be an important finding. However, epoxy`s cross linking is always a desired case and if carbon fiber in this form inhibits it, then it is not recommended to use. Nevertheless, findings which cannot prove the amount of the bubbles, it is scientifically required to stick to the case that mixture in the cast had bubbles to reduce even the modulus of the epoxy even if it would be pure. Another case to explain it is that there was a mistake of having enough hardener in the mixture, which is a result of human error.

There is a slight increase in modulus in case of pure sample which has no additive, but in order to track better, it also requires to narrow down the gaps between the hours by adding more casting samples by tracking in between hours 1 to 5, yet it also requires to track the further results after 24 hours of exposure.

For the case of cellulose, the highest modulus was obtained at 5 hours of exposure. It could be that UV light destroys the cellulose. Unlike other additives and also epoxy itself

cellulose is a natural material. It may be that handling of UV light for itself of this additive particular was not achievable.

*Table 7 Demonstration of where sigmas of each cast reaches maximum*

| Sigma max | 0h | 1h | 5h | 8h | 24h |
|---|---|---|---|---|---|
| no additive | 57,274 MPa | 58,421 MPa | 63,338 MPa | 64,137 MPa | 67,073 MPa |
| carbon | 39,658 MPa | 49,524 MPa | 56,813 MPa | 56,585 MPa | 60,937 MPa |
| glass fiber | 58,640 MPa | 62,283 MPa | 59,122 MPa | 63,759 MPa | 61,175 MPa |
| cellulose | 54,637 MPa | 55,693 MPa | 59,197 MPa | 61,256 MPa | 67,073 MPa |

Sigma max refers to the point where the stress on the material reaches its maximum. It was obtained by using =MAX(X1;X7471) function which excel then obtains the highest number (X in here refers to the column in excel table).

Rule of mixture tells that the additives in the epoxy will result in higher modulus but outcomes do not follow these rules. Possibly the bubbles in the material during the mixing sessions resulted these unpredicted results. However, it was not obvious in carbon fiber added mixture as it was black, but in glass fiber mixture the bubbles were clearly seen. Due to this, in comparison of additives by UV light exposure time remains more valid as the casts of the same mixtures must have same amount of bubbles because of they were casted in the same time.

*Table 8 Demonstration of what is the strain where sigmas of each cast reaches maximum*

| Strain at sigma is at max | 0 hours | 1 hours | 5 hours | 8 hours | 24 hours |
|---|---|---|---|---|---|
| no additive | 0,05412 | 0,05921 | 0,05763 | 0,05385 | 0,05225 |
| Carbon fiber | 0,06125 | 0,05746 | 0,05580 | 0,05406 | 0,06064 |
| glass fiber | 0,02323 | 0,02522 | 0,02284 | 0,02458 | 0,02333 |
| cellulose | 0,05488 | 0,05099 | 0,04589 | 0,04498 | 0,04944 |

Strain at sigma was obtained the strain that corresponding to maximum sigma.

By following the pure sample`s maximum strain to compare with cellulose at all phases, exposed cellulose samples remain lower than unexposed sample which means that UV light may have destroyed the sample as it lost modulus and strain. Apart from the material itself was destroyed could be that there is no any interphase in between additive and epoxy itself. Therefore, cellulose is not the right additive to deal with UV light aging.

When it comes to glass fiber, by referring to the calculations at section 2.6 if strength remains the same and if the modulus rises it is expected to see the change in strain. If sigma is constant and the modulus is rising, then epsilon must fall. By comparing pure samples with glass fiber samples it is observed that strain drops. This means material becomes brittle. Therefore, it can be concluded that the glass fiber does not protect the material.

In carbon fiber added casts results in many results casts remain lower by comparing with pure epoxy casts. But there is a slight increase in the strain in casts with carbon fiber. Therefore, it can be concluded that the carbon fiber protects the material as it is marking in higher strain that material does not become brittle.

In general, what was observed is in Table 7 was that UV radiation creates more bonds in the beginning. That can be seen so that modulus increases by time of exposure. But as soon as the modulus increases it results lowering the strain as it can be seen in Table 8. These both outcomes tell that higher modulus in the material was achieved by creating more bonds but it resulted a loss in strain as material became brittle.

Testometric machine create results in force over displacement. This would be also informative in a case that all casts are unified. However, due to the material shrinkage and wet sanding, casts are not totally the same in dimensions. In order to maintain calculations that dimensions would not differ, stress and strain calculations were made.

### 4.1.1 Virgin Unreinforced Epoxy

All outcomes of virgin epoxy casts were outlined in Table 9 and entire table was divided into sections in following tables 10 and 11.
Table 9 was created by plotting all data of virgin epoxy. It tells that sigma grows by the time of exposure to UV light.

*Table 9 The entire stress over strain slopes of unreinforced epoxy*
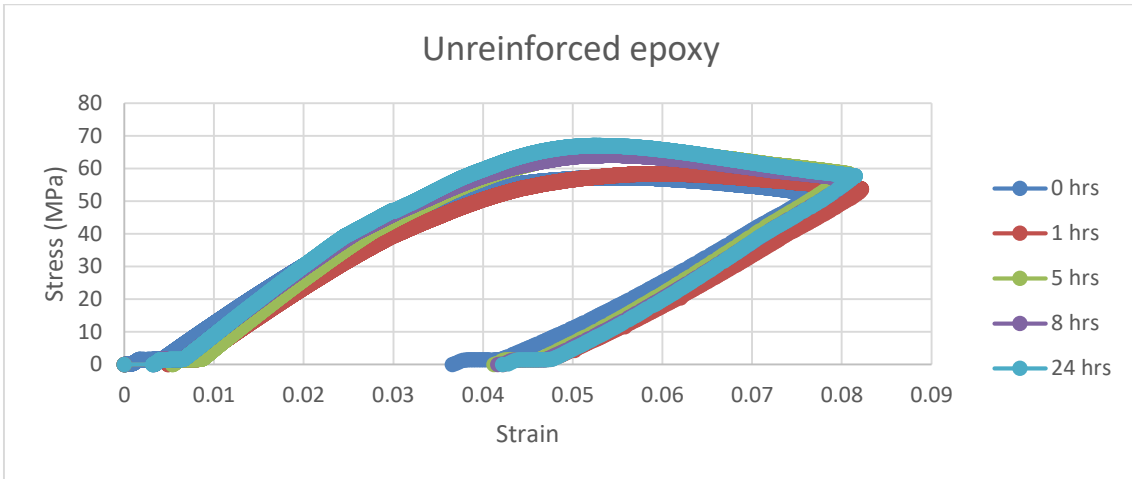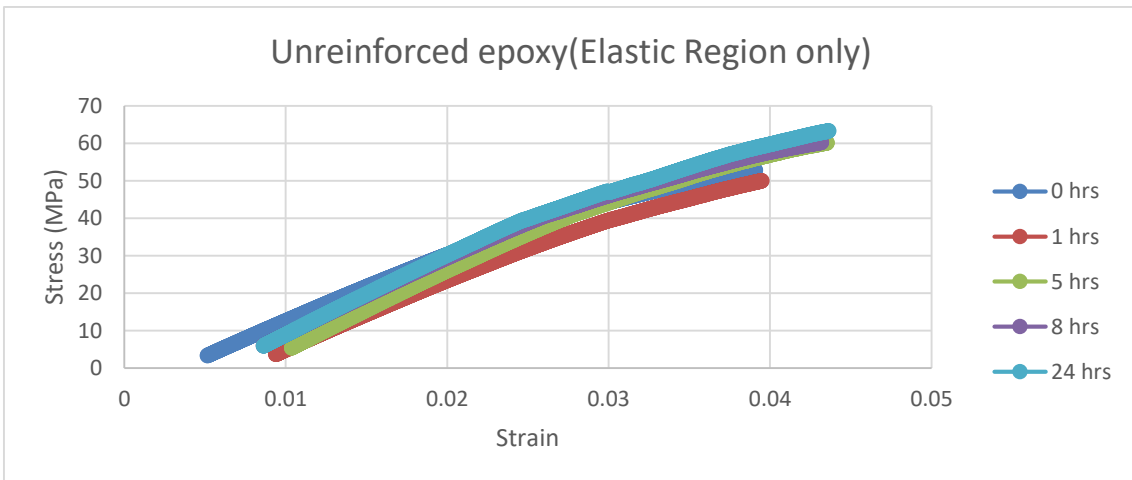


Table 10 shows us that modulus of the material increases by the time of exposure. Table points out that the modulus increases as the exposure time to the UV light increases.

*Table 10 Only elastic region focused stress over strain slopes of unreinforced epoxy*



Same trend of results was followed in Table 11. In overall, this tells that UV light post cured the material. The UV light exposure was not long enough to break the bonds in epoxy. The possible failure was to start the exposure procedures before the material reached to saturated levels in cross-linking.
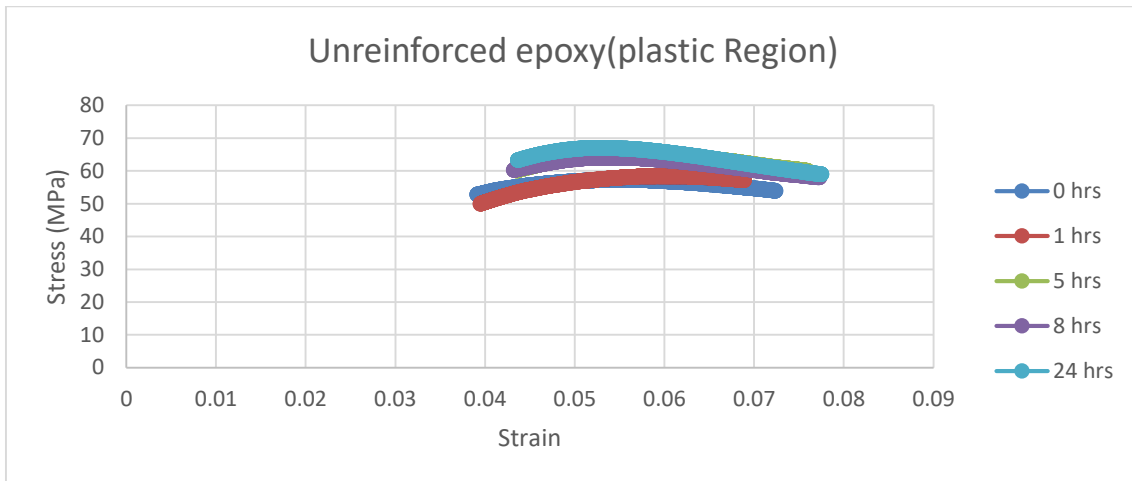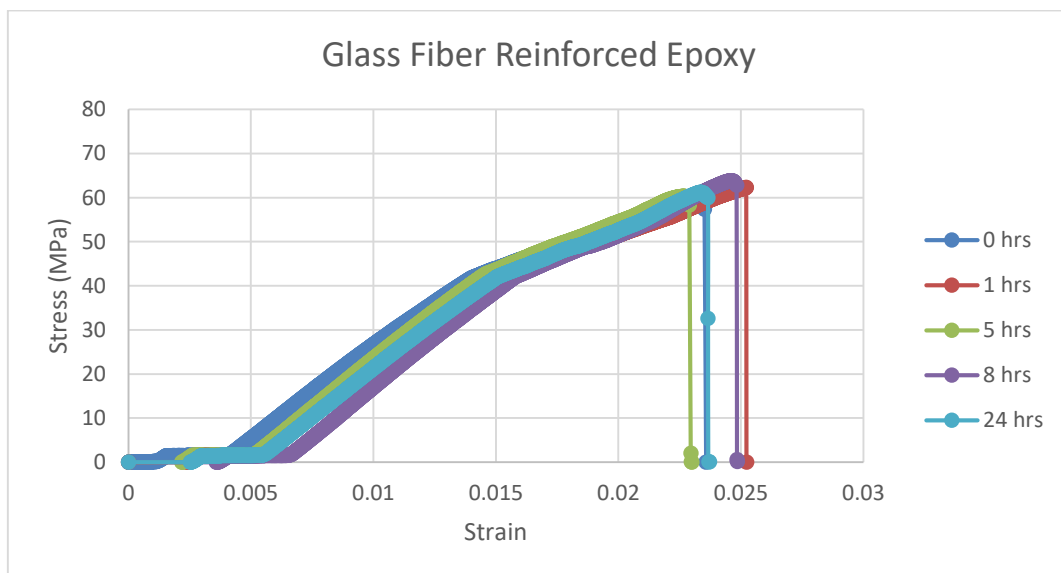
## 4.1.2 Glass Fiber Reinforced Epoxy

Stress-strain graph of the glass fiber added casts were gathered in Table 12. 24 hours exposure did not reach as high as the others in bending modulus but outcomes suggests that exposures that exceeds 24 hours should be also followed whether this drop is due to breaking bonds in the material or not.
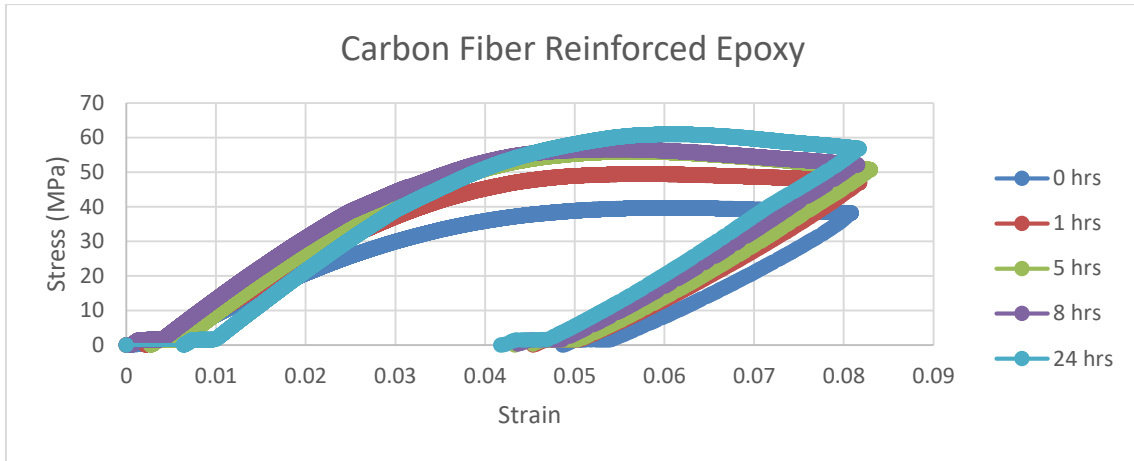
*Table 12 Stress over Strain graph of Glass Fiber Reinforced Epoxy Laminas*



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### 4.1.3 Carbon Fiber Reinforced Epoxy

Stress-strain graph of the carbon fiber added casts were gathered in Table 13. The gaps in the strain limits increase again by an increase in time of exposure to UV light.
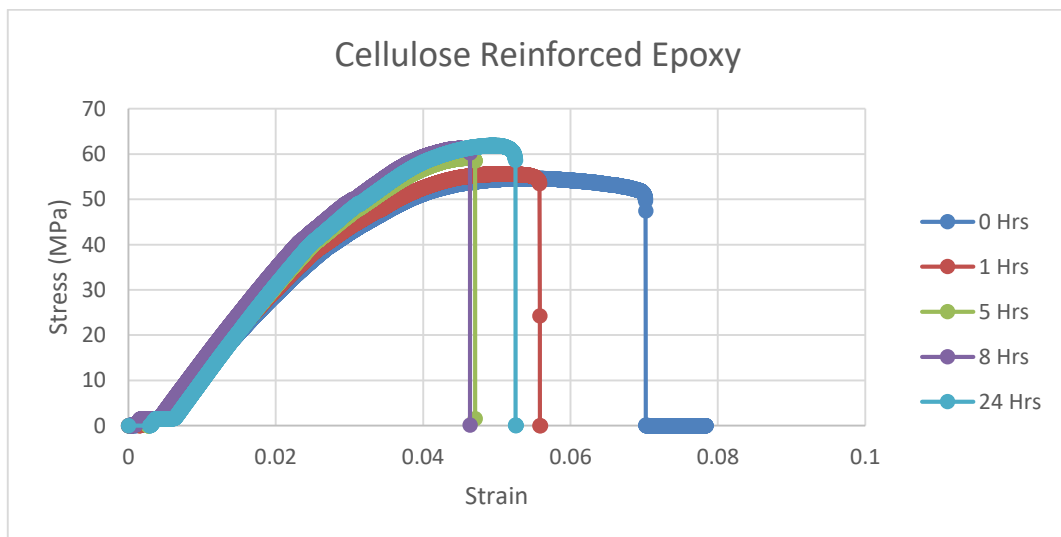
*Table 13 Stress over Strain graph of Carbon Fiber Reinforced Epoxy Laminas*



### 4.1.4 Cellulose Fiber Reinforced Epoxy

Stress-strain graph of the cellulose added casts were gathered in Table 14. Modulus of the cellulose increases by time while strain drops.

*Table 14 Stress over Strain graph of Cellulose Reinforced Epoxy Laminas*

## 4.2 FTIR SCANS

There are other researches with same findings which verifies the outcomes of this thesis in terms of FTIR scans. In Table 15 there is FTIR spectrum of uncured resins that was made by Basu et.al.,2008, and clarifies the peaks at the materials [41].

*Table 15 FTIR spectrum of uncured epoxy resin [41]*
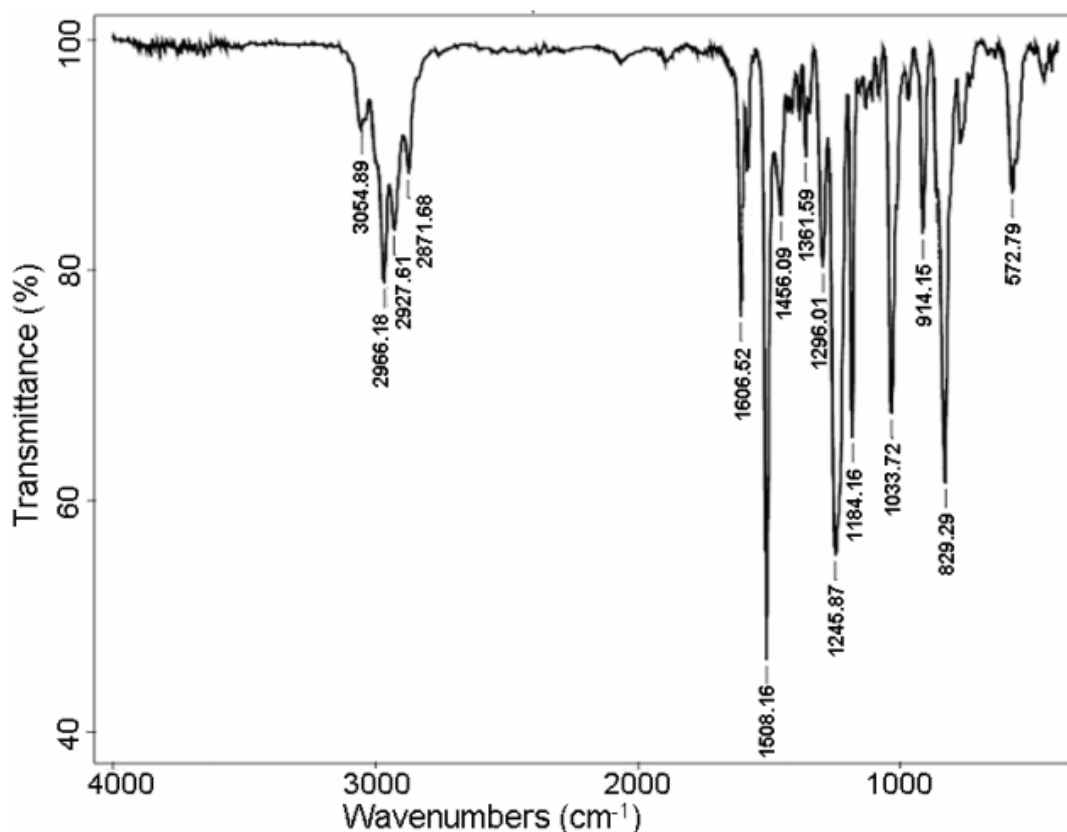


In Table 15 FTIR spectrum of uncured epoxy resin was outlined.

-3054.89 cm$^{-1}$corresponds to symmetrical & asymmetrical C-H stretch in aromatics.

-2966.18cm$^{-1}$corresponds to asymmetrical C-H stretch of –CH3 group.

-2927.61 cm$^{-1}$corresponds to asymmetrical C-H stretch of –CH2 group.

-2871.68 cm$^{-1}$ corresponds to symmetrical C-H stretch of –CH3 group.

-1606.52 cm$^{-1}$, 1581.44 cm$^{-1}$, 1508.16 cm$^{-1}$ and 1456.09 cm$^{-1}$ correspond to C-C stretching vibration in aromatic.

-1296.01 cm$^{-1}$ corresponds to asymmetrical –CH2 deformation.

-1245.87 cm$^{-1}$ and 1184.16 cm$^{-1}$ correspond to asymmetrical aromatic C-O stretch.

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-1033.72 cm$^{-1}$ corresponds to symmetrical aromatic C-O stretch.

-970.08 cm$^{-1}$, 914.15 cm$^{-1}$ (characteristic peak) and 862.03 cm$^{-1}$ correspond to epoxide ring vibrations.

-829.29 cm$^{-1}$ corresponds to –CH out of plane deformation in aromatic.

-460-580 cm$^{-1}$ corresponds to characteristics frequency of $C_6H_4X_2$-para. (X represents any functional group). [41]

*Table 16 Table shows the FTIR spectra of epoxy sample which was not subjected to any UV light*
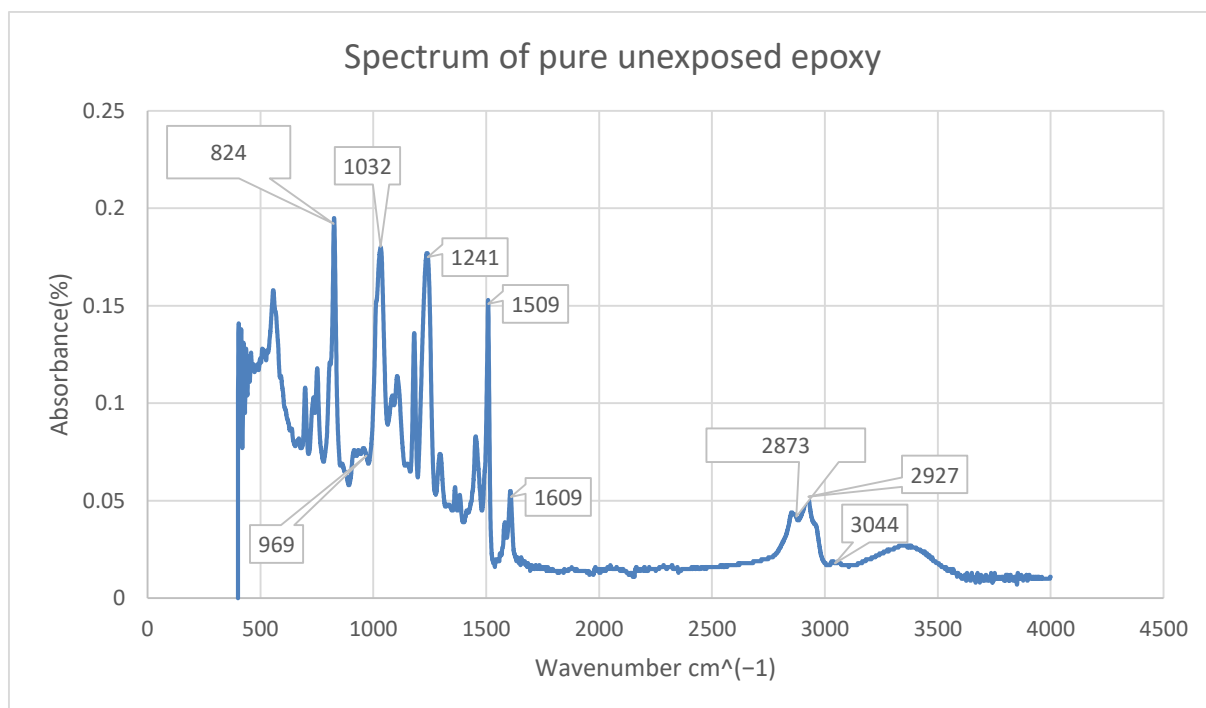


Before to start comparing Table 16 with, Table 15 it is necessary to mention our spectra`s condition. After mixing the both compartments of epoxy material it waited over a month before to be analyzed by FTIR machine. Specimens were kept in room conditions [42] until they were tested. It was expected that after mechanical tests were applied, during the three-point bending tests and the areas that the machine holds the specimen may show some differences in FTIR spectrum. These small discrepancies as well as the different additives in the products may vary the spectrums. However, spectra at Table 14 starts with functional groups and at 824 cm$^{-1}$the –CH peak appears while following epoxide ring vibrations shows up. At 1032 cm$^{-1}$ until 1241 cm$^{-1}$ , C-O stretch region appears. C-C interactions follows in the spectra which was labelled as 1509 cm$^{-1}$and 1609 cm$^{-1}$. Following area with a long break, methyl (-CH$_3$) and methylene($CH_2$) groups was expressed in the spectrum. Therefore, it can be concluded that FTIR tests which were used

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in this study verifies it`s reliability. For clarifying, wavenumbers also known as wave-numbers and its unit is $cm^{-1}$. $1$ $cm^{-1}$ is equal to $10^7 nm$.

$$\frac{1}{cm} \cdot \frac{1m}{100cm} \cdot \frac{10^9 nm}{1\ m} = 10^7 nm$$

Hypothetically, in order the break the bonds by doing work which was made to the casts, the work (W) should be higher than the energy of the bonds. $W > h\nu$ can be expressed mathematically and mentioned in section 2.3.

The Table 16 is showing the epoxy sample which is not subjected to any UV light. This is a base and solid piece to understand and expect about where the regions of peaks appear. Changes based upon the UV light, or additives will appear in the spectra but in order to judge those variables, it is important to follow the reference spectra. Nevertheless, UV light is expected to break bonds in the material and scans will be used to demonstrate those changes in the material.

*Table 17 Pure epoxy comparison by UV light exposures (*8hours exposed sample`s measurements could not be conducted due to shut down of University)*
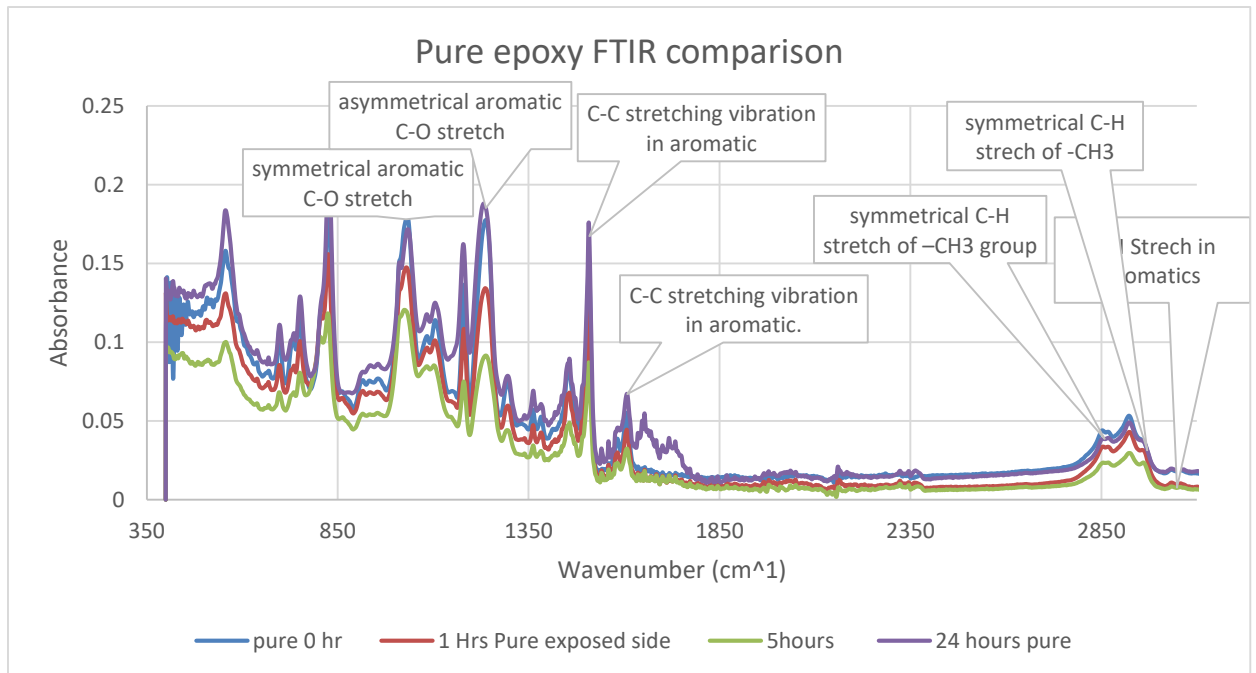


In Table 17, the blue line is epoxy unexposed to UV light, while red line is one hour, green line is 5 hours and purple is 24 hours of time exposed and exposed side of the

material was scanned to follow the change. Because the direct change in the material it is firstly expected to happen in exposed side.

Graph determines there is a peak loss which is correlating and following the base material, however peaks are dropping by their heights. However, in 24 hours spectra there is a jump more than the pure material.

To get a better view, Table 17 was divided to sections in following two tables.

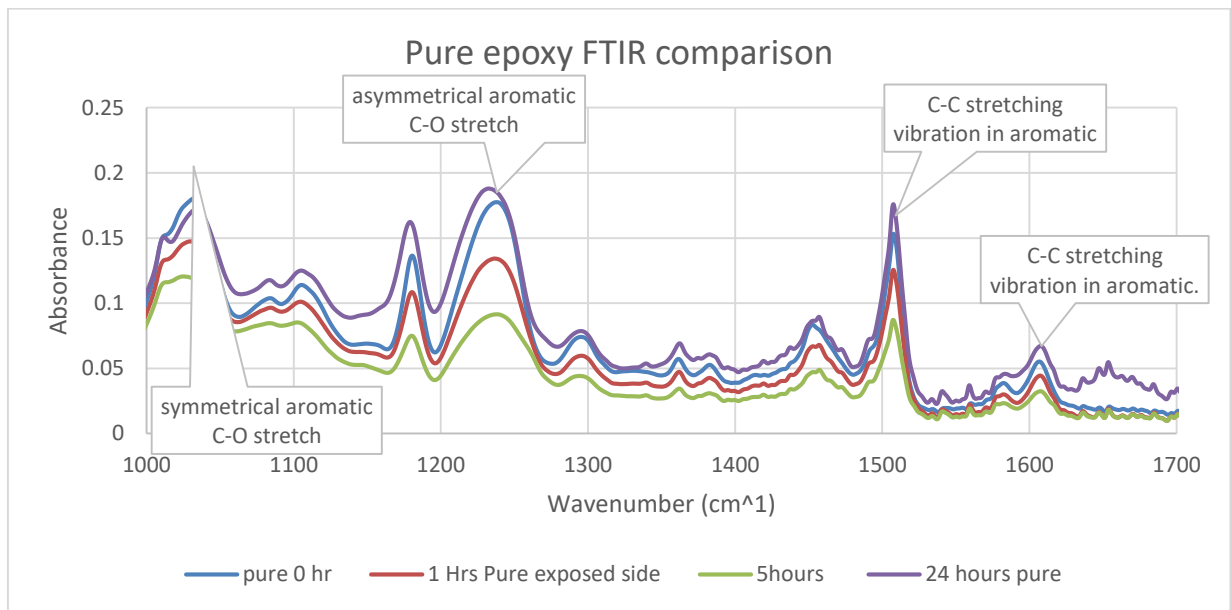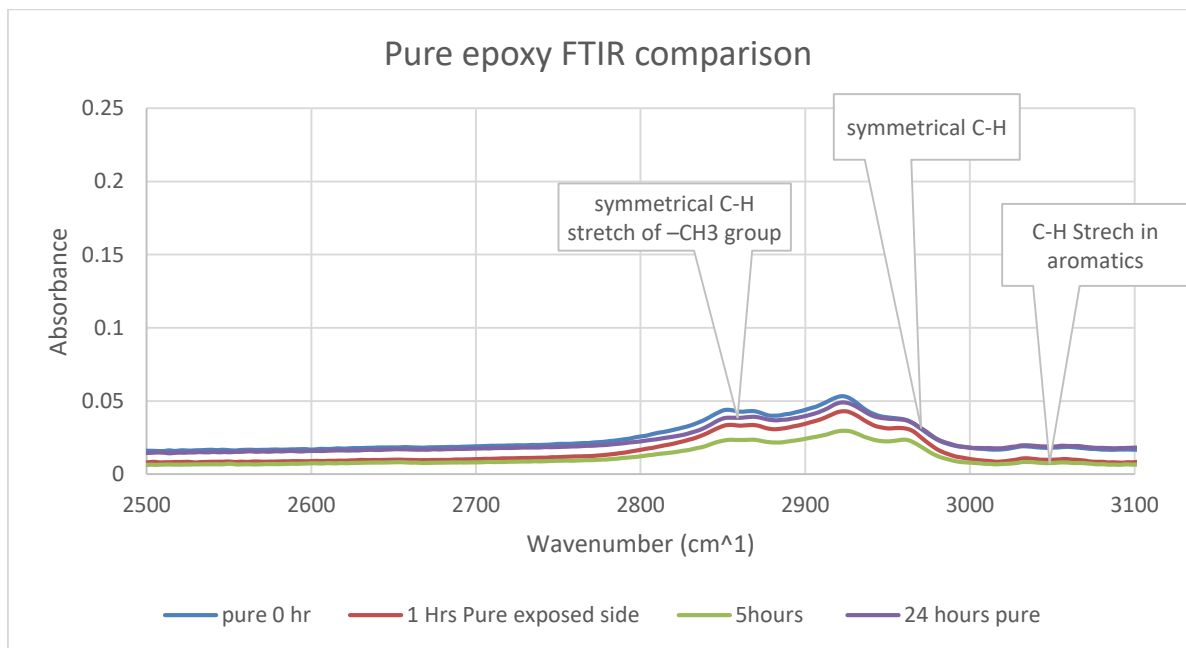*Table 18 Pure epoxy comparisons by time of exposure Wavenumbers 1000-1700 cm^-1*



*Table 19 Pure epoxy comparisons by time of exposure Wavenumbers 2500-3100 cm^-1*

Divided versions of the Table 17 show that in 5 hours of exposure material dropped to its lowest in absorbance while it is also low in 1 hour exposure. However, 24 hours exposed material showed the highest peaks in all sections on spectra.

*Table 20 Bending modulus of pure samples*

| slope | 0h | 1h | 5h | 8h | 24h |
|---|---|---|---|---|---|
| No additive | **1941.9** MPa | **1911.2** MPa | **2249.6** MPa | **2159.2** MPa | **2166** MPa |

By referring the modulus Table 20, also there is a slight increase in the modulus in 24 hours as well. However, the material behavior remains odd and some tests were unable to be conducted, while tests arises questions related whether material will deteriorate after 24 hours, or when is the time to see the rapid fall in results.

The exposed side of the material show a colour change from darker to its own colour of epoxy as moving to unexposed side.
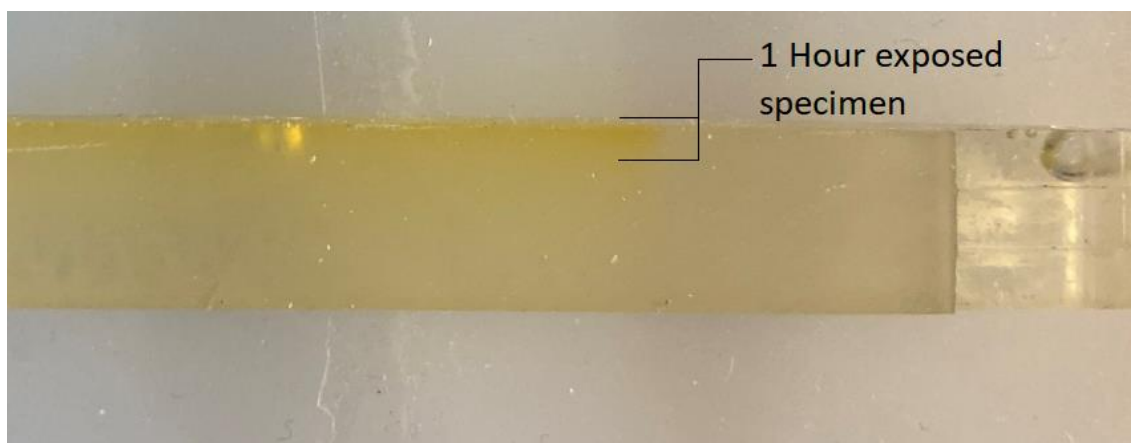


*Figure 19 1 Hour UV light exposed specimen.*

In order to compare the changes in material after exposure time, plot created by datas of using 1 hour exposed pure epoxy, over unexposed FTIR data. Mathematically can be modelled as follows.

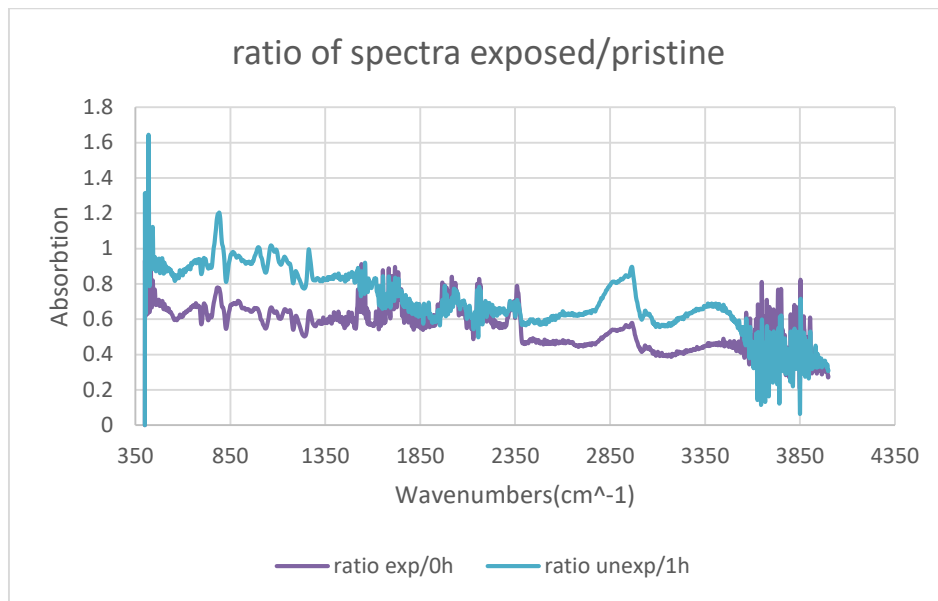$$F(v) = \frac{FTIR(t = 1\ hour)}{FTIR(t = 0\ hour)}$$

Table 21 shows the peak resides around at 750 wavenumbers. Regions where C-H interaction appears more around 2800 until 3200 $cm^{-1}$ and also in the region of C-O interactions which is residing around 1050 to 1250 $cm^{-1}$. Absorbance change between 2800 until 3200 $cm^{-1}$ reaches around 20% while it reaches around 40% at wavenumbers between 2800 until 3200 $cm^{-1}$.

The peak resides over 1 whereas in contrast. Arguably, at this peak it show that specimen receive an energy which only heated up the material but not to break the bonds. However, in exposed side it leaded to new cross-linkages. By referring to higher peaks in UV light exposed pure samples which was demonstrated in three-point bending results, either UV light did not break the bonds but built more crosslinks in the material, or UV light did break the bonds but was not enough to meet the ones that it created.

# 5  CONCLUSIONS

Having better stress levels but lower strain is bringing a case that in industry whether this would be applicable or not. It is questionable that whether in any case would it be a necessity after these results. Glass fiber prove itself in resulting in better modulus however, 24 hours of exposure again in local of glass fiber does not show the further results. In fact, due to covid-19 outbreak the additional tests which appear to be the necessity cannot be

granted under these circumstances. Nevertheless, for further suggestions, in terms of following where the cross-links of the epoxy breaks require reducing the gaps in between exposure hours to track material behavior more, while adding more casts to expose further than 24 hours. Carbon fiber reinforced casts clearly offers higher strain limits which definitely be observed in every results.

It is clear that UV light in this work proves that it changes the chemistry of the material which even eventually pays itself as well as in mechanical properties by giving brittleness. However, 24 hours of exposure does not point a clear case whether additives prove of prolonging its lifespan.

*Table 22 Effect of mixing time [43]*
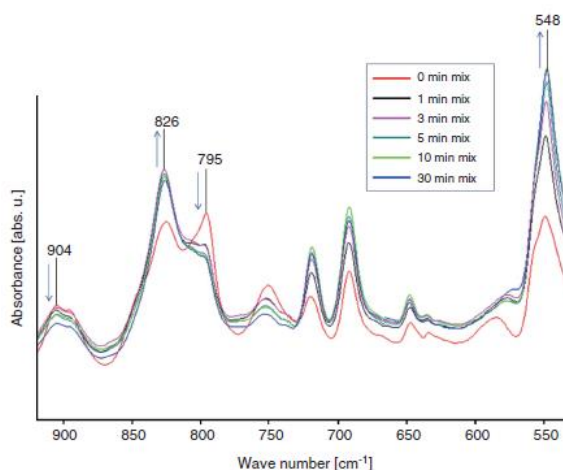


For improving the results in future studies about what would have been better, according to Table 22, study finds out that extending the time of mixing of epoxy gives higher absorbance in FTIR spectrums. Therefore, mixing the epoxy enhances the material interaction. The peak at 795 cm$^{-1}$ is because of the para-substituted benzene unit in GDAE decreased as mixing proceeded [43]. However, the peaks in Table 22 particularly pointed out are unable to be seen due to chemical deviation of the products in the market, claim of "extending the mixing time enhances material interactions" still remains a valid information, as in this thesis mixing time was set to 5 minutes and kept as a constant. Extending the mixing would reduce the post curing effects of UV light in this sense so it could be more possible to collect a data which has less effects of heating side effects. As Table 22 points out that specimens were being heated during the exposure time over 70°C.

Thesis plans also included cross sectional FTIR scans to prove the bond breakages change based upon function of depth. Unfortunately, due to the immediate actions that Arcada took to shut down the campus for COVID-19 restrictions, cross sectional scans, as well as 8 hours exposed FTIR specimen scans were unable to be conducted. Apart from these planned but could not finalized scans, the conclusion of studies after analyses strongly recommended to further analyzes. However, due to campus shut downs these plans also could not be made.

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# APPENDICES

    I.    MSDS for chemtrend 75 and biltema epoxy

**Danger**
Harmful to aquatic life with long lasting effects. Harmful if inhaled. Causes serious eye damage. May cause an allergic skin reaction. Causes severe skin burns and eye damage. Harmful in contact with skin. Harmful if swallowed.

[Show safety phrases](#)

Dispose of contents/container to hazardous or special waste collection point.

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

IF INHALED: If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing.

IF ON SKIN: Wash with plenty of soap and water.

IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

Wear protective gloves/protective clothing/eye protection/face protection. Wash hands thoroughly after handling. Avoid breathing dust/fume/gas/mist/vapours/spray. Keep out of reach of children. If medical advice is needed, have product container or label at hand.

Reference of this;
SAFETY DATA SHEET, Chemlease® 75 EZ,Chem Trend, Print date Feb 2019, according to Regulation (EC) No. 1907/2006 – GB

Biltema epoxy documentation, https://www.biltema.fi/en-fi/boat/boat-care/epoxy/laminating-epoxy-2000020523