UV Aging in Plastics

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Abstract:
The purpose of this thesis is to find out the expected lifetime of radiation aged thermoplastic material. The method is to irradiate PET and PP with UV radiation and measure the rate of degradation. The thesis focuses on the physical properties of the material and how UV radiation breaks bonds and/or cures the material. The UV source is a metal halide lamp and universal testing machine is used to record the properties of the samples. The samples are standardized dog bones. The plastics of the samples are tested for standard deviation. Then samples are exposed to UV light for ten hours and again tested for standard deviation to get knowledge of if the quality is good enough for the test. The samples are then exposed for a longer interval and periodically tested for stress strain and Young's modulus. The intervals are chosen in reference to the ten-hour exposure test. The result showed that both plastics degraded. Both PP and PET got stiffer and PET got stiff to the point that the material shattered. PP had a change of color that is a clear sign of change in the electron configuration. PET warped a lot but is not a result of uneven degradation due to the material being more transparent than PP.

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Sammandrag:
UV-degradering av plaster

Detta arbete är utfört för att fastställa den förväntade livslängden för plaster. Genom att bestråla plastbitar med starkt UV-ljus kan man på kort sikt mäta degradering. Metoden går ut på att två olika plaster föråldras och testas för mekanisk spänning, deformation och elasticitetsmodul. Med hjälp av resultaten kan man räkna ut raten av degradering. Plasterna PET och PP testas och med hjälp av olika plaster får man information om plaster föråldras på liknande sätt. Arbetet består av tre tester. Först testar man egenskaperna hos obestrålade provbitar i ett dragtest utfört med en universell testmaskin. Detta gör man för att få fram standardavvikelsen som behövs för att räkna ut kvaliteten på plasterna. De obestrålade provbitarna jämförs sedan med provbitar bestrålade i tio timmar för att se om någon förändring skett. Detta test är också utfört för att bestämma tiden och intervallerna provbitarna i det slutliga testet föråldras. Bestrålningstiden fastställs till 48 timmar och provbitarna testas med åtta timmars mellanrum för olika egenskaper för att få fram en syn på utvecklingen i materialen. Resultatet är att båda plasterna förändras på olika sätt av bestrålningen. PET:s två sista provbitar uppvisade en våldsam reaktion i dragtestet då de splittrades. PP däremot bytte färg till en svagare gul färg. PET:s elasticitetsmodul förändrade sig lite och höll sig huvudsakligen på samma nivå. Den mekaniska spänningen och deformationen hade en jämn ökning fram till de två sista provbitarna där plastens egenskaper gav efter. Resultaten stämmer bra överens med splittringen i dragtestet. Detta betyder att PET både brutit och bildat nya bindningar med energin från UV-strålningen.

PP:s mekaniska spänning föll i mitten av bestrålningstiden och steg tillbaka före slutet. Deformationen föll radikalt för de två sista provbitarna. Elasticitetsmodulen hade en gradvis stigande kurva vilket tyder på att plasten skapat nya bindningar och härdats. Standardavvikelsen visade att plasterna var av god kvalitet men blev ännu bättre efter tio timmars UV-bestrålning. för att få ännu noggrannare resultat kunde plasternas ursprungliga kvalitet vara bättre. PET-plasten böjde sig under bestrålningen och böjdes aldrig tillbaka. Detta kan vara ett resultat av att ställningen som håller upp provbitarna framför UV-källan blev varm och bildade märken där provbitarna rörde ställningen. PP kunde ha bestrålats lite längre för att man skulle få fram information om plasten fortsätter att bli styvare eller om den till slut ger upp. Som källor till arbetet användes vetenskapliga texter i bokform och elektronisk form. För formler och teorier användes internetsidor.

Nyckelord:	UV degradation, strålning, Elasticitetsmodul, termoplast, standardavvikelse
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FOREWORD

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List of symbols

F	force $\frac{kg\ m}{s^2}$
A	area m^2
l	length m
l_o	length original m
I	intensity W/m^2
I_o	intensity original W/m^2
σ	Stress MPa
$\boldsymbol{\varepsilon}$	Strain
t	Time h
r	radius m
f	frequency s^{-1}
h	Plancks constant $6.62607004 \cdot 10 - 34\ m^2\ kg\ /\ s$
Gy	Gray J/Kg
Sv	Sievert $J \cdot kg^{-1}$
Pa	Pascal $N \cdot m^2$
R	reflection
T	transmission
A	absorption

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1 INTRODUCTION

This thesis is conducted to determine the expected lifetime of radiation aged thermoplastic material. The samples are of PP and PET.

Young's modulus, stress and strain as function of aging time is determined using testometric testing machine. The aging is done by radiation from Osram metal halide lamp. The thesis focuses on the physical properties of the plastic after prolonged UV exposure measured in hours.

Polymeric material degrades in an unpredictable manner, bonds are destroyed or activated. It is important to know the rate a plastic degrades so it's expected lifespan can be determined. The expected lifespan is used to define maintenance intervals of materials or structural elements which gives companies or users of the material an expected maintenance cost. Sometimes the degradation is desired like in Biodegradable polymers. Degrading is a depolymerization or break out of molecular bonds. The breakage is related to the materials or molecules binding energy. Crosslinking is the formation of bonds that could be activated by radiation. Radiation activatable composites are for example used in tooth fillings. Photosensitizers are activated in the tooth filling paste by absorbing visible blue light. The paste is sensitive and must be contained in a lightproof packaging not to activate during shipping. [1]

Two different materials are tested to see if polymers degrade in a similar fashion. Shape of the specimen is standard dog bone injection molded by ENGEL CC 90 (figure 1).

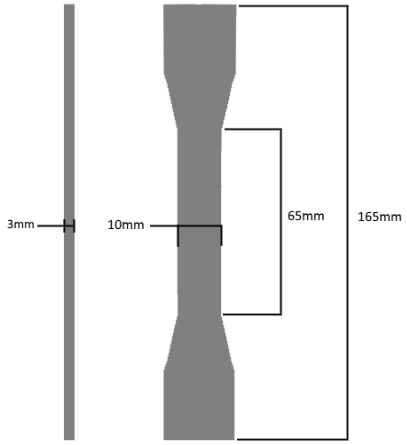

Figure 1. Schematic of dog bone.

Polypropylene and Polyethylene terephalate are tested. PP has a naturally white color and feels soft. PET is transparent and has a harder surface. These plastics where chosen to get knowledge of, if transparency and toughness makes a difference when exposed to UV radiation.

The experiment will be conducted by first measuring the initial properties. Further tests are done on aged samples, and relative changes due to aging are studied as function of exposure time. In this study the results are the rate of strain, strength and modulus change of function of exposure hours.

Two studies are made to establish the rate of aging.

2 LITERATURE REVIEW

The thesis hypothesis will be based on previous studies. The findings are summarized below.

2.1 Review of Massey's work

Liesel K. Massey's studies showed the aging by UV to be very different from case to case. According to Massey, one case of Urethan thermoplastic elastomer aged by 57% from 47 MPa to 27 MPa tensile strength in 1900 hours when threated in QUV. The method of QUV focuses on giving an accelerated natural outdoor degradation. It simulates sunlight, moisture and temperature of desired amount. There are a lot of different test standards and the material doesn't say which one it used. [2] The treatment time is far longer than what this thesis works with. With 1900 hours of exposure, much more data can be gathered. Massey worked with several different compositions of hydroxybenzotriazole and HALS. The first urethan mentioned to degrade by 57% is Dow Pellethane® 2103-80 AEF. It acted in an interesting way, getting stronger after 800 hours and then got weaker until 1500 hours. At 1500 hours it got a little stronger again. The second plastic tested is a mixture of urethane with 0,25% hydroxybenzotriazole and 0,25% HALS. The urethane first got weaker until 600 hours in. Then it started getting stronger until 1050 hours at which it was the same strength as before the exposure. Then it dropped back down after 1500 hours. Then it got a little bit stronger after 1700 hours of exposure.

The last urethan is a 0,5% HALS. It got weaker all the way to 1500 hours in when it jumped up a little in strength. It acted in the same way as the unstabilized urethane. Interesting to see is that all three plastics had a stress and strain curve that at some point gained strength. [3]

2.2 Review of PVC aging

A test from the book “Polymer degradation and stability” takes another approach to radiation degradation of plastics. By utilizing ultra-visible absorption spectroscopy, information of polymer chains being cut can be gathered.
Polyvinylchloride is mixed with DEHP and Tinuvium P. The mixture makes an irregular structure and prolonging the degradation. The test focuses on three mixtures of PVC plasticized with DEHP and how stabilizing additives protect Polymer chains from being cut. Radiolytic degradation is observed. The films are subjected to different doses of gamma radiation and the results are gathered by ultra-visible absorption spectroscopy. The doses are 10, 25 and 60 kGy.
The first mixture is a PVC 75% DEHP 25% film. The degradation was proportional to the irradiation dose.
The second film is PVC 75% DEHP 24,5% Tinuvin P 0,5%. The film with 0,5 Tinuvium P shows no bigger change in its molecular weight upon irradiation…
PVC 75% DEHP 24% Tinuvin P 1%
The film with 1% Tinuvium P shows an increase in molecular weight when exposed to 10 kGy but loses molecular weight when exposed to the higher doses of 25 and 60 kGy.

This experiment focuses on how molecular weight changes in different radiation doses. It doesn’t give information of how the strength of the material changes. The experiment is very fast, only about a minute. The experiment shows how UV stabilizers protect the material from polymer chains breaking.
The test successfully shows that Tinuvin P stabilizes the plastic with a maximum protection of 90%. This highlights the importance of plastic composition. [4]

2.3 Review of studies by Gijsman et. al.

Aging by different methods such as chemical corrosion was done by Pieter Gijsman, Guido Meijers and Giacomo Vitarelli. They used a similar approach as in this experiment and expanded it to also use chemical degradation and UV degradation along with temperature and humidity.

The tests focus on photodegradation of polypropylene, polyethylene, polyamide 6 and polybutylene terephthalate and how concentrations of chromophores changes it. To obtain information on how chromophores impact the photodegradation, PE, PP, PA6 and PBT are UV degraded while PP is thermos-oxidatively degraded in a comparable temperature. After the degradation, oxygen uptake is measured.
It has three different tests; Suntest, Weather-o-meter (WOM) and thermos-oxidative degradation.
The tests were done in an osilicate glass system.
The suntest used a xenon lamp with a filter filtering wavelengths under 290 nm (equivalent to normal sunlight). Temperature between 40 and 50 °C
The experiment used a Weather-o-meter which used a xenon lamp with same wavelengths as in the suntest, controlled temperature and humidity (55%) and had a raincycle. The machine records the oxygen uptake of the different plastics.
Thermooxidative degradation was done in an oilbath at 50 °C.
The test pieces where blown plastic films of 150 μm. The PA6 was a cast film of 50 μm. PBT was also a cast film but had a thickness of 25 μm
Carbonyl absorbance was recorded with IR spectra. [5]

Radiation in Finland

Finland is a northern country and doesn't get much UV rays from the sun compared to southern countries. Material degradation doesn't only happen from UV rays and Finland has an abnormally high radioactivity which contributes to material degradation. It is a natural radiation source in the ground. Finland and especially Eastern Uusimaa has a higher granite and uranium percentage in the ground. [6] The radiation goes up to 0,2 μSv/h in eastern parts of south Finland. [7]

3 THEORY

The specimen is a standard thermoplastic injection molded dog bone [8] in PP and PET. The mechanical properties of the dog bone are established by a universal testing machine (Testometric machine). [9] The measured quantities are Young's modulus, strength and strain. The first variation of properties is measured in unaged test pieces. Aging of material properties is measured on new dog bones exposed to predetermined hours of radiation. This will be used to determine the rate of aging. Figure 2 shows the setup for degrading the samples.

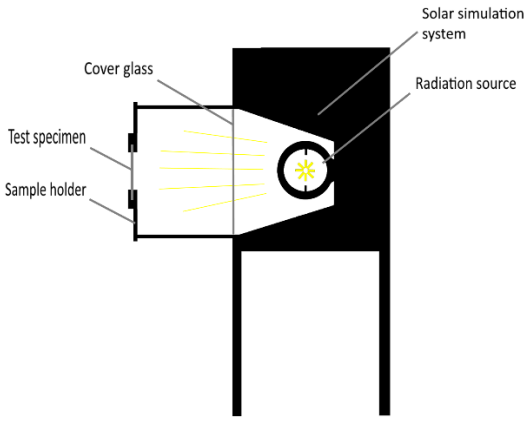

Figure 2. Sample holder.

Material

There are many ways of measuring degradation in plastic. Some tests use humidity and chemical treatments to lower material properties. UV-degradation is due to combined effects of photolysis and oxidative reactions. [5]

The behavior of Young's modulus in function of time $\frac{\Delta E}{\Delta t}$, stress $\frac{F}{A} = \sigma$ and strain $\varepsilon = \frac{\Delta l}{l_o}$ is not certain, thus it is necessary to determine the behavior of it.

3.1 Safety

For safety, operators of the universal testing machine should wear eye protection. The machine has a safety cover that is to be mounted when the machine is in use.
The metal halide lamp causes high luminance, UV radiation and has a high internal pressure during operation. The lamp may only be used in an enclosed casing specifically made for the purpose. Mercury will be released if the lamp is to break. The UV source gets hot and aging of high power radiation involves fire risks and should not be left unattended. The surrounding must be protected from the heat and radiation. Highly flammable material should not be in the line of the radiation. Looking into the light could cause eye damage. [10]

3.2 Mechanical properties

Hooks law [11]
Hooks law states that the force needed to extend or compress an object by a distance scales linearly in proportion to the length. This is only true if the object returns to its original state after releasing the force.

$$\sigma = \frac{F}{A} = E\,\varepsilon = E\frac{\Delta l}{l_o} \qquad (1)$$

Statistical data analysis [12]
Important statistics are the standard deviation and variance which you get by adding all squared values and dividing them with the number of values. Square root the variance to get the standard deviation.

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2} \qquad (2)$$

The standard deviation is then to be divided by the average of the values to get the relative variation which tells how high of a percentage the values vary from each other.

$$\frac{Standard\ deviation}{Average} = Relative\ variation \qquad (3)$$

Average of data [12]

The average, also called mean, is all results summed together and divided by the number of results.

$$\bar{X} = \frac{1}{N}\sum x_i \qquad (4)$$

Intensity of degradation

The intensity of degradation is calculated by the change in stress, strain or Young's modulus divided by the change in exposure hours. [13]

$$\frac{\Delta x}{\Delta t} = intensity\ of\ degradation \qquad (5)$$

3.3 Intensity of radiation

Intensity reduction in free space [14]

The intensity of the radiation from the UV source decays the further it gets from the source. This happens because the same amount of radiation spreads out on a bigger area. Watts per steradian and watts per area are used to measure radiation. When measuring radioactivity, Becquerel is used.

The intensity is inversely proportional to the distance from the source.
The radiation intensity decay for an isotropic source as function of distance by

$$I(r) = I_o \frac{1}{r^2} \quad (6)$$

Transmission, reflection and absorption at interface [15]
When the radiation hits a material it is reflected, transmitted and/or absorbed. when adding up absorbed, transmitted and reflected radiation energy it gives the value of the energy hitting the material.

$$1 = R + T + A \quad (7)$$

Intensity decay inside specimen (penetration depth)
The radiation intensity drop also occurs inside the specimen. [16]

$$I(r) = I_o e^{-\frac{t}{r}} \quad (8)$$

3.4 UV aging

Plastics age in different ways. The most known is the aging caused by UV-rays as it can be seen everywhere from plastic waste to outdoor furniture losing color from laying around in the sun. Degradation caused by UV radiation is photooxidative which means that polymer chains are broken and reduces molecular weight and creates free radicals. [17]
Polymers degrade by chemical, thermal, biodegradation, radiolytic, mechanical and photodegradation.
Plastics are not the only material degrading by UV. Plastics often have a supporting material in it to protect the plastic. Benzophenone and benzotriazole are common UV

blockers that protects the UV-rays and thereby makes the plastics last longer. The UV blockers doesn't last forever and only serve to lengthen the plastics lifetime. A good example of UV blocker usage is the car wax that is applied on cars before the summer. [18]

UV source.

The UV radiation source is a double-sided metal halide lamp with maximum 2500 W, 115 V, 25.6 A. The lamp is inside of an ATLAS Teleste SAT 430 solar simulation system that generates 230V Max 16 A. Figure 3 shows the UV sours after shutting it down.

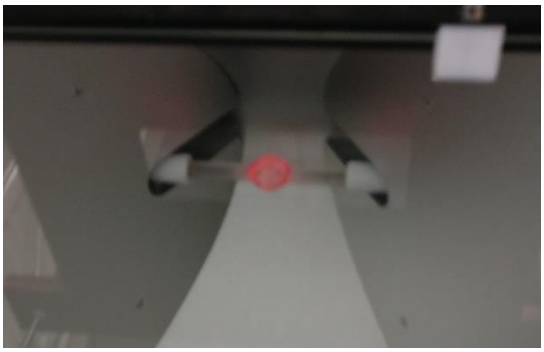

Figure 3. UV source.

The dog bones will be placed behind a metal sheet with a cut out so that only the area that is to be tested of the dog bone, is exposed. The dog bones are 200 mm from the light source cover glass. The sheet is fastened to the case with steel bars. The radiation source is on maximum at all time. Ten test pieces fit in the stand as seen in figure 4.

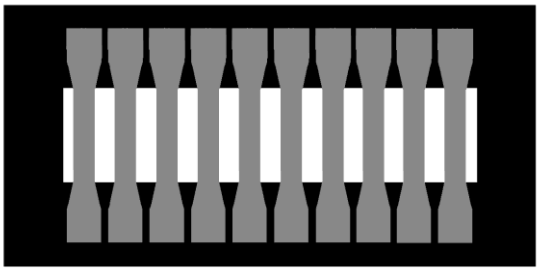

Figure 4. Stand for the dog bones.

3.5 Universal testing machine and objects

The universal testing machine is used to test durability of materials. It works by pulling or pushing an item. It has a strain sensor that records the strain and the elongation is determined by how far the clamp moves. The upper clamp moves at a constant speed while the lower stays put. The grips are self-aligned after a load is applied and the energy to pull or push starts being recorded. Figure 5 shows a universal testing machine.

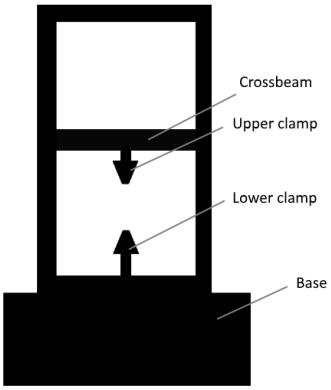

Figure 5. Universal testing machine.

The machine is the Testometric M350-5CT. [19] It can perform pulling, pushing and 3-point bending. The length of the test specimen (starting position) and the speed of the clamp must be chosen in the software before the test. The machine records energy applied, elongation and time.

Problems can occur if the clamps holding the dog bone aren't fastened tight enough and the test specimen starts to creep. It is easy to see if creeping has occurred since it leaves marks on the dog bone. Other things to take into consideration is to fasten the test piece straight. If it is angled, the test piece loses tested width as seen in figure 6. [20]

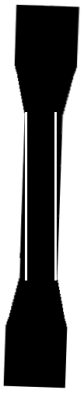

Figure 6. Width lost when angled.

Dog bone [8]

The dog bones are of measurement standard ASTM Designation: D 638 - 67 T.
The dog bone is of type I for dog bones under 7 mm thickness. The measurements standard requires: length 165 mm (+-no maximum) with the length between the clamps being 100 mm, width 19 mm (+-6 mm) width testing area 13 mm (+-0,5 mm)
The thickness must be under 7 mm and in this experiment 3 mm is used.
The PP dog bones are injection molded at a temperature of feed 280, rear 282, middle 278 and front 275 ^{o}C.
The PET dog bones are injected at 245 ^{o}C feed, 235 ^{o}C rear, 225 ^{o}C middle and 190 ^{o}C front.

PET [21]

Polyethylene terephalate is the most commonly used thermoplastic in the world. PET has many strong properties that makes it widely used. It has high chemical resistance, doesn't break easily, it is transparent and has a very high strength to weight ratio. It was first developed to be used as a textile fiber. Today PET is most known to be used in clothes and as packaging material in the food industry. The PET used in the test is transparent which could help with letting the UV rays penetrate further into the material.

PP [22]

Polypropylene is a widely used thermoplastic. It is known for being resistant to organic solvents and being flexible. PP oxidates at higher temperatures which has been a problem when using it in injection molding. PP could be transparent but is normally made in a milky white color like in this test.

3.6 Calculations

How to get Stress, strain, E module [23]

The testometric machine doesn't give the stress, strain and young's modulus right away. The machine only gives the elongation values, force and time. Only elongation and force are needed in the calculations.

stress

Stress calculation is made by the formula (9)

$$\frac{F}{A} = E \cdot \varepsilon = \sigma \qquad (9)$$

Locate the highest force in the test. Divide it by the cross-sectional area, which is

$$13 \cdot 3\,mm = 39\,mm^2$$

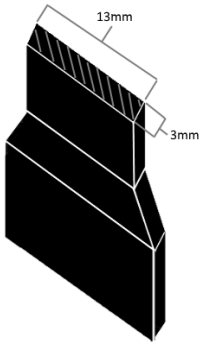

Figure 7. Dog bone cross-sectional area.

Strain

$$\varepsilon = \frac{\Delta l}{l_o} \quad (10)$$

The deformation at the time when the force is the highest divided by the tested length. Deformation/100 mm = Strain maximum in percent.

E module

To calculate the Young's modulus, tensile stress and extensional strain in the linear portion of the test must be known. Formula (11) shows the calculation.

$$F = \frac{EA}{l_o}\Delta l \quad (11)$$

$$Slope = tan\,\alpha = \frac{EA}{l_o} \quad (12)$$

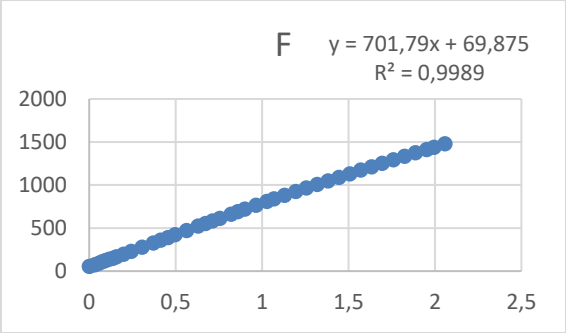

Figure 8. Tensile stress.

To get the elastic stress, linear part of the test must be located in the results. The elastic stress is in the start of the graph in the slope leading up to the maximum force. Creating a graph helps a lot with finding the linear stress section.

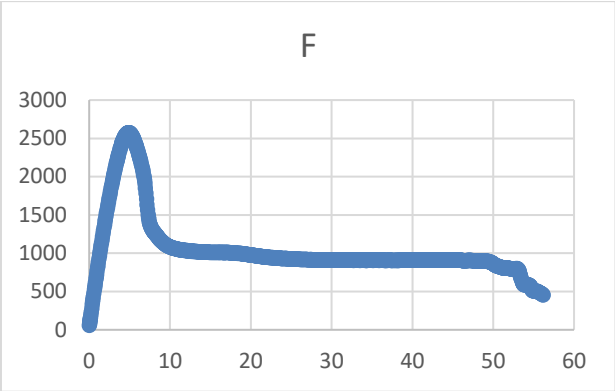

Figure 9. Stress and strain curve.

The tensile stress is calculated by the force divided by the increase in length in the linear region.

Take a part from the graph which looks straight and make a new graph of it. Make a trend line and make sure the R^2 (how much it correlates to being straight) is close to 0,999 like in figure 8. Multiply the trend line with the cross-sectional area and divide it with the tested length to get Young's modulus. Higher Young's modulus means higher stiffness of the material.

Potential energy

In physics, potential energy is the energy an object has because of a positional difference to another object. On earth, potential energy can be heightened by increasing an objects altitude thereby creating a greater fall.

In chemistry potential energy is a structural arrangement of atoms and molecules which mostly is binding energy of molecules. [24]

Binding energy means the energy a bond between atoms have. The higher the binding energy, the harder it is for other energies to break it. If an energy smaller than the binding energy hits a bond, it will only heat up the material or direct the energy to another bond. If all energies hitting a bond exceeds the binding energy, it will break the bond. If these broken bonds add up, it will result in the material aging. For macroscopic damage to be observed, a high number of bonds must break. The material will become more brittle.

Reflection and transmission doesn't contribute to material degradation, but transmission could direct the energy further into the material to a bond which could break. [25]

Photoelectric effect [26]

If the frequency of light is high enough, electrons or other free carriers are released from the matter it hits. Electrons released in this way is called photoelectrons.
Photoelectric effect is quantified and by treating the light as packets (photons) it solves the problem to why electrons are released even at low intensities. The photons have a greater amount of energy the higher frequency it has.

Plancks relation [27]

Plancks relation is an equation that changes the energy of a particle to a frequency times Plancks constant.

$$E = hf \qquad (13)$$

Ionization [28]

Radiation with high enough energy is ionizing which means that the rays destroy bonds in the material. The rays destroy bonds by hitting an electron and pushing it out from an atom. When an atom has fewer electrons it is called an ion. Electrons have an ionization energy threshold, which is the energy required to push away the loosest electron. The further away from the nucleus an electron is, the less ionization energy it has.

Expected results

This thesis speculates that the Young's modulus decreases or remains constant, after prolonged radiation. Strength of the material is expected to decrease. The strain limit of elastic deformation is decreased.

Some polymer chains could be uncured and in the earlier hours they could crosslink making the material stronger.
A problem could occur if the UV rays aren't penetrating the material deep enough and results in only one side degrading. This will make the Testometric test skewed.
Other thinks taking to consideration is that the lamp isn't strong enough and the material only heats up a bit leaving the material unchanged after cooling down.
The quality of the dog bones could be of a bad enough standard to make the results not visible.

4 METHOD

First of all, ten test pieces are tested in a universal testing machine. Testing the material for stress and strain gives a base value that can be used for comparison to the situation after UV treatment. It serves as a reference for further testing.
The testometric software is started on a computer that has contact to the testometric machine. The test speed is set to 40mm/minute. First the clamp has to be steered to the right height so the dog bone can be fastened. The dog bone is fastened vertically to the clamps and after the clamps are tightened a small load will appear in the software. The load is reset and the test can be started and continued until the dog bone breaks. The data should be exported to an external memory.

5 PERFORMING OF TESTS AND THEIR RESULTS

The PP and PET are tested for quality by calculating the standard deviation and relative variation of ten unaged dog bones.

5.1 Unaged sample PET

Table 1. Unaged PET

PET unaged	σ [MPa]	ε (MAX)	E [MPa]
	85,79333	0,04847	210,537
	84,18667	0,04782	205,245
	82,74667	0,05014	196,203
	86,27667	0,05012	203,076
	83,23	0,05073	197,787
	85,13667	0,048	209,67
	84,74667	0,04983	210,537
	84,06333	0,04683	209,406
	84,07333	0,04877	199,863
	84,05	0,04859	181,626
	81,82	0,04949	177,636
PET average	84,19303	0,048980909	200,1442
Standard deviation	1,296217	0,001186385	11,3924
relative variation	0,015396	0,024221373	0,056921

In unaged PET-samples E is 200,1442, sigma is 84,19303 and strain 0,048981, standard deviation is for E 11,3924, sigma 1,296217 and strain 0,001186. The E values vary by 5,6 %.

The dog bones didn't show any faults in the testing. The clamps aligned well and there were no big creep marks that could indicate loosely fastened clamps. Figure 10 shows that no creeping occurred.

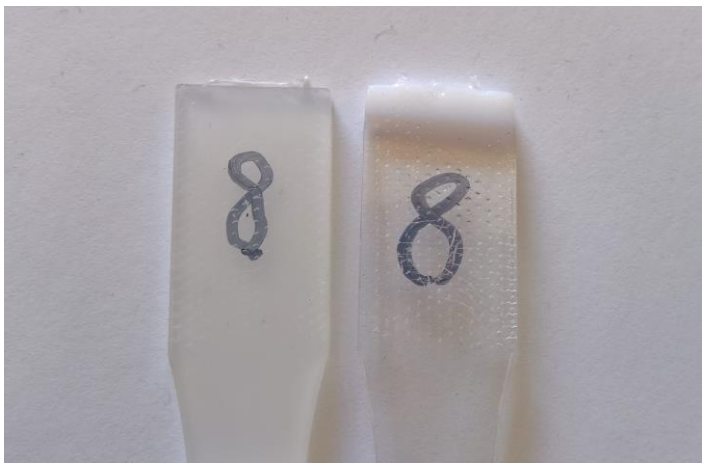

Figure. 10 small clamping marks on dog bones.

5.2 Unaged sample PP

Table 2. Unaged PP.

PP unaged	σ [MPa]	ε (MAX)	E [MPa]
	44,43	0,09399	125,799
	43,55667	0,09864	118,503
	42,02	0,09091	122,796
	43,88333	0,09822	123,813
	39,41667	0,0921	114,495
	44,09333	0,0922	126,078
	39,28333	0,09078	112,551
	43,05667	0,09204	124,338
	40,04	0,09194	115,29
	38,29	0,09177	110,547
PP average	41,807	0,093259	119,421
Standard deviation	2,325251	0,002861078	5,84969
relative variation	0,055619	0,030678837	0,048984

In un aged PP samples E is 119,421. sigma is 41,807 and strain 0,093259.
Standard deviation is for E 5,84969, sigma 2,325251 and strain 0,002861. The E values differs by 4%.

5.3 10-hour UV test for PP and PET

The dog bones are 200mm from the light sources cover glass. The radiation source is on maximum at full time. Ten test pieces fits in the stand.
To get knowledge of how the plastics act from UV radiation, ten dog bones of each plastic are Treated for 10 hours in front of the UV source. The UV treated dog bones are tested the same way as the ten reference dog bones by the universal testing machine and a general percent of how much the plastics degrade in ten hours is determined.

10-hour UV test.

Table 3. 10-hour UV exposure.

PET 10 hour exposure	σ [MPa]	ε (MAX)	E [MPa]
	90,10667	0,05211	200,859
	89,84	0,0525	199,665
	92,39667	0,05327	197,928
	91,28	0,05338	206,232
	91,76	0,05148	205,68
	92,74333	0,05449	204,594
	91,46	0,05442	199,212
	93,2	0,05558	198,159
	91,36	0,05359	202,434
	91,10667	0,0525	206,784
PET UV average	91,52533	0,053332	202,1547
PET average	84,19303	0,048981	200,1442
	0,919888	0,91841671	0,990055
Procentual difference	0,080112	0,08158329	0,009945
Standard deviation	1,065747	0,001245372	3,446065
relative variation	0,011644	0,023351306	0,017047

After 10 hours of UV treatment, PET's stress got better. The strain rose with about 8 % and the Young's modulus increased about 1 % making the material stronger. This could be because of un crosslinked polymer chains crosslinking from the energy of the UV light. This could also be a small enough change to just be a fluctuation in the dog bone quality and the PET hasn't degraded at all. Interesting is that the PET dog bones warped. The side closer to the lamp shrank or the back expanded. The stand that holds the dog bones in front of the lamp seemed to get hot since the dog bones changed color where they had contact with the stand (figure 11).

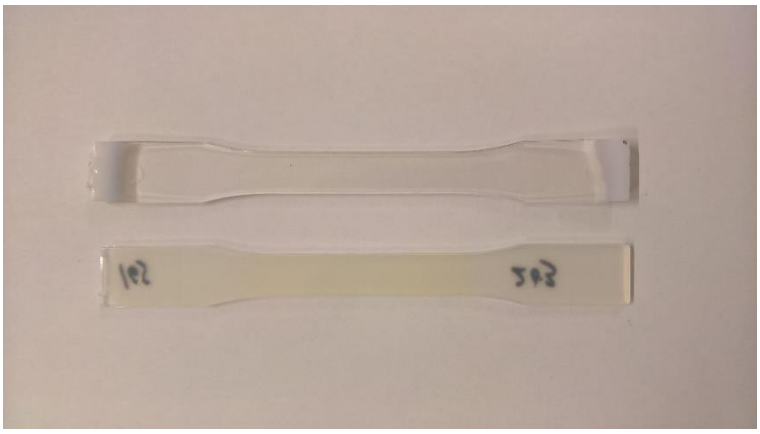

Figure 11. Dog bones after 10-hour exposure.

Table 4. 10-hour UV exposure.

PP 10 hour exposure	σ [MPa]	ε (MAX)	E [MPa]
	42,95667	0,10057	111,591
	43,32	0,10107	113,751
	42,13	0,10107	111,558
	43,71333	0,10025	116,301
	43,54	0,1004	114,063
	40,34	0,09899	111,327
	42,82	0,09932	111,573
	43,15667	0,10021	113,781
	43,15667	0,10021	114,783
PP UV average	42,7925933	0,100232222	113,192
PP average	41,807	0,093259	119,421
	0,97696813	0,930429336	1,05503
Procentual difference	0,02303187	0,069570664	-0,05503
Standard deviation	1,02661765	0,000700228	1,765919
relative variation	0,02399055	0,006986058	0,015601

PP had the stress rise with 2 % and strain with 7 %. The Young's modulus decreased with 5,5%. The UV treatment had made the material more elastic. The material didn't get any visible change. The color is intact and no warping visible.

Because of the ten dog bones not showing much degradation, a longer exposure is done. PP had a loss in Young's modulus by 5 % and PET only 1 %. The second test's objective is to radically degrade both plastics and get to know how they degrade.

One dog bone of each plastic is degraded for 48 hours. The possible irregularities of the dog bones will hopefully be irrelevant in this test, because of long exposure time making the degradation difference bigger than the differences in the dog bones. If the degradation is small, it won't be because of faults in the dog bones but rather the radiation being too small and the bonds not breaking. One dog bone of each plastic is put into the machine for 5 days during work hours (8 hours). By adding dog bones, more data can be gathered. By stopping UV treatment of one dog bone of each plastic every day, a better vision of how the dog bones are aging is realized.
6 PP and 6 PET dog bones are exposed for 8, 16, 24, 32, 40, 48 hours. Then the dog bones are tested in the universal testing machine and the rate of degradation is calculated.

5.4 48-hour aging of PP and PET

8, 16, 24, 32, 40, 48-hour UV test

The PET dog bones warped like in the 10-hour UV test, but no visual degradation is observable. The PP plastic didn't bend like the PET plastic, but the dog bones exposed for more than 16 hours got yellowing where the UV rays hit it.

PP

The first 8 hours gave the dog bones a loss in young's modulus. The Yong's modulus starts climbing and the last sample rose a lot. The Young's modulus curve looks to get steeper at the end reminding of a quadratic curve. The PP plastic has undergone curing and produced new bonds in the material. Table 5 shows the change in stress, train and Young's modulus for PP with 8-hour intervals.

Table 5. PP prolonged exposure.

Exposure time hours	σ [MPa]	ε (MAX)	E [MPa]
8	43,96	0,09463	140,283
16	42,72333	0,09475	126,126
24	37,29	0,09471	133,155
32	25,03	0,09458	132,771
40	45,38333	0,0934	136,782
48	45,06	0,09381	139,314
Standard deviation	7,862264	0,00056691	5,223146
average	39,90778	0,094313333	134,7385
relative variation	0,197011	0,006010918	0,038765

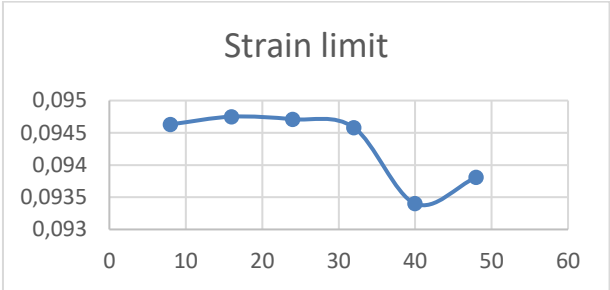

Figure 12. PP strain limit.

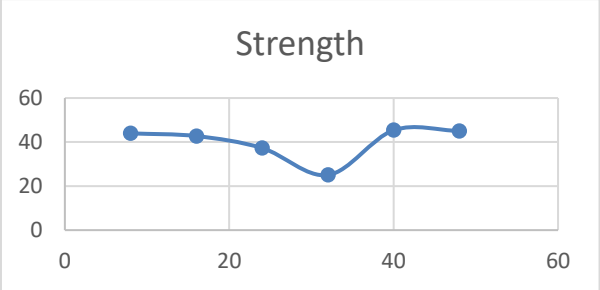

Figure 13. PP strength.

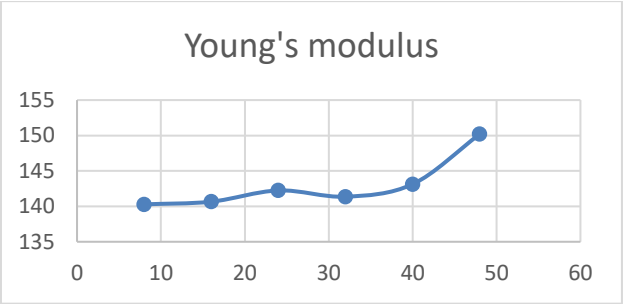

Figure 14. PP Young's modulus.

The stress and strain curves doesn't give information on degradation or curing. The Young's modulus curve on the other hand shows a steady rise in stiffness as seen in figure 14. The rise in Young's modulus is calculated to be 0,2478 MPa/h. Table 11 shows the difference in Young's modulus from piece to piece.

Table 6. PP Rate of curing.

Δ E/T	ΔMPa/h
0,047125	MPa
0,198125	MPa
-0,11025	MPa
0,220875	MPa
0,883125	MPa
0,2478	MPa

PET

The last two PET samples shattered in the Testometric test as seen in figure 15. It is a clear sign that the material has become extremely brittle. The mathematical results show the same results. The stress and strain both rouse sharply before the last two samples which means that the material is getting stiffer and, in the end, depleting the material. The last two samples show that the strength and strain limit drops which means that the material has become fragile and breaks more easily. Young's modulus doesn't change much and means that the material degrades and produces new bonds at the same time.

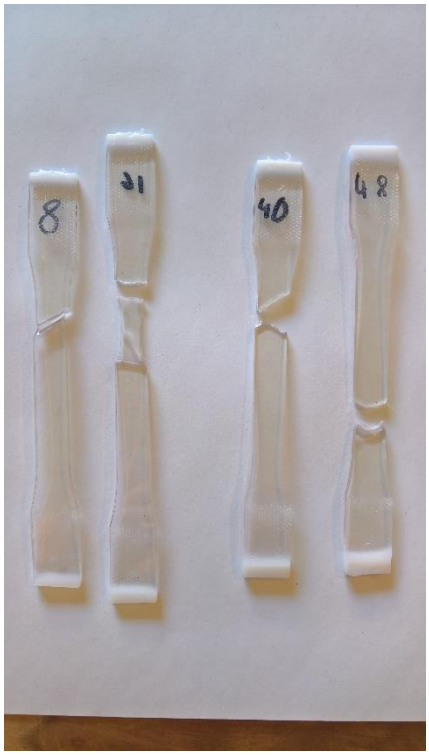

Figure 15. Shattered 40 and 48-hour dog bones.

The strength curve, seen in table 14, shows steady rising until the last two samples. The rate of reduction can be calculated by eliminating the two last samples. The rate of reduction is calculated to be 0,386 MPa/hour. Table 8 shows the change in MPa from piece to piece. The right column only takes the first four test pieces in to consideration. Table 7 shows the change in stress, train and Young's modulus for PET with 8-hour intervals.

Table 7. PET prolonged exposure.

Exposure time hours	σ [MPa]	ε (MAX)	E [MPa]
8	88,01333	0,05204	217,452
16	90,79	0,05373	199,122
24	93,46667	0,05456	214,902
32	97,27333	0,05697	198,879
40	96,89333	0,0555	206,433
48	96,39333	0,05469	225,84
standard deviation	3,768678	0,001658016	10,80784
average	93,805	0,054581667	210,438
relative variation	0,040176	0,030376791	0,051359

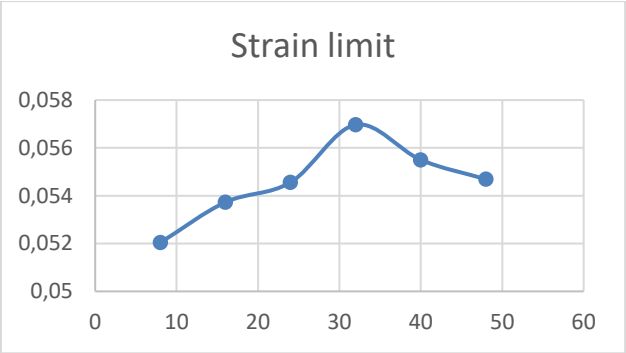

Figure 16. PET Strain limit.

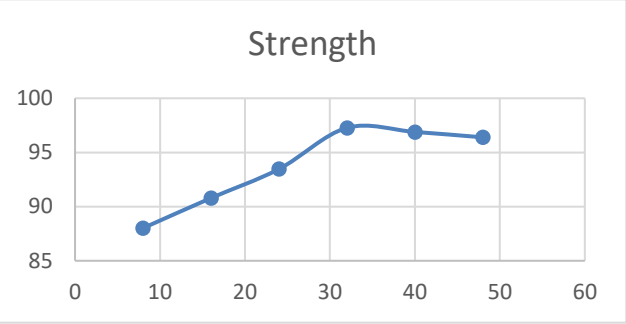

Figure 17. PET Strength.

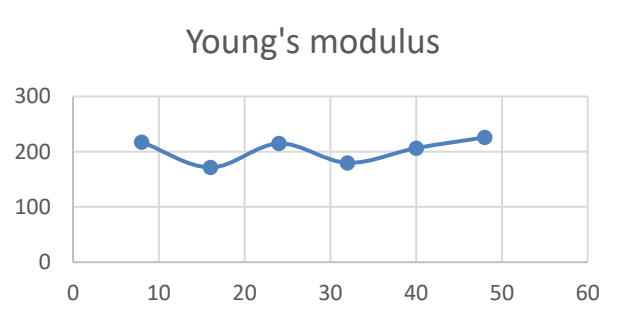

Figure 18. PET Young's modulus.

Table 8 shows the difference in Young's modulus from piece to piece.

Table 8. PET rate of reduction.

Δ σ/T	Δ σ/T	
0,34708375	0,347084	MPa/h
0,33458375	0,334584	MPa/h
0,4758325	0,475833	MPa/h
-0,0475		MPa/h
-0,0625		MPa/h
0,2095	0,385833	Mpa/h

6 DISCUSSION

The relative variation shows that the samples are of a good enough quality to show variation in the results due to UV exposure.

The methods used proved effective. Both types of plastics degraded, and in two different ways. The PET plastic shattered which is a sign that it degraded more homogenously and affected the whole sample due to the plastic being transparent and letting the rays trough. Interesting is that the PET warped aggressively as depicted in figure 19. It could be because of the stand holding the samples was hot and the plastic touched the wall only on one side. This is probably the case due to the PP not having the same marks where the dog bones touch the stand and the same not happening for it.

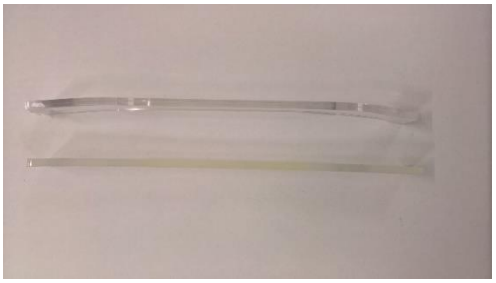

Figure 19. PP and warped PET samples.

Another reason could be that the sample's surface towards the UV source degraded more than the other side or the heat from the lamp affecting the surface somehow. PP is less transparent and the surface towards the UV source should degrade more than the surface of the PET.
The PP plastics Young's modulus rises a lot at the end. Longer exposed samples could have really helped in determining how far the material keeps on getting stiffer.
The test can't be compared to outdoor degradation due to the irradiation not being known. The temperature from the UV source is unknown and is a factor affecting when bonds are created and broken.

7 RECOMMENDATION FOR FURTHER STUDIES

The dog bones injection parameters weren't known when the experiment was performed. It doesn't affect the results but is good to know if the test is to be done again. Some dog bones may have been of bad quality, but the UV treatment averaged out the differences according to the relative variation calculations. By having good quality test specimen from the beginning, more precise results can be obtained.
More investigation could be done to get to know the reason to why the PET plastic warped so much and the PP didn't.
The test can be calibrated to simulate outdoor UV intensity by measuring the irradiance from the sun and putting the dog bones further away from the UV source to match the irradiance.
The UV source's power supply reference wasn't found.

8 SAMMANFATTNING

Syftet med arbetet är att lära sig räkna ut den förväntade livslängden för UV föråldrat termoplastiskt material. Genom att UV-bestråla plasterna och mäta mekanisk spänning, deformation och elasticitetsmodulen kan man räkna ut graden av degradering.

8.1 Metod

Metoden är att belysa PET och PP med UV strålning och mäta graden av degradering. Som strålningskälla används en metallhalogenlampa och för att mäta plasternas egenskaper används en universell testmaskin i ett drag test. Provbitarna är standardiserade ”dog bone”. Standardavvikelsen är uträknad för obestrålade provbitar och jämförd med tio timmar UV bestrålade provbitar för att få veta om kvaliteten av plasten är tillräckligt bra för att användas till testerna. De tio timmar bestrålade plasterna fungerar också som en referens till hur länge man skall bestråla för att se en trend i degraderingen. De längre bestrålade plasterna bestrålas i 48 timmar och är med åtta timmars mellanrum testade för mekanisk spänning, deformation och elasticitetsmodul.

8.2 Resultat och slutsats

Resultatet visar sig vara att båda plasterna förändrades på olika sätt. PET föråldrades på 48 timmar jättemycket och de två sista plasterna splittrades i drag testet vilket betyder att plastens elastiska egenskaper har tagit slut. PP blev också styvare men hade inte lika våldsam reaktion. Däremot visade sig att PP bytte färg till att bli mera gul-aktig vilket är ett tecken att plasten förändrats.
PET:s elasticitetmodul ändrades inte så mycket medan den mekaniska spänningen och deformationen steg tills de två sista provbitarna. Detta är ett exempel på att bindningar både bryts och bildas på samma gång. De två sista provbitarna bestrålades under 40 och

48 timmar och det visade sig att materialet utmattats. Genom att ta bort de två sista resultaten från räkningarna kan man få ut en grad av degradering.

Table 9. PET:s grad av degradering.

Δ σ/T	Δ σ/T	
0,34708375	0,347084	MPa/h
0,33458375	0,334584	MPa/h
0,4758325	0,475833	MPa/h
-0,0475		MPa/h
-0,0625		MPa/h
0,2095	0,385833	Mpa/h

PET:s grad av degradering är uträknat till 0,386 MPa per timme.
PP reagerade till UV strålningen med att bilda mera bindningar i materialet och elasticitetsmodulen höjdes ju längre tid plasten bestrålades. Den mekaniska spänningen föll i mitten av de 48 timmarna och deformationen föll under de 16 sista timmarna. Den jämnaste kurvan hade elasticitetsmodulen och med att räkna ut graden av reducering så kom man fram till 0,248 MPa per timme.

Table 10. PP:s grad av reducering.

Δ E/T	
0,047125	MPa/h
0,198125	MPa/h
-0,11025	MPa/h
0,220875	MPa/h
0,883125	MPa/h
0,2478	Mpa/h

Med flera provbitar kunde man få fram hur långt plasten härdar och om egenskaperna till slut ger efter.

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