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Effects of Heat, Moisture and UV-irradiation on the Properties of Polyurethane Membranes

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Civil Engineering

by

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ABSTRACT OF THE THESIS

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Professor Michael K. Stenstrom, Chair

Punched membranes as fine pore diffuser material have become available in the last ten years because they are more efficient. Heat, moisture and UV light are three main factors causing degradation of plastics and rubber membranes. In order to better understand the impact of sunlight on membranes, a series of outdoor tests were conducted on actual membranes. Results of this experiment showed that heat decreased hardness values; existence of UV light resulted in decreased modulus values; heat only had very slight effect on thickness and weight. To prevent membranes from degradation, it is suggested that they are stored in water as deep as at least 24 cm and they are covered with UV filter, especially when the weather is hot and UV light is strong.

The thesis of Tan Zou is approved.

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University of California, Los Angeles

2014

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1 Introduction

1.1 Fine pore diffusers

Aerobic biological processes are important in wastewater treatment. By diffusing oxygen through orifice into wastewater, bacterial growth is encouraged. In 1916, porous diffuser plates were used for aeration. There are two types of diffusers: course bubble diffusers and fine bubble (fine pore) diffusers. Course bubble diffusers produce bubble diameter of 10 to 20 mm, while bubble size produced by fine bubble (fine pore) diffusers is 2 to 4mm (Cincinnati, n.d.).

Fine pore diffusers were originally named fine bubble diffusers, but later the name fine pore was adopted to indicate that the small bubbles are created by passing gas through fine pores or orifices (Cincinnati, n.d.). Advantages of fine pore diffusers are high oxygen transfer efficiency (OTE), high aeration efficiencies (AE, mass oxygen transferred per unit power per unit time), satisfying high oxygen uptake rate (OUR), adaptability to existing basins for plant upgrades, and lower volatile organic compound stripping. Disadvantages of fine bubble diffusers are that they are susceptible to chemical/ biological fouling and chemical attack and their performance may be affected by airflow distribution (Mcgee & Pearson, 1999).

Materials of diffusers can be ceramic, plastic, or flexible sheaths. The type of fine pore diffusers is determined by materials used, which include (Cincinnati, n.d.):

1. Porous ceramic plates, discs, domes, and tubes
2. Porous plastic plates, discs, and tubes

3. Flexible sheath tubes

Another way to classify fine pore diffusers is by their shapes (Cincinnati, n.d.):

1. Plate diffusers
2. Tube diffusers
3. Dome diffusers
4. Disc diffusers
5. Strips and panels

Each design has its own advantages and disadvantages. Plate diffusers were widely used throughout the 1920s, but had a number of disadvantages. The long distances created pressure drop which made it difficult to have uniform flow. Also it was difficult to replace the plates, which had to be cemented into the tank bottoms. These problems caused their decline. Tube diffusers and tube assemblies can be constructed from stainless steel or durable plastic to prevent corrosion, but it is was still difficult to obtain uniform bubble distribution. Dome diffusers were introduced to America from Europe. Each diffuser has approximately 254.34 cm^2 area. Air flow rate per diffuser ranged from 0.2 to 0.25 L/s/diffuser and were usually less than 1L/s and strongly affected oxygen transfer efficiency (OTE). Operation at air flow rates less than the manufacturer's minimum rate resulted in poor air distribution causing excessive fouling in spots with low air flow. Disc diffusers were developed in part to overcome to disadvantages of dome diffusers. The use of a locking ring and O-ring gasket in disc diffusers creates an air tight seal, which minimizes OTE reductions caused by foulants, and prevented diffusers breakage (Cincinnati, n.d.).

Important characteristics of fine pore media include: permeability, uniformity, dynamic wet pressure, strength, chemical stability, resistance to heat, and density (weight). Factors that may affect aeration systems performance are: wastewater characteristics, process type and flow regime, loading conditions, basin geometry, diffuser placement and performance characteristics, changes in performance due to fouling, mixed liquor DO control and air supply flexibility, mechanical integrity of the system, operator expertise and quality of preventive maintenance (Cincinnati, n.d.).

One of the largest problems that a diffuser may have is fouling. Local flux rate, which is defined as the air flow rate per unit area of a small defined segment of a given diffuser, affect fouling rate. High local flux rates may increase fouling rate, and then flux rate may be reduced. Their combined effect may result in uniform bubble distribution. At the places where foulants accumulate, pores are blocked and pore diameter is reduced. As a result, DWP may increase and OTE may also increase, but the backpressure may exceed the capabilities of the air supply system and cause operational failures (Cincinnati, n.d.). Performance of diffused aeration systems are also determined by wastewater characteristics, process type and flow regime, loading conditions, basin geometry and others (Mcgee & Pearson, 1999).

1.2 Membrane materials

The most common materials used for diffuser membrane construction are ethylene propylene diene monomer (EPDM), polyurethane (Polyurethane), nitrile (NBR), silicone, polyethylene (PE), and polyvinyl chloride (PVC). Each one can be used for different purpose in fine pore diffusers. No materials are suitable for all types of wastewaters. These materials can be further classified as plastics and rubber. Plastics materials include PE, Polyurethane, PVC, polypropylene (PP), and others. Most important rubber materials are EPDM and silicone rubber. Rubber can be natural rubber and synthetic rubber.

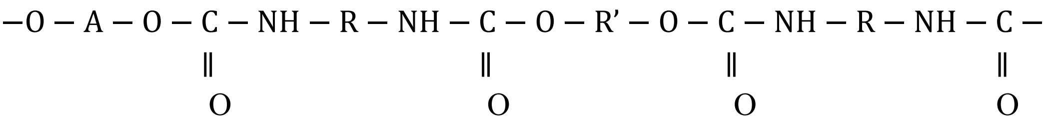
Formation of Polyurethane material starts with reaction between a block polymer with OH end groups and a diisocyanate. Chain extension can be described as (Corish, 1959).

$$\begin{gathered}-\mathrm{OH}+\mathrm{OCN.R.NCO}+\mathrm{HO}-\mathrm{OH}+\mathrm{OCN.R.NCO}+\mathrm{HO}-\\ \downarrow \\ -\mathrm{O.OC.NH.R.NH.CO.C}-\mathrm{O.OC.NH.R.NH.CO.O}-\end{gathered}$$

If excess diisocyanate exists, further chain extension continues. When water, glycol, or diamine is added, urea or diurethane groups are formed. The reaction is (Corish, 1959):

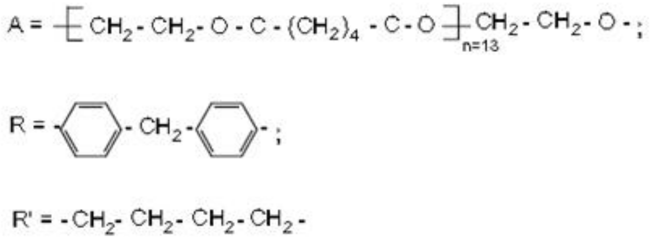
$$\begin{gathered}\mathrm{OCN}-\mathrm{NCO}+\mathrm{H_2O}+\mathrm{OCN}-\mathrm{NCO}+\mathrm{H_2O}+\mathrm{OCN}-\\ \downarrow -\mathrm{CO_2} \\ \mathrm{OCN}-\mathrm{NH.CO.NH}——\mathrm{NH.CO.NH}-\end{gathered}$$

Chemical structure of the synthesized Polyurethane (Rosu, Rosu, & Cascaval, 2009):



$$-O-A-O-\underset{\substack{\| \\ O}}{C}-NH-R-NH-\underset{\substack{\| \\ O}}{C}-O-R'-O-\underset{\substack{\| \\ O}}{C}-NH-R-NH-\underset{\substack{\| \\ O}}{C}-$$

Where



The urethane group NH-(C=O)-O- is the link.

If isocyanate polymer exists, cross linking may appear, and the products will be highly elastic and resistant to tearing and extensibility (Corish, 1959).

Properties of membranes that are important for diffuser materials include endurance, thickness, test strength, tensile strength, maximum allowable extractible oil content, hardness, opening size and oxygen transfer in standard clean water and in-process water (International, 2005b).

Table 1 shows advantages, disadvantages and usages of some common and new diffuser materials (International, 2005a):

Table 1 Properties of different materials (International, 2005a)**:**

Polymer	Low temp	High temp	Resistant to	Attacked by
EPDM	-60℃	150℃-S, 177℃-P	Heat, oxygen, ozone, animal and vegetable fats	Solvents, aromatic, hydrocarbons
Fluoroelastomers	-40℃	200℃	Oils, acids, chemicals, fuel and oxygen	KETONES, low MW esters
Silicone	-65℃	315℃	Heat, ozone, oxygen, concentrated bases	Solvents, oils, acids
Nitrile	-40℃	120℃	Oils, fuels, fates, hydrocarbons	Ketones, esters, aldehydes
Polyurethane	-68℃	80℃	Oils, solvents, high abrasion resistance	Acids, ketones, esters
HNBR	-30℃	150℃	Heat, ozone, oils, chemicals	Ketones, esters, aldehydes
Neoprene	-40℃	120℃	Ozone, acids, fats, greases	Acids, ketones, aromatic hydrocarbons

1.3 Weathering

Factors that influence membrane properties include solar radiation, microorganisms, bacteria, fungus, high humidity, ozone and oxygen, water (vapor, liquid, or solid), thermal energy and pollutions (industrial chemicals) (Shah, 2007).

Heat is transferred through three processes: radiation, conduction and convection. Sun is a natural source of radiation. Contact between objects results in heat transfer through convection (gas or liquid phase), conduction and advection (Park, 2001). Air and water surfaces are heated by convection. Higher temperature accelerates degradation process. Temperature of materials exposed to heat is not always the same to ambient temperature, and materials with darker color become hot more rapidly than those with lighter color (*Accelerated and Outdoor Durability Testing of Organic Materials, Issue 1202*, 1994).

Some chemicals can enhance EPDM’s resistance to heat. Stabilizers in EPDM are efficient in retarding oxidation under 100℃. Softeners have very small effects. Above this temperature, carbon black stabilizes EPDM membranes under 150℃. A high concentration of carbon black is recommended. Oxidation also takes place very rapidly when EPDM is exposed to radiation and rain. As a result, part of tensile strength of material is lost (Delor et al., 1998).

There are two main types of moisture: relative humidity and wet time. Relative moisture is used to measure the relative amount of water vapor in the air, while wet time is the length of time material has water on the surface. The worst condition occurs when high temperature and high humidity occur at the same time (Davis & Sims, 1983).

Moisture accelerates degradation of membrane through three types of processes. In hydrolytic processes water chemically reacts with material, causing chalking. Cycling of moisture, which means repeated drying and wetting, results in mechanical stresses in materials. When water on the surface of plastics dries, stresses at the interface increases after evaporation. Water as a solvent may cause plasticization (loss of flexibility), and expose the material to dissolved oxygen. Oxygen diffusion working with solar radiation starts photo-oxidation reactions (Andrady, Hamid, &

Torikai, 2011)'(Mark, 2013)'(Boubakri, Elleuch, Guermazi, & Ayedi, 2009).

Figure 1 shows destruction of polymer by water molecule diffusion (Mark, 2013):

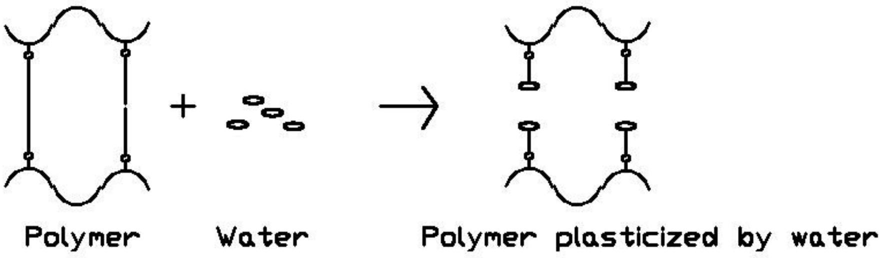


Figure 1 Destruction of polymer by water molecule diffusion

Oxygen, ozone and shear cause chain scission and cross-linking. Chain scission will cause softening and weakness in materials, as mentioned before. Cross-linking is caused by radical cross-linking reactions, which may produce more cross-links in materials. As a result, materials such as EPDM will become stiffer (*Handbook of Specialty Elastomers*, 2010).

Radiation with different wavelengths has different effects on membrane material. Infrared light and visible light at longer wavelength have optical effects and result in photo-chemical effects. They are also called non-ionizing radiation. UV light at shorter wavelength has higher energy that can break chemical bonds and even damage DNA, and is defined as ionizing radiation (US EPA, 2006). Table 2 and 3 show types of radiation and relationship between wavelength and irradiance. Irradiance is measured in units of Watts/cm^2 or mW/cm^2. Energy density is mostly commonly measured in units of J/cm^2.

Table 2 Types of radiation in the electromagnetic spectrum (US EPA, 2006)

	Non-ionizing					Ionizing		
Type of radiation	Extremely low frequency	Radio	Microwave	Infrared	Visible light	Ultraviolet	X-ray	Gamma rays
Effects	Non-thermal		Thermal	Optical		Broken bonds		
	Induces low currents		Induces high currents, heating	Excited electrons, photo chemical effects		Damages DNA		
Source	Static field	Power line, AM radio	AM radio, FM radio TV, microwave, oven	Heat lamp, tanning booth		Tanning booth, medical x-rays		

Table 3 Relationship between irradiance and wavelength (*Coatings Technology Handbook, Third Edition*, 2005)

Sunlight, Xenon with daylight filter							
Wavelength (nm)	260-280	280-300	300-320	320-340	340-360	360-380	380-400
Irradiance (W/m^2/nm) (approximate)	0	0-0.1	0.1-0.25	0.25-0.5	0.5-0.75	0.75-0.95	0.95-

Ultraviolet radiation (UV) has electromagnetic spectrum between X-rays and visible lights. types of UV light and their wavelengths are listed in Table 4 (“Ultraviolet Radiation,” n.d.):

Table 4 UV light and wavelength

UV	Vacuum UV	Far UV	UVC	UVB	UVA
Wave length	40-190nm	190-220nm	220-290nm	290-320nm	320-400nm

Not all types of UV light will cause damage on materials. When UV light has a wavelength that corresponds to specific bond energy in polymer chain, it may cause a reaction. This response can break chemical bonds, and this process is called chain scission (*Characterization and Failure Analysis of Plastics*, 2003). UV C kills bacteria. UV B is the most destructive type of UV radiation, with energy high enough to cause photochemical damage. UV A only has a pigment-darking effect, so it is often called "black light." UV A lamps are widely used in phototherapy and tanning booths as a UV light source ("Ultraviolet Radiation," n.d.). Results of chain scission include embrittlement, discoloration, and reduction, affecting physical and electrical properties of membranes. Artificial lights sources include xenon arc lamps, fluorescent lighting, and sun lamps (Shah, 2007).

Light energy is a function of wavelength. Longer wavelength penetrates more deeply into membranes but it has less energy, while shorter wavelength have greater effect on the surface of material (*Characterization and Failure Analysis of Plastics*, 2003). So the energy of UV light is higher than that of visible and infrared light.

Not all plastics and rubbers would be damaged by UV radiation after exposure. Chemical bonds are broken by radiation (also called chain scission) when bond energy in the polymer corresponds to particulate photo energy. For different materials, UV light with different wavelength has different effects. Longer wavelength goes deeper in the materials, but its effect may not be the strongest due to increasing hardness after absorbance. Energy shorter wavelength can be absorbed within a few micrometers of thickness, and the membrane surface may be destroyed (*Characterization and Failure Analysis of Plastics*, 2003). After exposed to UV radiation, photochemical degradation occurs with scission of urethane group and photo oxidation of the central CH_2 group between aromatic rings. These processes result in yellowing of polyurethane materials (Rosu et al., 2009).

Material that is UV resistant absorbs less UV radiation compared with other materials. Plastics resistant to UV light are polytetrafluoroethylene (PTFE), polymethylmethacrylate (PMMA), PP, polyethylene (PE), and polymethylpentene (TPX). To reduce photo-oxidation caused by UV light,antioxidants, UV absorbers, UV light screens, quenchers, radical scavengers or traps can be added to the material (Wright, 2001).

Wavelengths that some types of polymer are sensitive to are showed in Table 5 and Figure 2:

Table 5 wavelength of maximum photochemical sensitivity (*Characterization and Failure Analysis of Plastics*, 2003)

Polymer	**Wavelength**	
	nm	**Å**
Polyesters (various formulations)	325	3250
Polystyrene	318	3180
Polyethelene	300	3000
Polypropylene (nonheat stabilized)	370	3700
Polyvinyl chloride	320	3200
Polyvintl chloride, copolymer with polyvinyl acetate	327-364	3270-3640
Polyvinyl acetate	280	2800
Polycarbonate	285-305,330-360	2850-3050, 3300-3600
Cellulose-acetate-butyrate	296	2960
Styrene-acrylonitrile	290,325	2900,3250

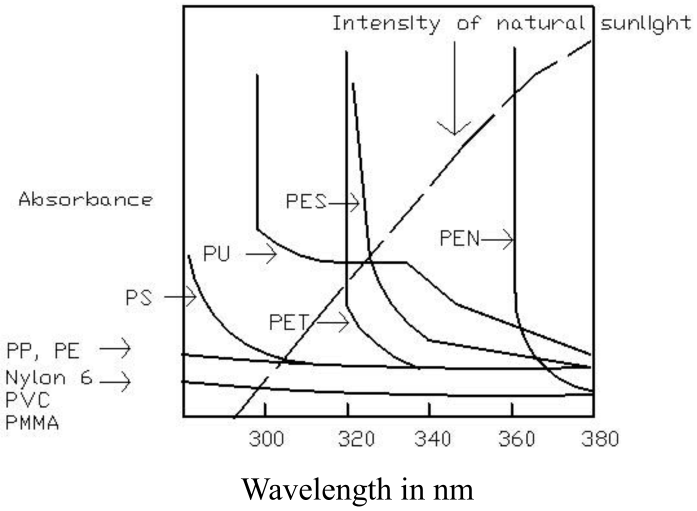


Figure 2 UV absorbance of various plastic compared with the intensity of natural sunlight (Wright, 2001)

UV light introduces more free radical oxidations into rubber and then causes damage. The combination of light, heat and humidity worsen this situation. The color of the material also matters. Black compounds will absorb more heat, but they are more resistant to UV light (*Handbook of Specialty Elastomers*, 2010).

Methods used to block UV light include using antioxidants, UV absorbers and light screens, quenchers, radical scavengers or traps (Wright, 2001). Chemicals added to membranes to protect it from UV light include two groups: UV absorbers and UV stabilizers. The best pigment by far in absorbing UV light is carbon black, which transfers this radiation to other type of less destructive radiations. UV stabilizers use chemical means to prevent chemical scission or dissipate the energy to lower and less harmful levels (Shah, 2007).

Other factors accelerate deterioration of materials include pollutants, like inert particulate matter, biologically active material and reactive gases. Dust may accumulate on the surface of specimens. Sulfur compounds, ammonia, oxides of nitrogen, other volatile pollutants and their derivatives may chemically or physically damage material (Davis & Sims, 1983).

Polyurethane materials are composed of polyester chains (flexible segments) and urethane groups (hard segment). Micro phase separation of the two segments determines its properties. Properties of polyurethane change though biodegradation. H_2O_2 and OH* initiate free radical reaction and then cause oxidation. Polyurethane exposed to UV light loses physical integrity and color. This process is followed by enzymatic (hydrolytic) degradation as another possible reason for biodegradation. Interaction between the two segments decreases crystallinity and hydrogen bonding in the hard part and increases photooxidation (Oprea & Oprea, 2002). For UV aging, urethane linkage bonds breaks first, then results in the phase separation between the two segments (Jana & Bhunia, 2008).

1.4 Weathering tests

There are two types of weathering tests: the accelerated test and the actual outdoor exposure test (Shah, 2007). The accelerated indoor test accelerates the degradation process by using an artificial light source with a much higher intensity. It cannot completely simulate the natural environment but may save time and all parameters are controllable. Actual outdoor exposure means no special equipment is required and the sun is the only light source. To study a product's service year, the outdoor test may take more than five years before failure of material (Chin, Nguyen, XIAOHONG, Byrd, & Martin, 2006). Temperature and humidity depend on the weather, and all weather conditions are not reproducible. This type of test is time consuming, and conditions of most factors may change rapidly and unpredictably. As a result the reason for the change of properties may not be known. An advantage of the outdoor test is that conditions are the same to actual field exposures and can provide more natural and reliable results. Outdoor testing is also straight forward and easy. Sometimes both of the two tests fail to simulate real industrial environment (Shah, 2007).

Major accelerated weathering tests include exposure to carbon arc lamps, xenon arc lamps (cloest to natural sunlight) and fluorescent UV lamps (Shah, 2007). Acceleration tests can be done by increasing the use rate of the product, increasing the intensity of the exposure to radiation, aging rate of the products, and increasing the level of stress or use combination of several methods. Accelerated tests always require extrapolation, and it is important to minimize the amount of extrapolation and potential errors (Escobar & Meeker, 2006).

Accelerated tests used to be required to simulate outdoor tests as close as possible since outdoor testing is the de facto standard. But this goal is hard to achieve and there is no reliable relationship already found between results of indoor and outdoor test. One reason is that data from outdoor tests are hard to normalized and standardized. One possible solution to this question is to use the results of lab experiments as standard, and try not to simulate the natural environment. To have more precise and reliable results, indoor tests might as well cover as large a range of exposure conditions as possible, while still considering the natural limits (Chin et al., 2006).

Outdoor tests are always long, but sometimes outdoor weathering test of several months may also give us useful results (ZHANG & Grewdson, 2010).

1.5 Weather in Los Angeles

The irradiance and meteorological data sets were available on the Loyola Marymount University (Los Angeles, California) RSR web site ("LMU Daily Data," n.d.). The data were collected from April 28th to June 16th.

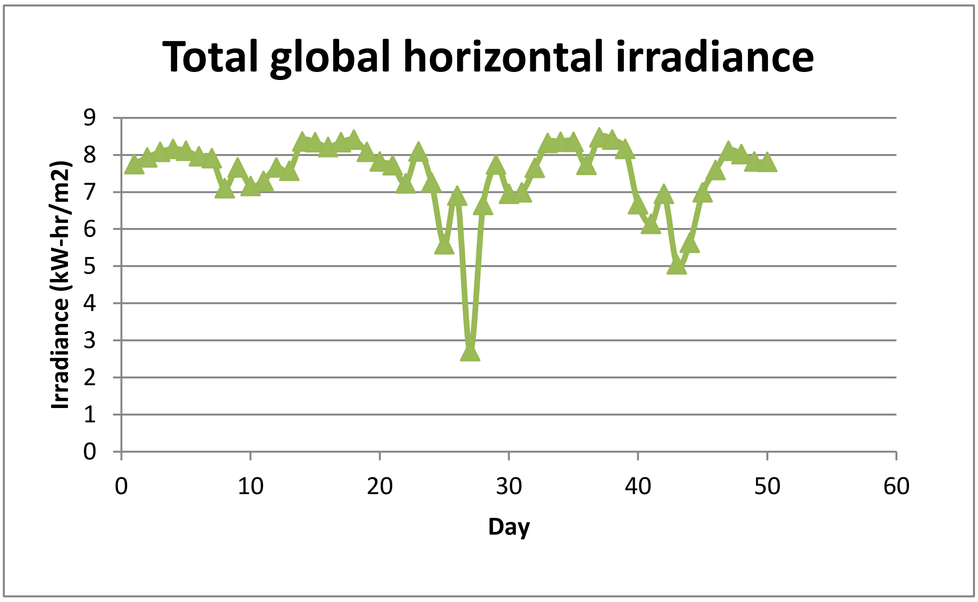


Figure 3 Total global horizontal irradiance in LA (From 4/28/2014 to 6/16/2014)

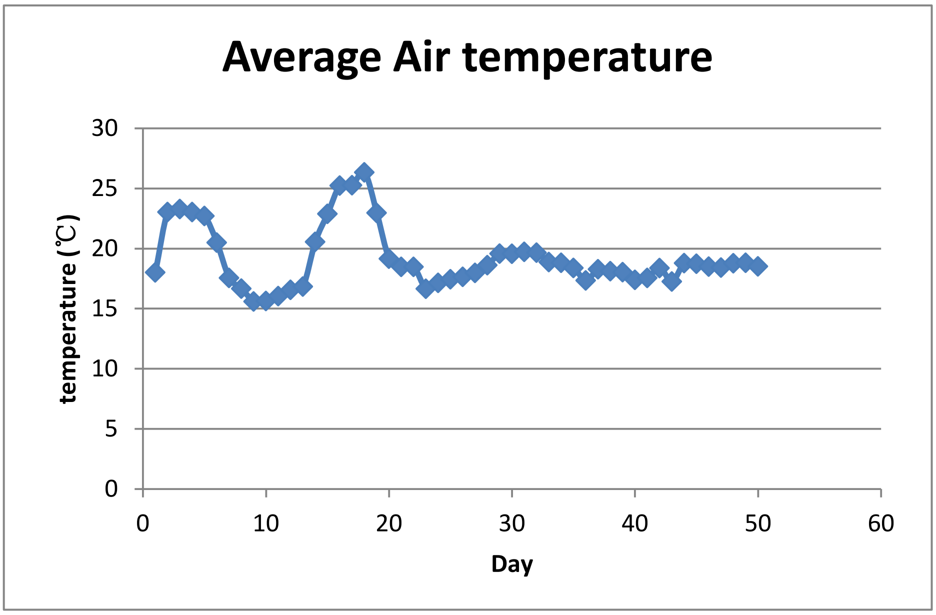


Figure 4 Average air temperature in LA
(From 4/28/2014 to 6/16/2014)

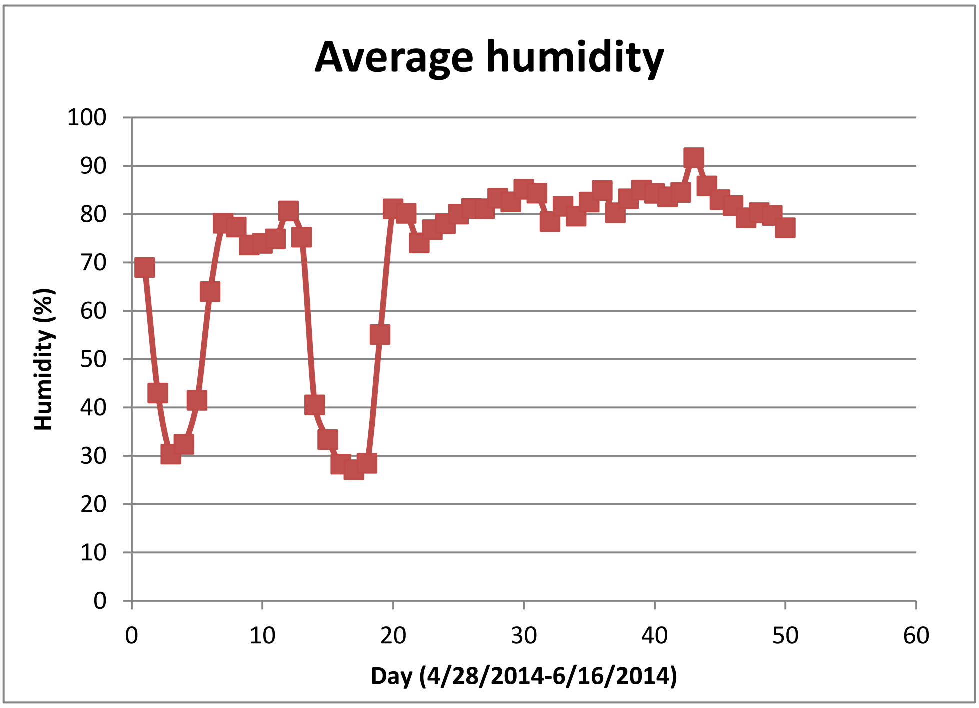


Figure 5 Average humidity in LA
(From 4/28/2014 to 6/16/2014)

From April to June in Los Angeles, the values of energy density, temperature and humidity values were stable. The total daily horizontal intensity varied from 7kw-hr/m2 to 8kw-hr/m2. The daily temperature was around 20℃, which was not so high. The daily average humidity was around 80%.

2 Experiments design

2.1 Materials

The material of specimens used in this experiment was polyurethane. All of the specimens were divided into five groups: O1, O2, O5, O6 and I8. There were five specimens in each group for repeated measurement. The five specimens in the same group received identical treatment. Difference of different treatments was whether the specimens absorbed heat, water or UV light. Heat, moisture and UV light were the three factors considered here and they were represented by A, B, and C respectively. Four plastic boxes (dimension: $20 \times 14 \times 16$ inches) were labeled 1, 2, 3, and 4. Each of them contained one group of specimens (five specimens). The Specimens of group I8 were stored indoors. Water in the box was as deep as 24cm. The temperature in the lab was 20 ± 2 ℃ and the relative humidity was between 65% and 70 %. Labels of five groups and five treatments are given in Table 6:

Table 6 Labels of specimens

Labels	Group	Factors	Details	Tank No.
O11, O12, O13, O14, O15	O1	A	Outdoor, UV filter	1
O21,O22, O23, O24, 025	O2	B	Outdoor, UV filter, water	2
O51, O52,O53, O54, O55	O5	A+C	Outdoor	4
O61, O62,O63,O64, O65	O6	B+C	Water, outdoor	3
I81, I82, I83, I84, I85	I8	-	Indoor, control group	

The shape of all of the specimens was rectangle, according to the standard ISO527 (Plastics – Determination of Tensile Properties). The width, length and thickness of specimens were 2.5cm, 15cm and 0.5mm respectively.

2.2 Light filter

An ideal light filter for this experiment should be: inexpensive, easy to install, able to block most UV light and not increase or decrease temperature of specimens. The materials used to block UV light include fabrics, PE foils, and plastic. A nylon fabric can absorb more than 98% UV A and UV B. It is always cheap (about $10/yard) and flexible enough to cover a container with any shape. Some plastic UV filter films are stable and only block lights in a narrow wavelength range, but they are expensive. PE foil is widely used in the lab but it will block most sunlight and increase temperature in a system.

The EasyShade Blk90 Sunblock Black 90% Shade Cloth UV (Hayward, California, United States) resistant fabric is inexpensive and soft, and it is made of 100% UV stabilized HDPE. An experiment was conducted to find out what percentage of the total UV light and IR light would be blocked by this resistant fabric. In this experiment, the temperature and UV light intensity were measured every hour, both above and under the filter. The equipments used here included UV light meter UV340B (Hong Kong, Hong Kong) and thermometer. The fabric was 12ft x 10ft in dimensions. The tank was 30.5 cm wide and 30.5 cm high.   The UV-blocking fabric completely covered the tank containing the specimens, protecting them from the sun.

The details are provided in Figures 6, 7 and 8:

Figure 6 Tank and light filter

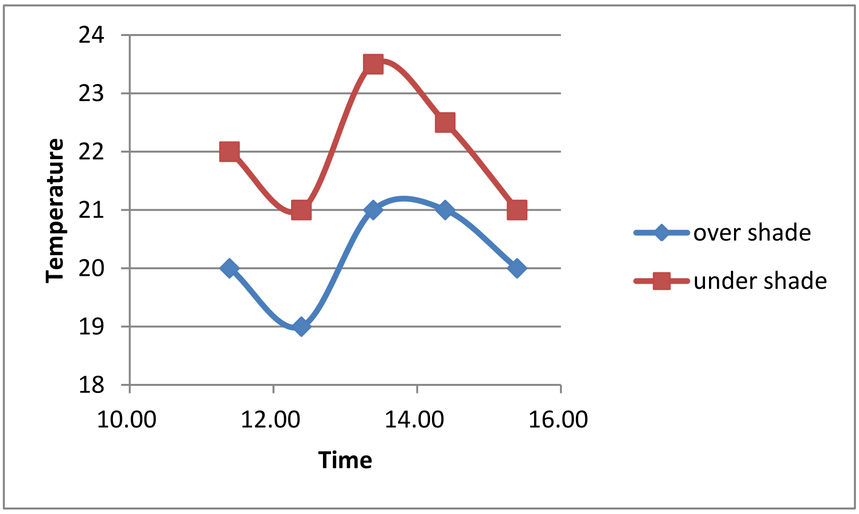


Figure 7 Time and temperature over and under the shade

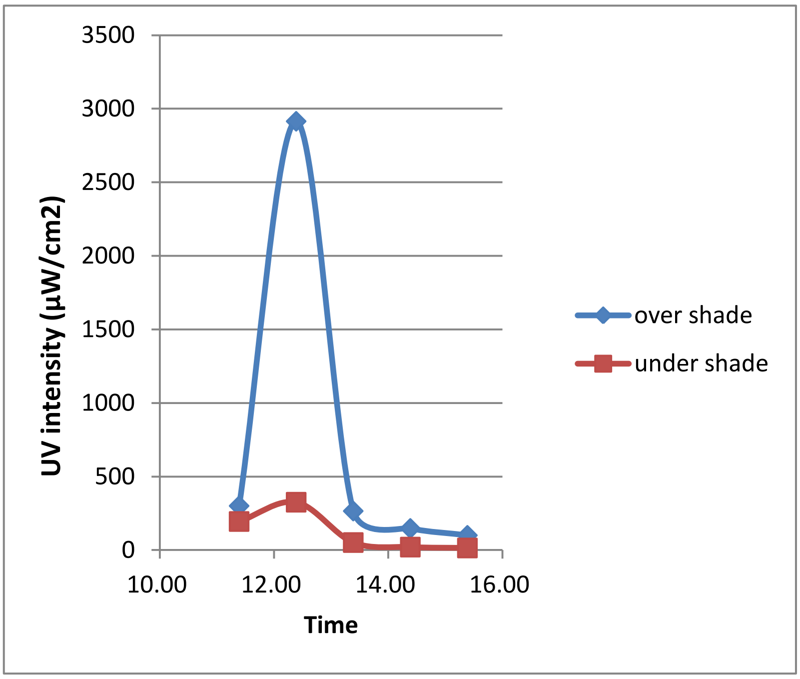


Figure 8 Time and UV intensity over and under the shade

The air temperature under the shade only increased 10%. Most of the UV light was filtered, and the UV light intensity was close to zero. The EasyShade fabric was an ideal material to filter UV light for this experiment.

2.3 Test methods

This experiment was conducted outdoors. Most of the specimens were exposed to the sun with or without UV filters. One week was called a cycle. Before each cycle, the specimens were collected, washed, conditioned at room temperature for 24 hours and then their properties were measured.

For the specimens stored indoors (control group), the temperature and humidity were stable. The room temperature was around 21℃. The daily average humidity in the lab was about 67%. There was no UV light source in the lab.

The outdoor membranes were exposed to UV light and heat. Heat, moisture and UV light played important roles in membrane damage. In this experiment, water was used to absorb heat, but it also introduced moisture. The EasyShade fabric was used to block UV light.

To decide depth of water, we used the Beer-Lamber Law (or called Beer's Law). According to the Beer-Lamber Law, the light intensity absorbed by the liquid is proportional to the path length of light and wavelength-dependence absorptivity coefficients. Absorbance means radiation energy is converted to heat. The equation to calculate absorbance (Trussell, Howe, & Hand, 2012):

$$log\frac{I}{I_0} = -k_A(\lambda)x \tag{1}$$

Where

I = light intensity after passing through a solution of known depth containing constituents of interest at wavelength λ, mW/cm^2

I_0 = light intensity after passing through a blank solution (i.e., distilled water) of known depth (typically 1.0cm) at wavelength λ, mW/cm^2

λ = wavelength, nm

x = length of light path, cm

$k_A(\lambda)$ = absorptivity at wavelengthλ, cm^{-1}, or called absorption coefficient, decided by temperature, pressure, salinity, concentration and wavelength (Bass et al., 2009).

This equation can also be written as (Robinson, 1996):

$$A = -\log T = -log\frac{I}{I_0} = abc = k_A(\lambda) \tag{2}$$

Where

A = absorbance, dimensionless, if length of light path equals to 1cm, absorbance is equal to absorptivity $k_A(\lambda)$

T = transmittance = $\frac{I}{I_0}$

I = light intensity after passing through a solution of known depth containing constituents of interest at wavelength λ, mW/cm^2

I_0 = light intensity before passing through the solution at wavelength λ, mW/cm^2

a = absorption coefficient, or called molar absorptivity, M^{-1}cm^{-1}

b = path length of the light through the solution

c = concentration of the solution, mol/L

Equations 3 and 4 were used to calculate the fraction of light absorbed as a function depth and wavelength.

$$x = \frac{log\frac{I}{I_0}}{-k_A(\lambda)} \tag{3}$$

$$\frac{I}{I_0} = 10^{-k_A(\lambda)x} \tag{4}$$

The average light intensity can be calculated by integrating I over the depth of the water (Trussell et al., 2012):

$$I_{avg} = \frac{\int_0^d I_0 e^{-\alpha x} dx}{d} = \left(-\frac{I_0}{\alpha} e^{-\alpha x}\Big|_0^d\right)/d = \frac{I_0}{\alpha d}(-e^{-\alpha d} + 1) \quad (5)$$

$$\alpha = 2.303 k_A(\lambda) \quad (6)$$

$$\frac{I_{avg}}{I_0} = \frac{1}{2.303 k_A(\lambda) d}(-e^{-2.303 k_A(\lambda) d} + 1) \quad (7)$$

Where

d = length of light path, cm

Although application of Beer-Lambert Law is limited due to chemical factors of solution and instrumental factors (Kaur, 2007), it can be used to approximately estimate the percentage of infrared light and UV light absorbed by the solution at a certain depth. The average intensity of the light is more appropriate to represent the percentage of light radiation absorbed by a certain volume of water or other solution, because the absorbed radiation changes along the depth. Figure 9 shows relationship between average intensity and real intensity:

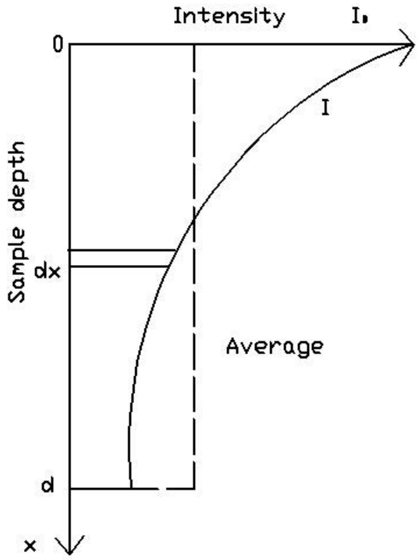


Figure 9 Change of intensity of light along the depth (Trussell et al., 2012)

The length of light path x, or called optical path length (OPL) in a homogeneous medium is the product of thickness and refractive index of the medium, as shown in equation 8 (Wayne, 2013):

$$x = \mathrm{OPL} = ns \tag{8}$$

Where

OPL = optical path length, cm

n = refractive index of medium

s = thickness of medium

In the air, the refractive index equals to 1.00, while in other medium, n is greater than 1.00. As a result, the OPL value is always equal to or greater than the thickness of the medium.

For light with different wavelengths, absorptivity changes. Table 7 shows relationship between depth and absorptivity in water (assuming n = 1):

Table 7 Light and absorptivity

x(cm)	**λ(nm)**	**Light**	**$k_A(\lambda)$ (cm^{-1})** (Bass et al., 2009)	**I/I_0**	**$1-I/I_0$**	**I_{avg}/I_0**	**$1- I_{avg}/I_0$**
50	300	UV	0.00141	85.016%	14.984%	92.304%	7.696%
50	400		0.000171	98.051%	1.949%	99.022%	0.978%
50	500	Visible	0.000257	97.085%	2.915%	98.535%	1.465%
50	600		0.00244	75.509%	24.491%	87.180%	12.820%
50	700		0.0065	47.315%	52.685%	70.398%	29.602%
50	800		0.0207	9.226%	90.774%	38.084%	61.916%
50	1000	IR	0.33	0.000%	100.000%	2.632%	97.368%
50	10000		700	0.000%	100.000%	0.001%	99.999%
50	1000000		130	0.000%	100.000%	0.007%	99.993%
24	300	UV	0.00141	90.719%	9.281%	95.284%	4.716%
24	400		0.000171	98.826%	1.174%	99.412%	0.588%
24	500	Visible	0.000257	98.240%	1.760%	99.117%	0.883%
24	600		0.00244	84.489%	15.511%	92.025%	7.975%
24	700		0.0065	63.826%	36.174%	80.561%	19.439%
24	800		0.0207	23.933%	76.067%	53.192%	46.808%
24	1000	IR	0.33	0.000%	100.000%	4.386%	95.614%
24	10000		700	0.000%	100.000%	0.002%	99.998%
24	1000000		130	0.000%	100.000%	0.011%	99.989%

We can conclude from Table 7 that a water depth of 24cm is needed to absorb 90% of the infrared light radiation. Notice that value of n is greater than 1, and for water, it is approximately1.3(Bass et al., 2009), which means the real percentage of light radiation absorbed is greater than that given by Table 7. In contrast, a very low percentage of UV light radiation (<1%) will be absorbed by water as deep as 24cm. As a result, water is a good medium to absorb IR but not UV light. The percentage of visible light radiation absorbed varies from 1% to 90% (the rest is reflected). However, all the values are estimates, as temperature, salinity, pressure, species and concentration vary continually in water. During the experiment, the water samples were not contaminated so effects of turbidity, light scattering and beam attenuation(Bass et al., 2009), on light intensity were not considered. A water depth of 24cm was effective in absorbing IR light (i.e., absorb heat).

By adding water, heat was absorbed and stress on the surface of specimens did not increase due to evaporation. When specimens were under water, the wetness their physical and chemical properties were changed. Water absorbed heat, but at the same time exposed specimens to moisture.

2.4 Measuring

In this experiment, properties like hardness, Young's modulus, thickness, weight, width, and length were measured. The equipments and their companies are listed in Table 8:

Table 8 Equipments and brands

Measure	Equipments	Brands
Hardness	Durometer	Shore Type A
Young's modulus	Load frame	-
Thickness	Micrometer	Mitutoyo 0.01mm
Weight	Balance	Denver Instrument XL-1810
Width, length	Ruler	
UV intensity	Light meter	DVM1300 Velleman
Heat	Thermometer	
Photos	Microscope, camera, light source	LEICA MZ12, Nikon coolpix 995, NCL 150

2.4.1 Hardness

Thickness of the test piece should be at least 6mm. Errors may occur in thinner piece because specimens are deeply penetrated by the indenter. "Apparent" hardness values can be used if this requirement is not satisfied, which may not be precise but can be used for comparison (Gent, 2012).

The equipment used in this study to test hardness was Shore Type A durometer (Los Angeles, CA). The type A durometer with a blunt rod-shaped indentor was appropriate to measure hardness of soft materials, like PU membranes. Other types of durometers with sharper indentors are used for harder plastics (Lokensgard, 2008). The standard ASTM D224 provides a standard method on how to use the durometer and measure hardness.

2.4.2 Young’s modulus

Young’s modulus was measured after hardness. Parallel-sided strip specimens were used in this experiment (Gent, 2012), with the size described in the standard ISO527.

The specimens are stretched and the expansion of membranes at a corresponding stress were measured and recorded, then plotted to show the stress-strain curve. The specimen is in its elastic region at the beginning and the relationship between stress and strain is linear when the elongation is small. Young’s modulus is the slope of the beginning part of a stress-strain curve which is straight. In this experiment, the original length of the specimens was 61mm. After they were stretched to 63mm, the final elongation was 3.3%. Slope of the straight part of stress-strain curve was calculated by using least squares method (Kaliman, Rosso, Leu, & Stenstrom, 2008).

The load frame used here to measure Young’s modulus was similar to the one described in ASTM D412 and other researcher’s paper (see Figure 10) (Kaliman et al., 2008). According to the standard ASTM D412, constant rate of elongation was required to assure precise results. According to the standard ASTM D638, speed limit of stretching was 5mm/min.

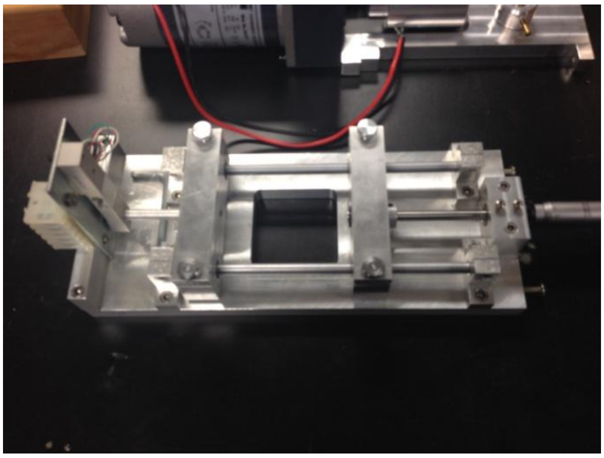


Figure 10 The load frame used to measure Young's modulus

The load frame was connected to the Omega DP25-s-a (Stamford, CT). The Omega DP25-s-a is a strain indicator, and the output unit is volt. For convenience, units can be converted from volts to grams. Because the reading of DP25-s-a meter can be scaled by hand, the values of the loaded weight on samples can be read directly from the screen.

2.5 Statistical methods

According to George E. P. Box, all models are wrong, but some are useful (Willink, 2013). Sample sizes are usually not large enough to fit a perfect model, but there are still some models good enough to find out whether the change is statistically significant and which factor is more important. In this experiment we had longitudinal data with missing cells, so a linear mixed-effect model was used. The Tukey and ANOVA tests were used to compare two data sets, which helped us to compare properties of the specimens from different groups. Plots were also a useful method to compare several groups of data, and we could see how the properties changed over time.

All the models used here were entered into the software RStudio (Boston, Massachusetts). There are thousands of packages in R providing models and methods for different purposes. Each model has its own hypotheses. For a null hypothesis test, p-value is the probability of a hypothesis used to decide whether we feel confident to accept or reject a hypothesis. A threshold p-value of 5% was used for this experiment. If the P-value is smaller than 0.05, it indicates that we failed to accept the hypothesis. Larger p-value indicates that we failed to reject the hypothesis.

2.5.1 Repeated measures design/longitudinal factorial design

To study the difference between individual means, a Tukey multiple comparison tests was applied, the results of which tell us whether the effect of each factor or each treatment is significant. The null hypothesis is:

$$H_0: \mu_a = \mu_b$$

Where μ is the mean value; a and b represent two different treatments or levels.

Analysis of variance (ANOVA) is a very useful statistical technique to find out important factors and compare different models. At the same time it does not increase Type I error (reject a true null hypothesis) (Rutherford, 2001). For example, by comparing the p-values with a threshold value, we will know whether effect of a certain parameter is significant, or which model is more appropriate.

There were three environmental factors in this experiment: heat (A), moisture (B) and UV light (C). Each factor had two levels: low level (-1) and high level (+1). For heat, low level was prepared by adding water into container. Water as deep as 24cm absorbed 46.8% visible light and nearly 100% IR light. Heat was at a high level when there was no water in the container, and the specimens were exposed to air and directly absorbed heat from the sun. The moisture level was high (+1) when the heat level was low (-1), and vise versa. When the UV filter was applied, less UV light was absorbed by the specimens, and the level of UV light was recorded as -1. High UV light means there was no UV filter outside the container. Details of this factorial design are provided in Table 9. It was a completely randomized experiment.

Table 9 Factors and levels

Treatment No.	Treatment	Factor			
		A	B	C	Combination
O1	Outdoor, UV filter	1	-1	-1	A
O2	Outdoor, UV filter, water	-1	1	-1	B
O5	Outdoor	1	-1	1	A+C
O6	Outdoor, water	-1	1	1	B+C
I8	Indoor, control group	-1	-1	-1	-

When more than two factors would have effect on response and each factor has two or more levels, the factorial design was more appropriate. The assumption for factorial design is that response is almost linear when one factor changes from one level to another. The advantage of the factorial design is that it requires only small number of runs (Montgomery, 2008).

In this experiment, data was observed and collected every week, and specimens were measured repeatedly. This type of data is called longitudinal data. This was a repeated measures design, which means the same subject is measured several times at the same times or the same subject is measured repeatedly at different time. A design is called mixed designs when the levels of some factors are independent (random) and the levels of other factors are related (fixed) (Rutherford, 2001). Mixed-effects model was used to analyze our longitudinal data in this repeated measures design because time and environmental factors were fixed and labels of specimens were considered a random factor (Tiwari & Shukla, 2011).

Since we had three factors and each factor had two levels, a complete factorial design was required $(2 \times 2 \times 2 =)$ 8 treatments. Here we only had 5 treatments (see Table 9), so it was a repeated measures design with missing cells. Under this condition, mixed linear regression model used to evaluate main effects was preferred to factorial design using ANOVA. Even though the AMOVA method evaluated not only main effects but also interactions, which would give us more details about the results, unreliable results would occur because of the three missing treatments.

Package “nlme” in the comprehensive R archive network (CRAN) can be used to fit and compare several linear or nonlinear mixed-effects models. Function “lme” is used to fit a linear mixed-effects model and it allows for nested random effects. Before a model is fit, a within-group variance-covariance structure must to be decided. Different structures have different assumptions. The default assumption is that there is no within-group correlation. The assumption for the autoregressive structure is that observations closer to each other are more correlated than other observations, which is a possible condition for repeated measures data (“Repeated Measures Analysis with Splus/R,” n.d.)'(José Pinheiro, Bates, & R-core, 2014). Each model has its own AIC and BIC values. A model with smaller Akaike information criterion (AIC) and Bayesian information criterion (BIC) values is preferred. The function “gls” can also be applied to fit a linear model. The advantage of this function is that it allows for correlated errors and/or unequal variances (JC Pinheiro & Bates, 2000).

2.5.2 Plots

The main effect plots and interaction plots showed how the membrane's response changes when one or two factors changed from one level to another. Plots of responses over time and response of each treatment showed how properties of specimens changed in two months.

2.5.3 Error analysis

Type I error (probability is α) occurs if we accept the alternative hypothesis when the null hypothesis is true. By setting value of α, ANOVA and p-values controls probability of Type I error.

3 Results

3.1 Hardness

3.1.1 Repeated measures design/longitudinal factorial design

The results of Tukey multiple comparison tests (95% family-wise confidence level) showed whether hardness of specimens changed significantly over time:

Table 10 3.1.1 Results

	Durometer	**Difference**	**Adjusted p-value**
Week1	88.49	-	-
Week2	87.957	-0.533	0.00004
Week3	89.49	1.533	0
Week4	88.77	-0.720	0
Week5	88.444	-0.326	0.051
Week7	87.897	-0.547	0

According to the small p-values, hardness changed significantly between every two weeks.

First the function “lme” in the package “nlme” was used to fit a linear mixed-effects model by using maximum likelihood. We built two models, one with within-group correlations and the other one without. ANOVA was used to compare the results of different models, and it showed that the model without within-group correlations had smaller AIC and BIC values, so this model was preferred. Details of the preferred model:

Table 11 Preferred model

	Value	**Degree of Freedom**	**P-value**
A	-0.041	21	0.025
B	-0.041	21	0.569
C	-0.039	21	0.473

The p-value of A (0.025) was smaller than 0.05, so only heat had a significant effect on the hardness change. The negative value -0.041 meant that heat decreased hardness.

ANOVA was also used to compare models with and without a time factor. The p-value was smaller than 0.0001, which meant there was a time effect, and hardness changed significantly in seven weeks.

Then function “gls” in the package “nlme” was used to fit a new model comparing the specimens in the other four groups and the specimens in the control group, and studying the time effect. The orthogonal polynomial components for time included linear, quadratic, and cubic patterns over time. The results showed that no parameters in this model had a significant effect on hardness values.

3.1.2 Plots

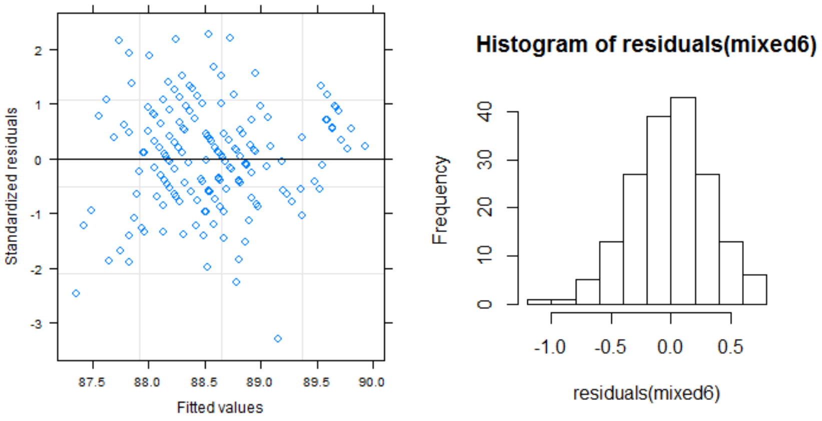


Figure 11 Residuals plots of linear mixed-effects model

In the residuals plots of the linear mixed-effects model, the variance was constant, and the distribution in histogram was normal, according to the bell–shaped curve, indicating that assumptions of the model were satisfied.

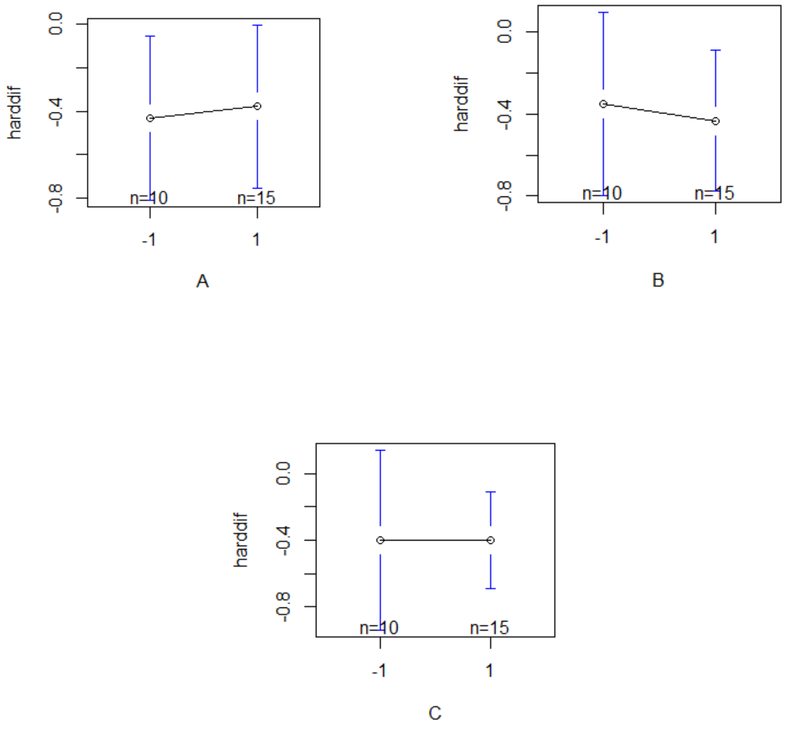


Figure 12 (a) Main effect plots

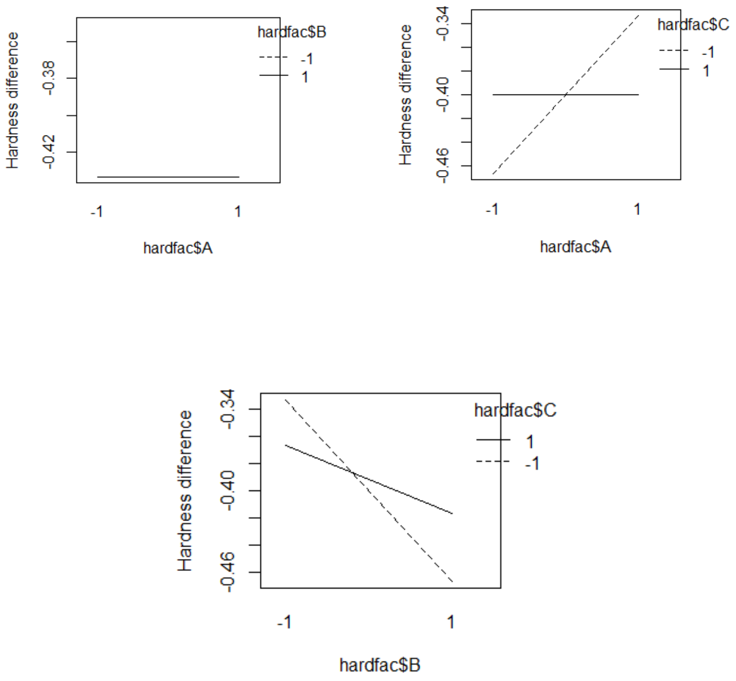


Figure 12 (b) Interaction plots

The hardness difference was the difference between the hardness values of specimens in the last week and the hardness values of specimens in the first week. The main effect plots showed that hardness did not change significantly, whether or not heat, moisture or UV light existed. The AB, AC and BC interaction plots indicated that hardness always decreased. Hardness decreased faster under the condition with moisture and without UV light, or the condition without heat and without UV light.

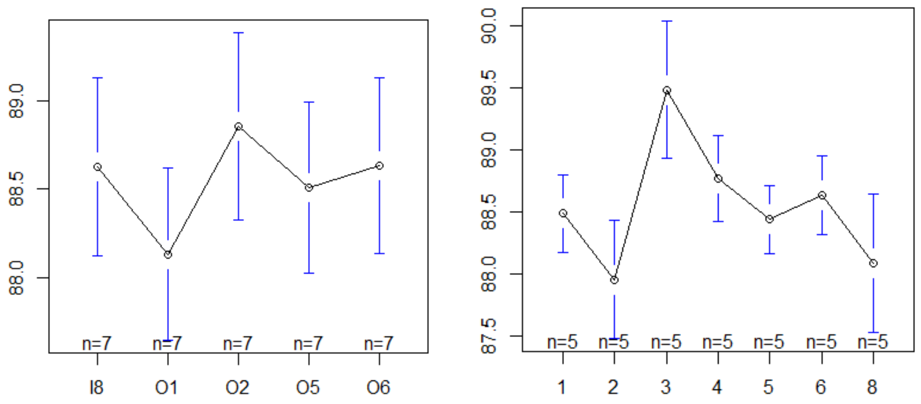


Figure 13 Hardness change over time

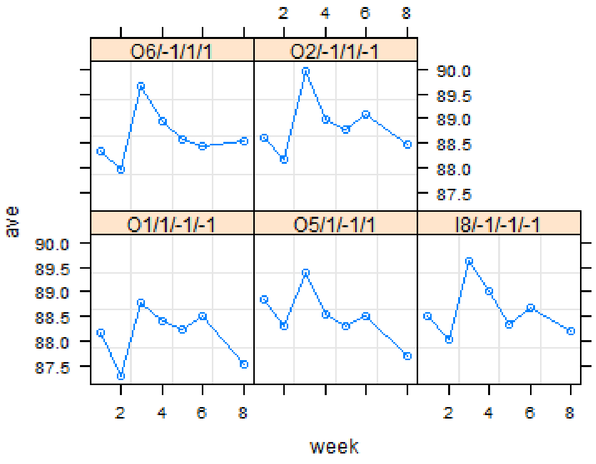


Figure 14 Hardness changes of specimens in six groups

Figures 13 and 14 showed the changes of hardness in seven weeks and in five groups.

3.1.3 Summary

The results of repeated measures design showed that heat significantly decreased hardness values. ANOVA proved that there was a time effect. Hardness changed significantly over time, and under all conditions, hardness decreased.

3.2 Modulus

3.2.1 Repeated measure design/longitudinal design

ANOVA was used to compare the results of different models, and it showed that the model without within-group correlations had smaller AIC and BIC values, so this model was considered as the better one:

Table 12 3.2.1Results

	Value	**Degree of Freedom**	**P-value**
A	-139653	21	0.020
B	-211584	21	0.001
C	-199194	21	0.000

The p-value of A, B, and C were smaller than 0.05, so heat, moisture and UV light had a significant effect on the modulus values change. The negative signs before all the values meant that heat, moisture and UV light decreased the modulus values.

Output of the function “gls” are in Table 13 (only list significant effects):

Table 13 “Gls” function output

Coefficients	Standard error	T-value	P-value
Intercept	119901.7	104.244	0.000
Factor(No)O5	169566.6	-3.926	0.001
Factor(No)O6	169566.6	-4.195	0.001
Poly(week, degree =3) 1	709347.8	-3.062	0.008
Poly(week, degree =3) 2	709347.8	-2.226	0.042
Factor(No)O5:poly(week, degree =3) 2	1003169.3	3.241	0.005

The small p-values indicated that modulus of specimens in group O5 and group O6 differed from those in control group. The factors week, week^2, and interaction between treatment O5 and week^2 were significant.

The p-value of ANOVA comparing models with and without a time factor was smaller than 0.0001, which meant there was a time effect, and the modulus values changed significantly over seven weeks.

3.2.2 Plots

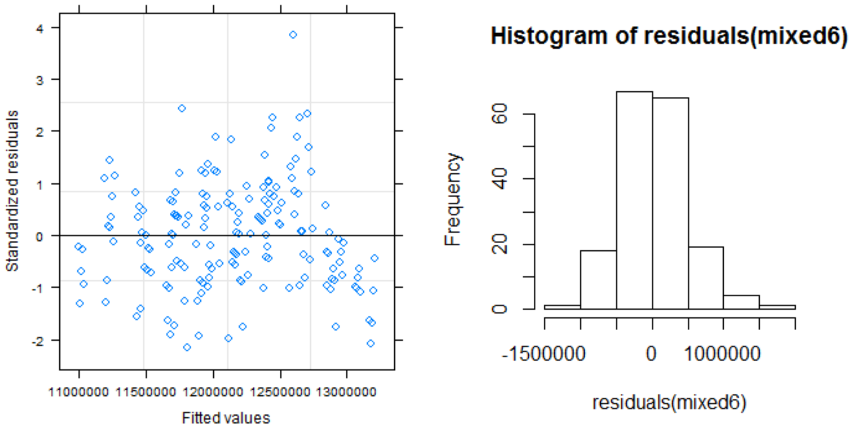


Figure 15 Residuals plots of linear mixed-effects model

In the residuals plots of linear mixed-effects model, the variance was constant, and the distribution in histogram was normal according to the bell–shaped curve, indicating the assumptions of the model were satisfied.

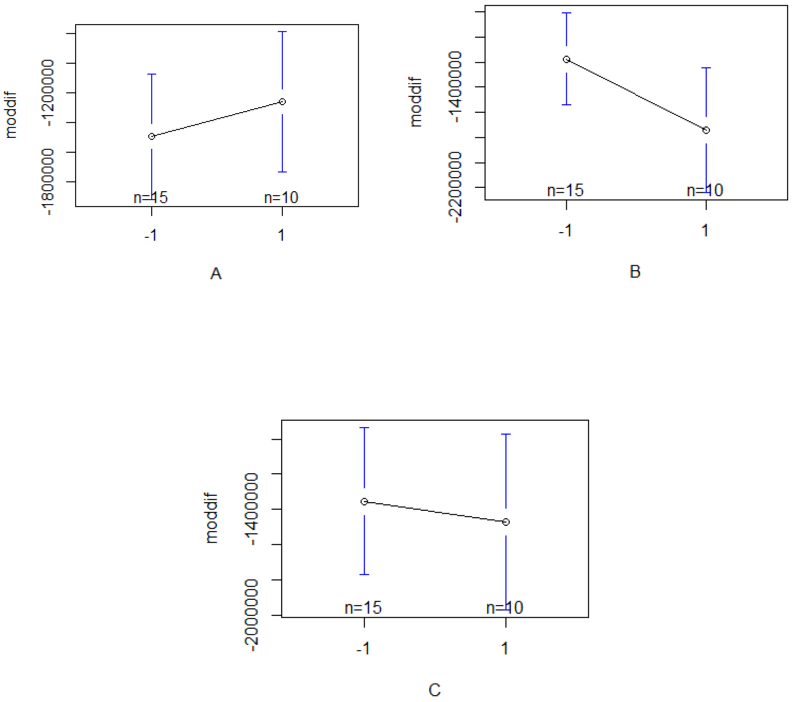


Figure 16 (a) Main effect plots

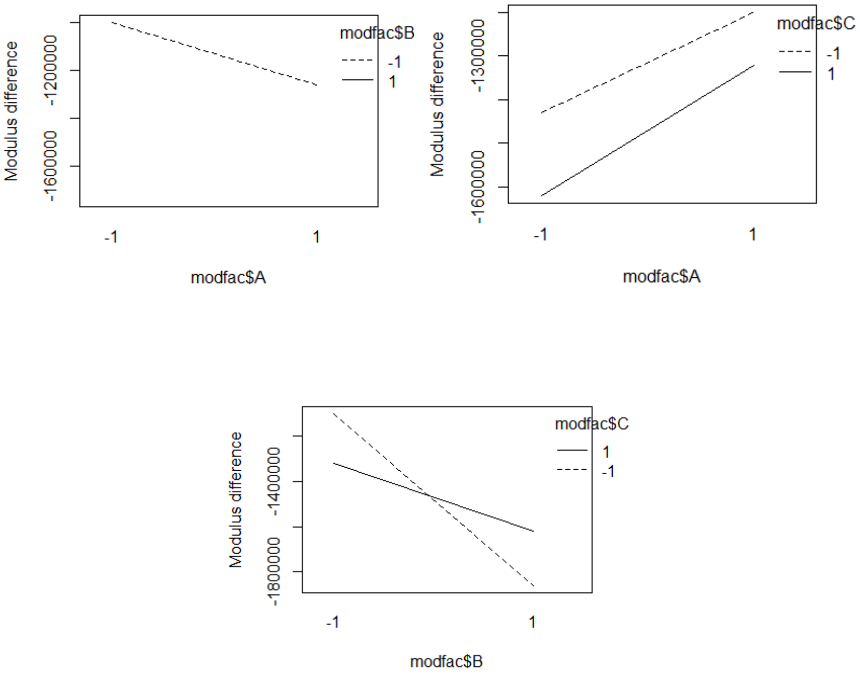


Figure 16 (b) Interaction plots

The modulus difference was the difference between the modulus of specimens in the last week and those in the first week. The main effect plots showed that the modulus under all conditions decreased. The modulus difference was smaller when there was moisture, no heat, or no UV light. The AB, AC and BC interaction plots indicated that the modulus decreased the most rapidly when there were moisture and no UV light; and the modulus decreased slower when there were no heat and no moisture.

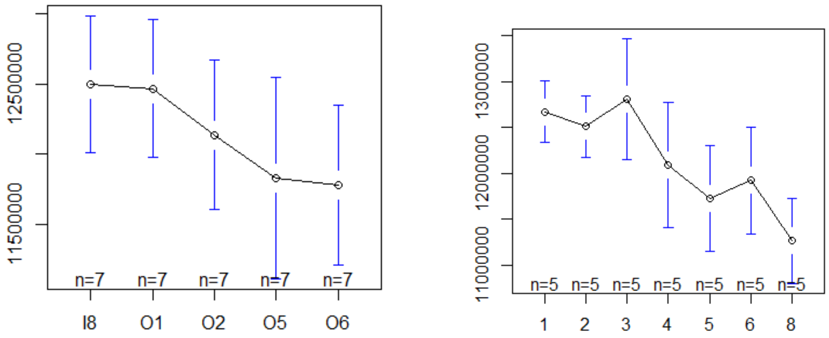


Figure 17 Modulus change over time

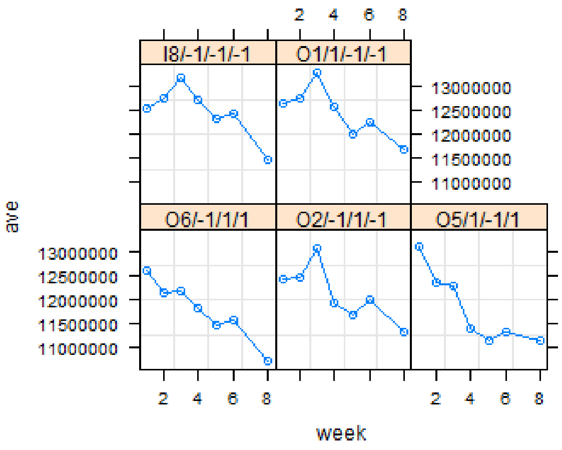


Figure 18 Modulus changes of specimens in six groups

The modulus value of specimens in the control group was the highest, and specimens in the O5 and O6 group had the lowest modulus value. Modulus of all specimens decreased over time.

3.2.3 Summary

The change of Modulus values in the group 5 and group 6 were different from that of specimens in the control group, indicating that moisture significantly decreased the modulus values. Results of the repeated measures design showed that all of the three factors decreased the modulus values over time.

3.3 Thickness

3.3.1 Repeated measure design/longitudinal design

The significant changes found in Tukey multiple comparison tests (95% family-wise confidence level) are in Table 14:

Table 14 3.3.1 Results

	Thickness(mm)	Difference(mm)	Adjusted p-value
Week4	0.605	-	-
Week5	0.618	0.013	0.014
Week6	0.603	-0.015	0.003

Thickness increased from the fourth week to the fifth week and decreased from the fifth week to the sixth week.

Results of the linear mixed-effects model showed that the model without within-group correlations had the smallest AIC and BIC values. Summary of the results are in Table 15:

Table 15 Results

	Value	Degree of Freedom	P-value
A	0.006	21	0.051
B	0.001	21	0.783
C	-0.001	21	0.615

The p-value of factor A was close to 0.05, so only heat had significant effect on the thickness change. The sign was positive, which means heat slightly increased the thickness value.

Output of function “gls” (only list significant effects here):

Table 16 Results

Coefficients	Standard error	T-value	P-value
Intercept	0.003	221.742	0.000
Factor(No)O1	0.004	-2.343	0.033
Factor(No)O5	0.004	-3.445	0.004

The small p-values indicated that the thickness values of the specimens in the group O1 and O5 differed from those in the control group.

The P-value of ANOVA comparing models with and without a time factor was smaller than 0.0001, which meant there was a time effect, the thickness changed significantly over the seven weeks.

3.3.2 Plots

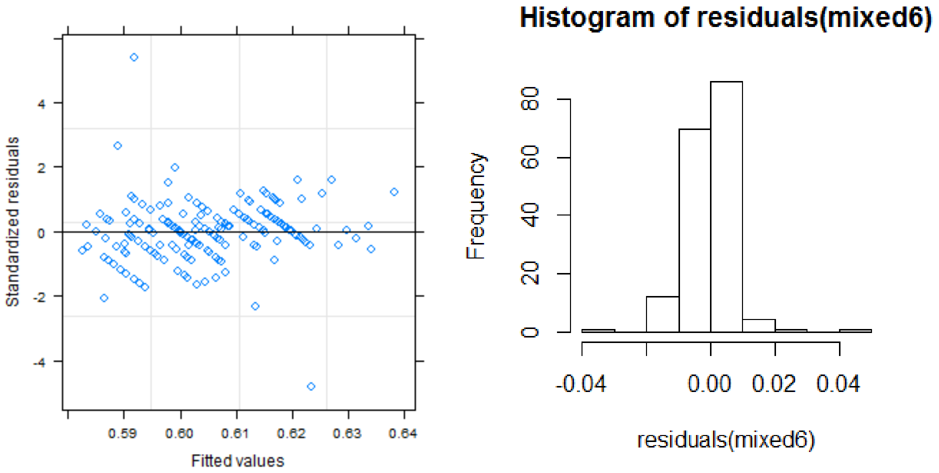


Figure 19 Residuals plots of linear mixed-effects model

In the residuals plots of linear mixed-effects model, the variance was constant, and the distribution in histogram was close to normal distribution, indicating the assumptions of the model were satisfied.

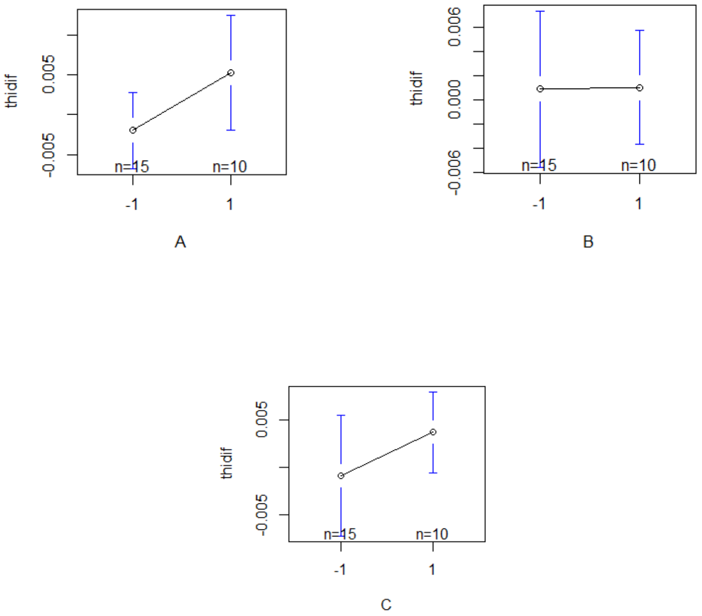


Figure 20 (a) Main effect plots

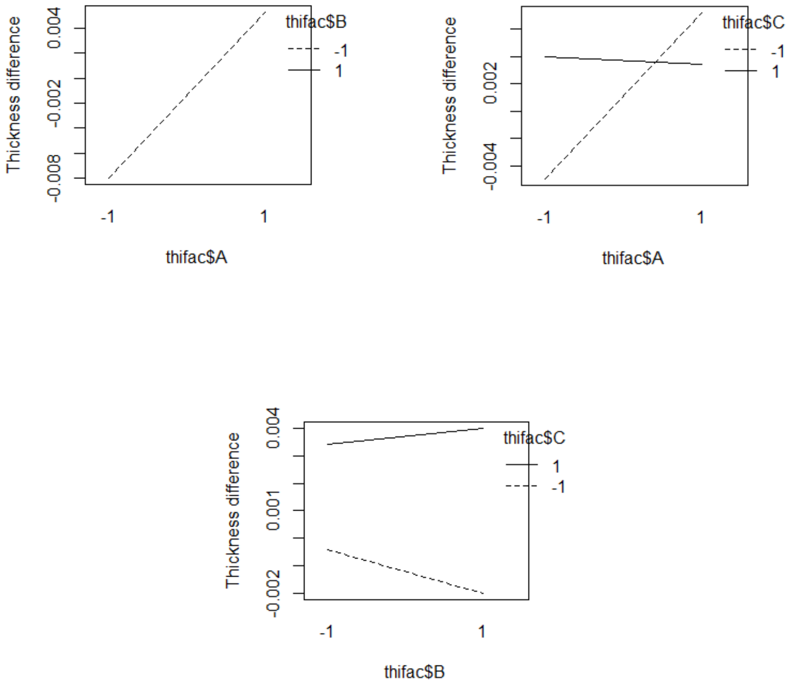


Figure 20 (b) Interaction plots

The main effect plots and the interaction plots showed that there was small change (about 1%of original thickness) in thickness over time and the thickness values of the specimens from different groups were not significantly different.

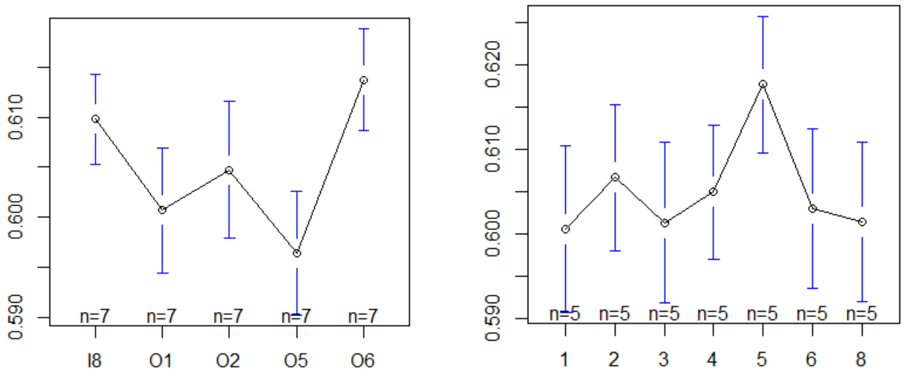


Figure 21 Thickness change over time

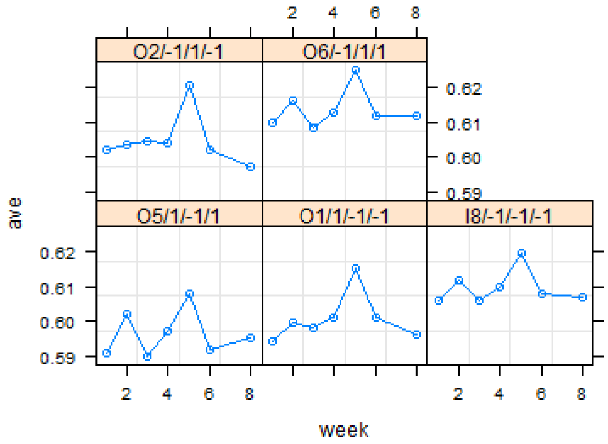


Figure 22 Thickness change of specimens from six groups

There is no statistically significant change of thickness over time.

3.3.3 Summary

Heat had a slight effect on the thickness values. Thickness of the specimens in all of the five groups did not change significantly over time.

3.4 Weight

3.4.1 Repeated measure design/longitudinal design

There was no significant change in the weight, according to results of the Tukey multiple comparison tests (95% family-wise confidence level).

ANOVA showed that the model considering within-group correlations had smaller AIC and BIC values, so this model was prefered:

Table 17 3.4.1 Results

	Value	Degree of Freedom	P-value
A	0.035	21	0.038
B	0.005	21	0.757
C	-0.003	21	0.804

The P-value of A (0.038) was smaller than 0.05, so only heat had a significant effect on the weight change. The positive value 0.035 meant that heat increased weight.

The ANOVA results showed that there was a time effect, and the weight changed significantly over the seven weeks.

The output of the function “gls” (only list significant effects):

Table 18 Results of the function “gls”

Coefficients	Standard error	T-value	P-value
Intercept	0.003	1008.850	0.000
Factor(No)O1	0.004	-18.254	0.000
Factor(No)O2	0.004	-3.580	0.003
Factor(No)O5	0.004	-18.293	0.000

The small p-values indicated that the weight of specimens in the group O1, O2 and O5 differed from those in the control group.

3.4.2 Plots

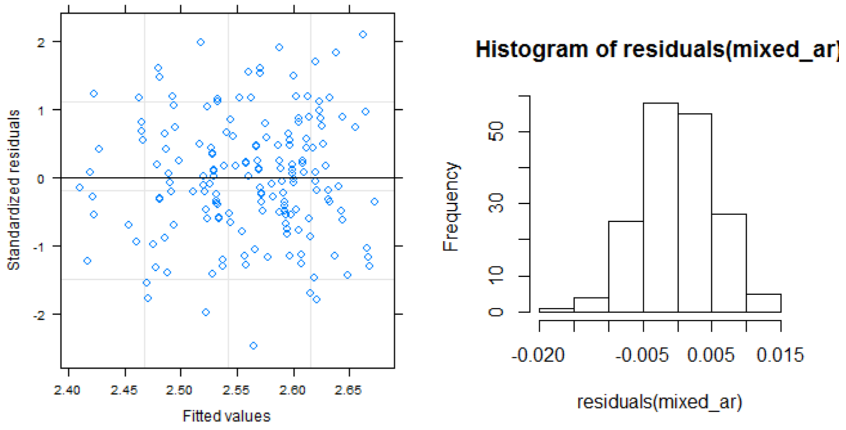


Figure 23 Residuals plots of linear mixed-effects model

In the residuals plots of the linear mixed-effects model, the variance was constant, and the distribution in histogram was normal according to the bell–shaped curve, indicating that assumptions of the model were satisfied.

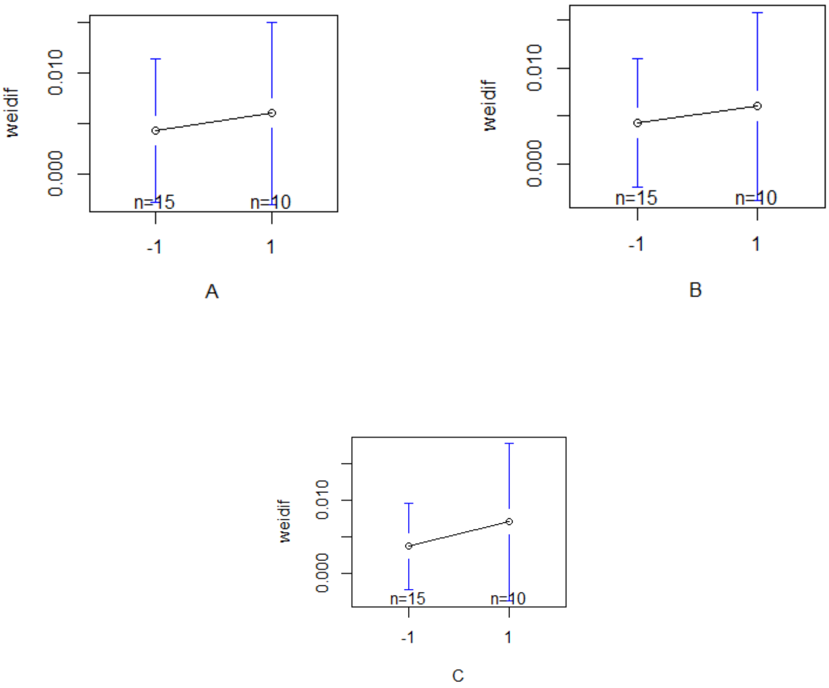


Figure 24 (a) Main effect plots

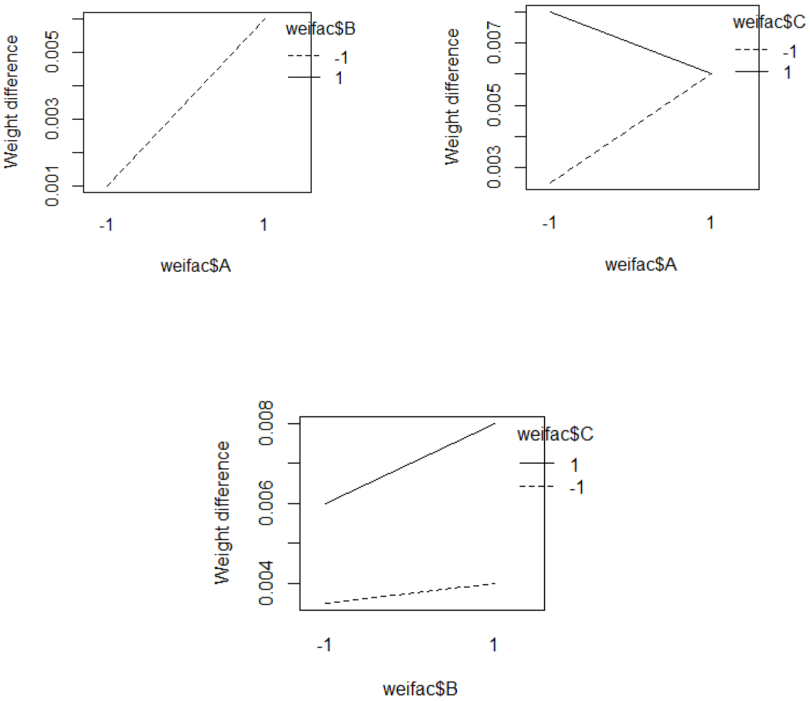


Figure 24 (b) Interaction plots

The main effect plots and interaction plots indicated that the change of weight (smaller than 1% of the original values) after seven weeks was not significant.

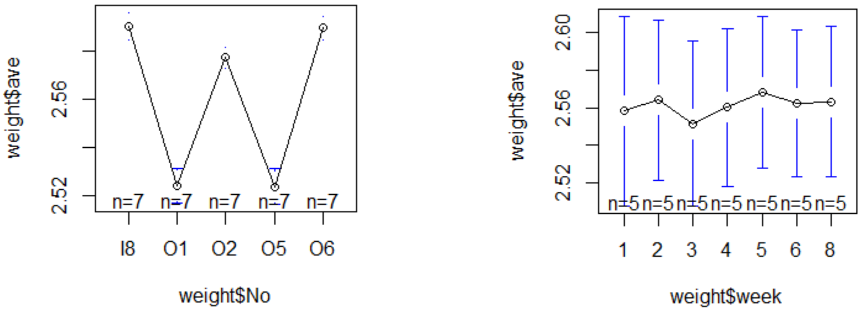


Figure 25 Weight change over time

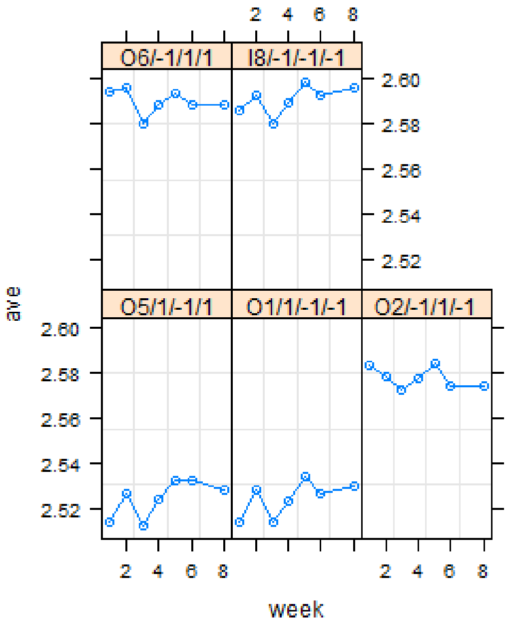


Figure 26 Weight changes of specimens from six groups

Figure 25 and 26 showed that the weight was almost constant over time.

3.4.3 Summary

Heat slightly increased the weight values, but the change was not statistically significant.

3.5 Width

3.5.1 Repeated measure design/longitudinal design

The significant difference between weeks found in Tukey multiple comparison tests (95% family-wise confidence level):

Table 19 Results

	Width(cm)	Difference(cm)	Adjusted p-value
Week1	2.534	-	-
Week2	2.473	-0.061	0.000

The width only changed significantly from the first week to the second week.

The results of ANOVA showed that the model without within-group correlations had smaller AIC and BIC values, so this model was the final model:

Table 20 Results

	Value	Degree of Freedom	P-value
A	-0.009	21	0.578
B	-0.018	21	0.269
C	0.001	21	0.909

The large p-values showed that none of the three factors had significant effects on the change of width values. ANOVA comparing models with and without a time factor showed that there was a time effect, and the width changed significantly over seven weeks.

Output of the function “gls” (only list significant effects):

Table 21 Results

Coefficients	Standard error	T-value	P-value
Intercept	0.006	387.881	0.000
Factor(No)O2	0.009	5.663	0.000
Factor(No)O5	0.009	3.263	0.005
Factor(No)O6	0.009	2.303	0.036
Poly(week, degree =3) 2	0.037	3.005	0.009

The small p-values indicated that the modulus of the group O2, O5 and O6 differed from the modulus of the control group, and the effect of time^2 was statistically significant.

3.5.2 Plots

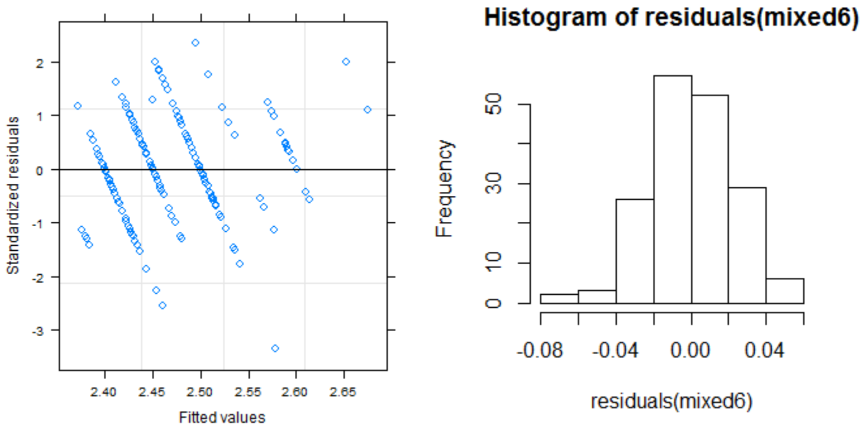


Figure 27 Residuals plots of linear mixed-effects model

In the residuals plots of the linear mixed-effects model, the variance was constant, and the distribution in histogram was almost normal distribution, indicating the assumptions of the model were satisfied.

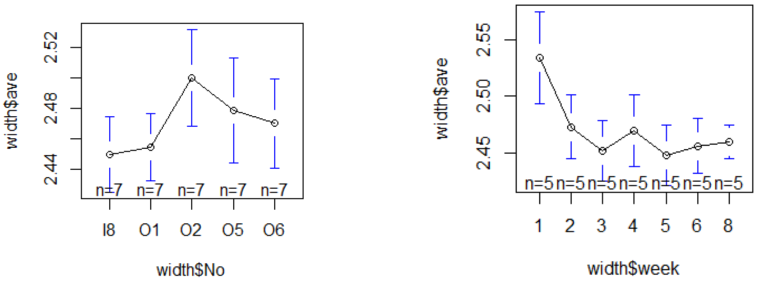


Figure 28 Width change over time

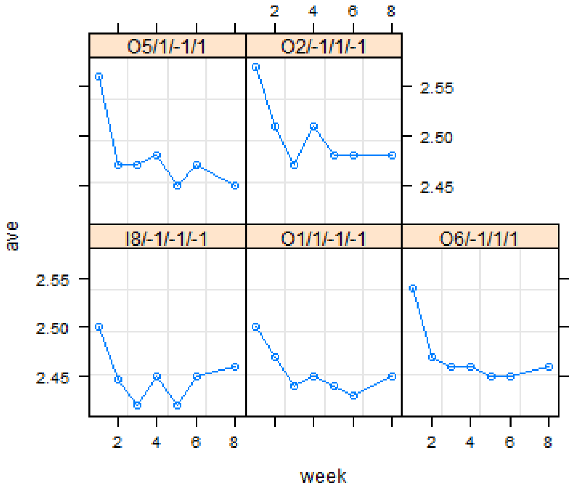


Figure 29 Width changes of specimens from six groups

Width of the specimens decreased a little bit over time, but the change (<5% of original width) was not significant.

3.5.3 Summary

The repeated measures design showed that none of the three factors determined how width changed.

3.6 Length

3.6.1 Repeated measure design/longitudinal design

There was no significant difference between each two weeks found in Tukey multiple comparison tests (95% family-wise confidence level).

The results of ANOVA showed that the model without within-group correlations had smaller AIC and BIC values. So this model was preferred:

Table 22 Results

	Value	Degree of Freedom	P-value
A	-0.009	21	0.740
B	0.024	21	0.408
C	0.010	21	0.655

None of the three factors had a significant effect on length change.

Output of the function “gls” (only list significant effects):

Table 23 Results

Coefficients	Standard error	T-value	P-value
Intercept	0.010	1676.861	0.000
Factor(No)O1	0.013	4.601	0.000
Factor(No)O2	0.013	-5.275	0.000
Factor(No)O6	0.013	-2/132	0.050

The small p-values indicated that the length of the group O1, O2 and O6 differed from the length of the specimens in the control group.

3.6.2 Plots

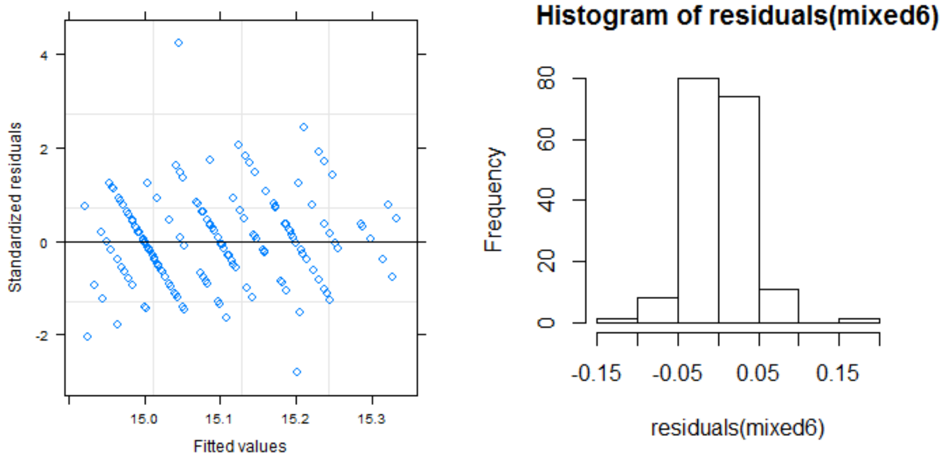


Figure 30 Residuals plots of linear mixed-effects model

In the residuals plots of linear mixed-effects model, the variance was constant, and the distribution in histogram was normal according to the bell–shaped curve, indicating the assumptions of the model were satisfied.

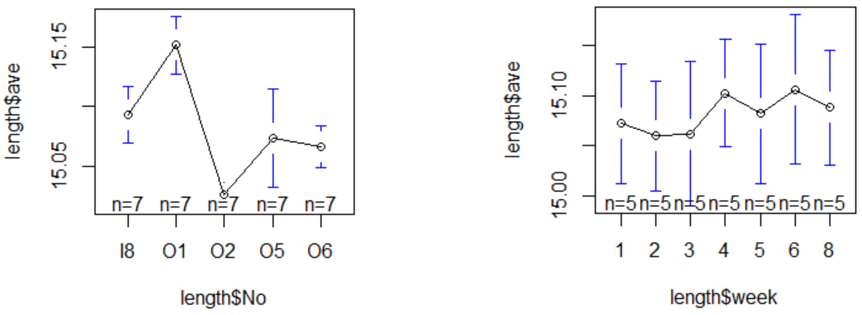


Figure 31 Length change over time

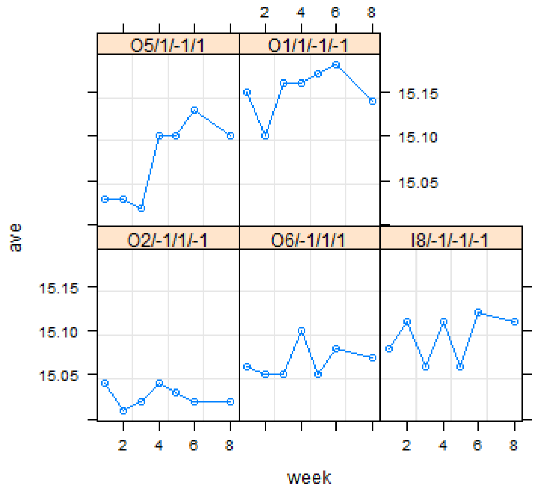


Figure 32 Length changes of specimens from six groups

The length did not change a lot over time (smaller than 0.7% of the original length).

3.6.3 Summary

The results of repeated measures design showed that none of the three factors had significant effect on the length. The length values of all specimens were stable over time.

4 Comparisons and discussions

After seven weeks, the specimens submerged in water became yellow-while color of the other specimens almost remained the same, as shown in Figures 33 and 34.

Figure 33 Photo of all specimens before test

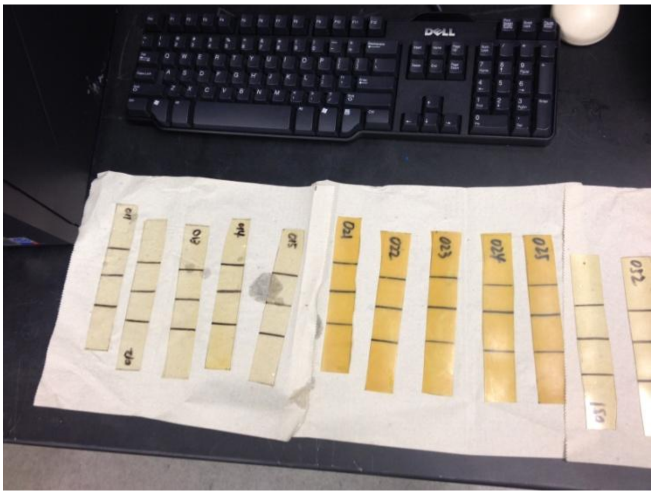


Figure 34 (a) Photos of specimens after test 011-025 (from left to right)

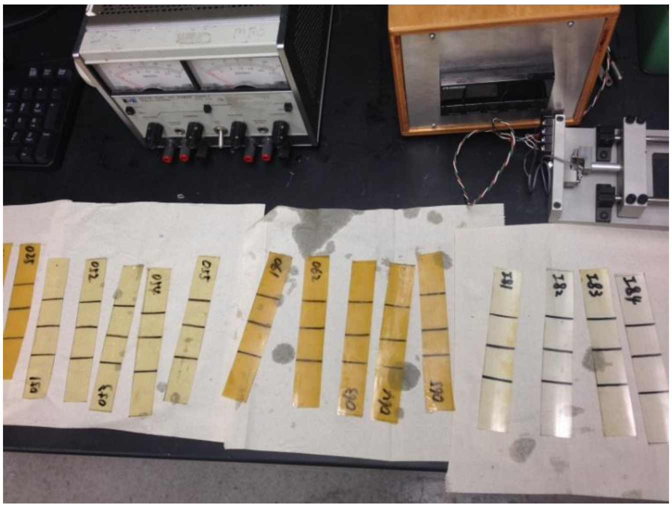


Figure 34 (b) Photos of specimens after test 051-I85 (from left to right)

The statistical methods were used to compare different models or different data sets. The results of the Tukey test shows whether the values of parameters changed significantly every two weeks. ANOVA was a good way to study the relationship between two groups of data. For repeatedly measured data, a longitudinal factorial design is precise enough and helps us to decide whether there is a time effect. And plots are the most obvious way to show change.

When there was heat, hardness decreased. UV light might have the most significant effect on the decreased modulus values, but heat and moisture also decreased the modulus values. Heat had slight effect on thickness and weight.

Hardness of the specimens in all of the groups decreased a little bit. The modulus of all specimens decreased significantly over time. The values of thickness fluctuated significantly over time. The weight, width and length values of all specimens were almost constant. This result could be caused by two reasons. First, this test was not taken for a long time. An outdoor experiment requires several years to determine a materials’ service life. Second, during the test, the temperature in Los Angeles was not too high, and the intensity of UV light was not always as strong as that of an artificial light source.

5 Conclusions

The longitudinal factorial design, ANOVA and Tukey tests are very useful for a longitudinal data analysis. When parameters are measured repeatedly, a longitudinal factorial design (function "lme" and "gls" in R) shows whether a factor is important. ANOVA is useful in studying the difference between two data sets or two models. A Tukey test is applied when we want to know whether values increase or decrease significantly.

This experiment proved that heat, moisture and UV light had significant effects on membrane properties like hardness, modulus, thickness, weight, width and length. The results suggested some good ways to prevent PU membranes degradation. To prevent their hardness from decreasing, which is caused by heat, PU membranes can be stored in water deeper than 24cm to avoid temperature increase caused by hot weather. When membranes are stored with exposure to UV light, their modulus values will decrease. To avoid this problem, membranes can be covered with a light filter like EasyShade Blk90 Sunblock Black 90% Shade Cloth UV resistant fabric, which is inexpensive and can decrease membrane temperature at the same time. Thickness, weight, width and length are not good indicators for damage in an outdoor test.

According to the results of this experiment, the next step is to conduct an indoor accelerated tests using an artificial UV light source with higher light intensity, because UV light was the most important factor causing decreased modulus values. Also, all of the methods must be standardized. Future work also includes studying the relationship between orifice openings versus the backpressure (DWP), which is recommended as a possibly good predictor for the decline of diffuser performance (Kaliman et al., 2008).

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