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Weathering of Polymeric Materials in New Zealand

NJ Marston and MS Jones



Foundation for RESEARCH SCIENCE & TECHNOLOGY

Tuāpapa Rangahau Pūtaiao

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External reviewer

Dr Peter Plimmer, The University of Auckland, New Zealand.

WEATHERING OF POLYMERIC MATERIALS IN NEW ZEALAND

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N J Marston and M S Jones

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Abstract

Most of the commercial organic-based polymers used in the building and construction industry undergo photolytic and photo-oxidative reactions during exposure to solar UV radiation. The premature failure of these building polymers is a major concern to the building and construction industries, and the right choice of materials for a specific application is critical in maximising the lifetime of building products.

An understanding of the durability and degradation of polymers within specific environments is required to assist the building industry in making correct decisions on materials. New Zealand's climatic variables, such as UV radiation, temperature, humidity and sea spray, significantly affect the durability of polymeric materials, and reliable assessments for New Zealand Building Code durability requirements can sometimes be difficult.

Research into the natural weathering of a number of building plastics at nine exposure sites around the country has shown that there are significant differences in the rates of photo-degradation of polymeric materials at the different sites. The development of New Zealand weathering indices maps for clear polyolefin materials is beneficial in understanding the durability of building polymers within the environment. In reality, most commercially available products will contain additive packages, such as UV stabilisers and anti-oxidants, to enhance durability. That said, the findings reported here do underline that manufacturers and specifiers need to be aware that the correct choice and accurate incorporation of these additives is crucial to obtaining any significant service life from exposed polyolefin and other polymeric materials.

Keywords

Polymer, weathering, weatherability, durability, UV radiation, degradation, construction, photo-oxidation.

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1. INTRODUCTION

The durability, performance and rate of deterioration of polymer-based products are all significantly influenced by both the material composition and the climatic conditions to which they are exposed. To date, polymers have predominantly found applications in non-structural items, such as cladding, plumbing and coatings. That said, there is a continued increase in the use of polymeric materials, particularly polymer-based composites, for structural applications within the building industry. However, the weathering of thermoplastics, thermosets and composites, due to variations in temperatures, moisture/rainfall and UV radiation, is not fully understood. More understanding of the durability and weathering of these materials would enable the useful lifetime of building products to be predicted to a greater accuracy, as well as enable plans to be made for maintenance and replacement of key building components.

This research has investigated whether climatic variations within New Zealand have a significant effect on the weathering and durability of building plastics. The main emphasis of the research is on the large variations in solar UV radiation within New Zealand, and the resulting photo-degradation reactions occurring from exposure at each of the nine sites across the country. To facilitate this investigation some of the materials exposed were chosen on the basis of their being highly susceptible to UV degradation. Therefore, they are not representative of materials usually specified for outdoor exposure, but are critical to developing the desired understanding of climatic effects.

Most of the commercial organic-based polymers used in the building and construction industry undergo photolytic and photo-oxidative reactions during exposure to solar UV radiation. The polymers contain chromophoric groups, such as carbon-carbon double bonds (C=C) and carbonyl groups (C=O) as shown in Figure 1, which are capable of absorbing UV energy and are involved in the photo-reactions that result in the degradation of the polymer. These chromophoric groups can exist: within the regular structure of the polymer, or as a result of impurities present, or through thermal processing of the materials involved.

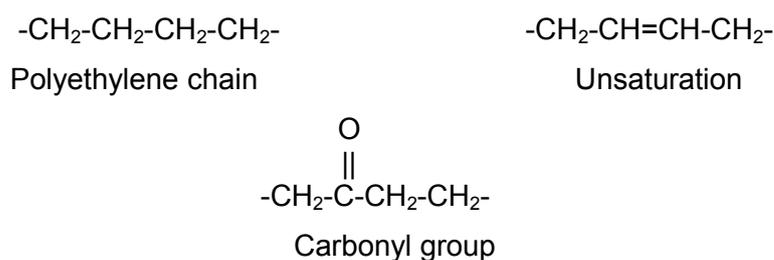
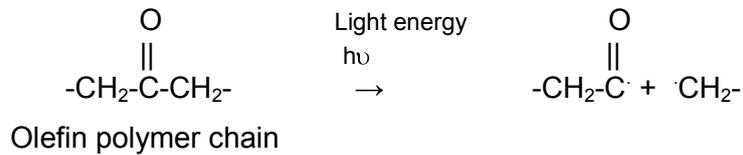


Figure 1. Structure of the polyethylene chain and chromophoric groups

This is the situation with the polyolefins, polyethylene (PE) and polypropylene (PP), which are severely affected by the presence of UV radiation. Although they have no carbonyl or C=C bonds within their regular structure, the chromophoric moieties are introduced into the backbone or side groups through the high temperature injection moulding and extrusion processes involved in producing the plastic building products. It is also understood that the metal-based additives contained within the polyolefins catalyse oxidation reactions resulting in photo-oxidative and thermo-oxidative degradation. Initiation of the photo-chemical degradation reactions can occur via free radical mechanisms, leading to the formation of hydroperoxides and chain scission as shown schematically in Figure 2, which eventually cause catastrophic failure of building components. However, it is important to note that the careful selection of UV

stabilisers, pigments and other additives can reduce this damage to the point where most polymeric materials can be fit-for-purpose for their specific applications in construction.

Chain scission



Peroxide formation

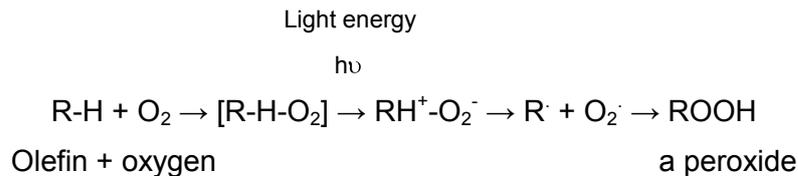


Figure 2. Photo-oxidation of polyolefins

Degradation effects that occur within polymer-based materials range from discolouration on the polymer surface, which affects the aesthetic appeal of the material, through to extensive mechanical damage to the polymers, severely affecting the performance of the building product. The colour changes mainly occur as a consequence of chemical changes within the polymer structure, resulting in yellowing or darkening of the polymer.

The more serious effects of photo-degradation include micro-cracking and embrittlement of polymeric substrates. These effects are often accompanied by extensive deterioration in the mechanical properties of the materials, such as tensile strength, impact strength and elongation, all of which are important parameters in the performance of a building product.

It is therefore necessary to be able to predict the performance of building products in specific environments, particularly regarding the expected lifetime of materials. This research has allowed the development of a method for lifetime prediction for plastic materials based upon a knowledge of material formulation coupled with an understanding of climate and climate change within New Zealand.

Approximately 47,800 tonnes (te) of polymer was used in construction in 2005, about 16% of all polymer usage (Plastics NZ 2006). This has grown significantly since 2003 when the figure was 36,400 te, equating to 15% of national consumption. As New Zealand has no domestic polymer production (polymerisation) industry, all polymer used, approximately 260,000 te in 2005, was imported (Plastics NZ 2006).

Polyvinylchloride (PVC) materials remain the major polymeric material used directly by the construction industry in New Zealand, with about 26,000 te being used domestically in 2005 (Plastics NZ 2006). This represents about 63% of all PVC consumption in New Zealand. Higher total figures than this have also been given (Plastics NZ 2007). Unplasticised PVC (uPVC) materials find applications in potable and waste water piping, spouting, ducting, cladding, windows and trims. When correctly formulated these uPVC materials are able to perform well in exposed applications and have an extensive history of use in New Zealand. Flexible, plasticised, PVC represents approximately 10% of PVC consumed (Plastics NZ 2007). Plasticiser additives modify the material properties for applications such as cable sheathing, flooring, seals and gaskets. When used in exposed positions the plasticiser can migrate from the matrix, accumulate at the surface and the products will embrittle.

High density polyethylene (HDPE) usage in construction is significantly less than PVC, at approximately 6,700 te per annum (Plastics NZ 2006). This is approximately 14% of all HDPE used in New Zealand. HDPE materials find applications in waste water piping, building wrap, damp-proof membrane (DPM), ducting and trims. Careful choice of formulation is needed if exposed HDPE components are to resist the effect of solar radiation.

Expanded polystyrene (EPS) is consumed in very high volumes by the construction industry, in the form of insulation. This volume translates into a annual mass consumed of approximately 4,000 te and represents about 57% of all EPS use in New Zealand (Plastics NZ 2006). EPS insulation is hidden, and so fit-for-purpose. Polystyrene has very poor resistance to solar radiation exposure.

Low density polyethylene (LDPE) is used directly in construction at the rate of about 2,500 te per annum (Plastics NZ 2006), equating to only about 4% of national annual consumption. This LDPE consumption will be almost entirely as DPM, as used below concrete slabs. However, it is believed that a significant quantity will also be used in packaging of building materials that is not accounted for in the figures derived by Plastics NZ.

Of course, other polymeric materials are used within the construction industry. While these account for only about 0.4% of annual total polymer usage in New Zealand some specific types are worthy of note. PP materials are consumed by the construction industry at a rate of about 400 te per annum (Plastics NZ 2006), being mainly used as DPMs, but also for building wraps. Polycarbonates (PC), polyesters (predominantly polyethylene terephthalate – PET) and polymethylmethacrylate (PMMA) can be used as glazing materials which are exposed to the full effects of sunlight. Nylons, polyesters and PP are used in carpets, which will be partially exposed to the effects of the sun after filtering by window glass.

2. WORK PROGRAMME

The experimental work undertaken as part of this project was focused upon examining the performance of organic polymers when exposed in the New Zealand environment.

Polymers offer a wide range of properties that often represent a step change in performance compared to many incumbent building materials. However, polymers can be expensive when compared to contemporary materials and so their use only makes sense if the whole life cost WLC of the project is considered. Then polymers may have a significant advantage over other materials due to their reduced requirement for maintenance, and this is the prime motivator for their widespread adoption.

For this reason the choice of materials for study was carefully considered and based upon knowledge of the existing and likely trends in the use of polymers in construction.

2.1 Polymeric materials

Proprietary pipe products, made from white uPVC and black high density PE, were selected for study. White uPVC injection moulded 90° joint pieces matching the uPVC pipe were also obtained. A summary of these materials is given in Table 1.

Table 1. Pipe materials selected for experimental work

Sample name	Generic matrix resin type	Pigments	Pipe diameter / mm	Pigment concentration / %	Wall thickness / mm
PE pipe	high density polyethylene	carbon black	32	1.9	3.5
uPVC pipe	polyvinylchloride	rutile titanium dioxide	68	4.2	1.8
uPVC 90° joint	polyvinylchloride	rutile titanium dioxide	–	–	1.8

The plastic samples selected for the outdoor exposure study were all commonly used within the building and construction industry as discussed in Section 1. Extruded polymer sheets of different generic types were used for this study. A summary of the materials used is given in Table 2.

Table 2. Materials selected for experimental work

Sample name	Generic matrix resin type	Pigments	Pigment concentration / %	Thickness / mm
PC	polycarbonate	unpigmented	–	3
PE	high density polyethylene	unpigmented	–	2
PE	high density polyethylene	unpigmented	–	3
PE	high density polyethylene	carbon black	1.7	3
PET	polyethylene terephthalate	unpigmented	–	3
PMMA	polymethyl methacrylate	unpigmented	–	3
PP	polypropylene	unpigmented	–	2
uPVC	unplasticised polyvinylchloride	rutile titanium dioxide	5.4	2

The unpigmented, clear, PE and PP sheets were selected on the basis that they did not contain any UV stabilisers. They are not representative of materials that would typically be specified for outdoor use, but are an essential part of the project as it was expected that they would degrade quickly enough to yield results within a timeframe of 1 – 5 years.

2.2 Outdoor exposure

Initially four identical exposure sites were established at sites across the country in 2001. These four sites were located at Kaitaia, Paraparaumu, BRANZ at Judgeford and Invercargill.

These sites were supplemented by the establishment of a further five sites in 2005 to more systematically cover variations in climatic conditions with latitude. These extra sites were located at Auckland, Rotorua, Westport, Christchurch and Cromwell.

The exposure sites lay at latitudes from 35° South to 47° South. The majority of the sites were located within 15 km of the coast. The exceptions were the Rotorua site, and the Cromwell site in Central Otago. In both cases the coast was over 100 km distant. The altitudes of all sites are not far removed from sea level, with Rotorua being the highest at about 400 m above sea level.

The exposure sites were specifically positioned across the different zones of temperature, moisture/rainfall and UV radiation that exist throughout the country.

The climate in the most northern sites, in Kaitia and Auckland, is distinguished from the other sites due to it having a typical annual solar irradiance of over 5.30 GJ/m² per year (NIWA 2007a). The site in Rotorua and those near Wellington (Judgeford and Paraparaumu) have a typical annual solar irradiance closer to 5.10 GJ/m² per year. The trend of decreasing solar radiation intensity continues for the sites further south, with Westport and Christchurch having typical annual solar irradiance of 4.67 and 4.83 GJ/m² per year respectively. Central Otago, due to the clean air, has higher annual solar irradiances. The Cromwell site typical has an annual solar irradiance of about 5 J/m² per year. Finally, at the southern extreme of the exposure sites, Invercargill receives an average annual solar irradiance amounting to roughly 4.4 GJ/m² per year.

The solar irradiance at a given location can also be simply represented in terms of the UV index. The UV index scale is derived from the intensity of the incident sunlight, weighted to the sensitivity of human skin. The approximate locations of the exposure sites and the maximum annual UV index values across New Zealand are shown schematically in Figure 3 (NIWA 2007b).

UV levels in New Zealand are higher than Europe and parts of North America, while the most populated centres correspond to latitudes equivalent to the Mediterranean or California. These low latitudes mean that New Zealand is more sunny than most of Europe, and added to this more UV is received due to the lack of pollution and closer approach to the sun during summer than for the northern hemisphere.

Rainfall also varies between the different site locations. Most sites receive about 1000 mm of rain per annum. Rainfall at BRANZ's site at Judgeford, near Wellington, varies between about 1000 and 1500 mm per annum. Considerably more rain falls in Westport, approximately 2000 mm per annum, due to its position on the west coast of the South Island. Conversely, both Christchurch and Cromwell have an annual rainfall of less than 750 mm per annum. A map showing details of median annual rainfall is shown in Figure 4 (NIWA 2007c).

Daily average maximum and minimum temperatures vary predominantly in line with the latitude of the exposure sites. The exception is Cromwell, where mountainous surroundings of the site results in maximum temperatures over 30°C and minimum temperatures around -5°C. The daily average maximum and minimum temperatures maps are shown in Figure 5 and Figure 6 (NIWA 2007c). The approximate locations of the exposure sites are also included in these figures.

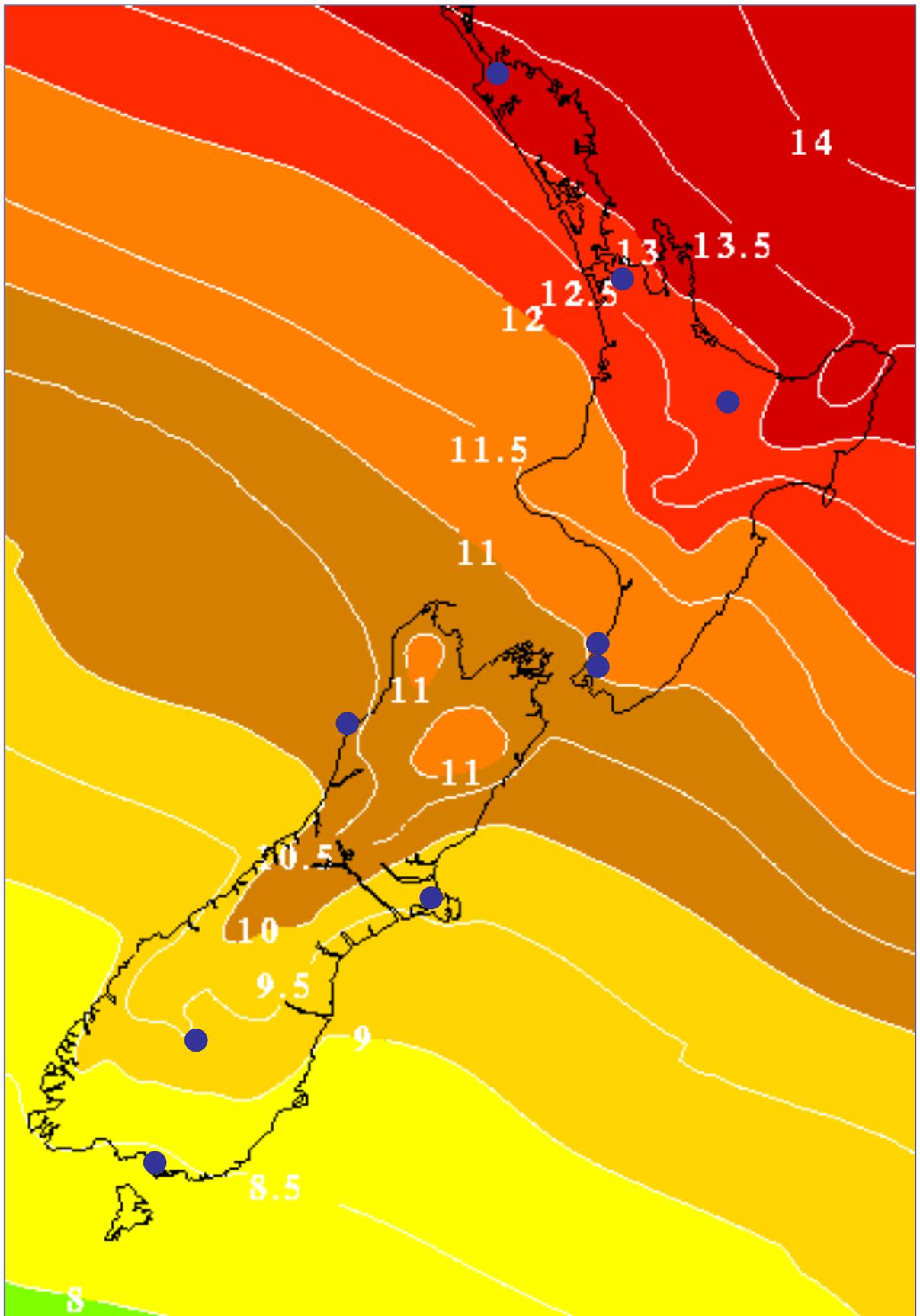


Figure 3. Maximum annual UV index at BRANZ exposure sites (UV index map provided by NIWA)

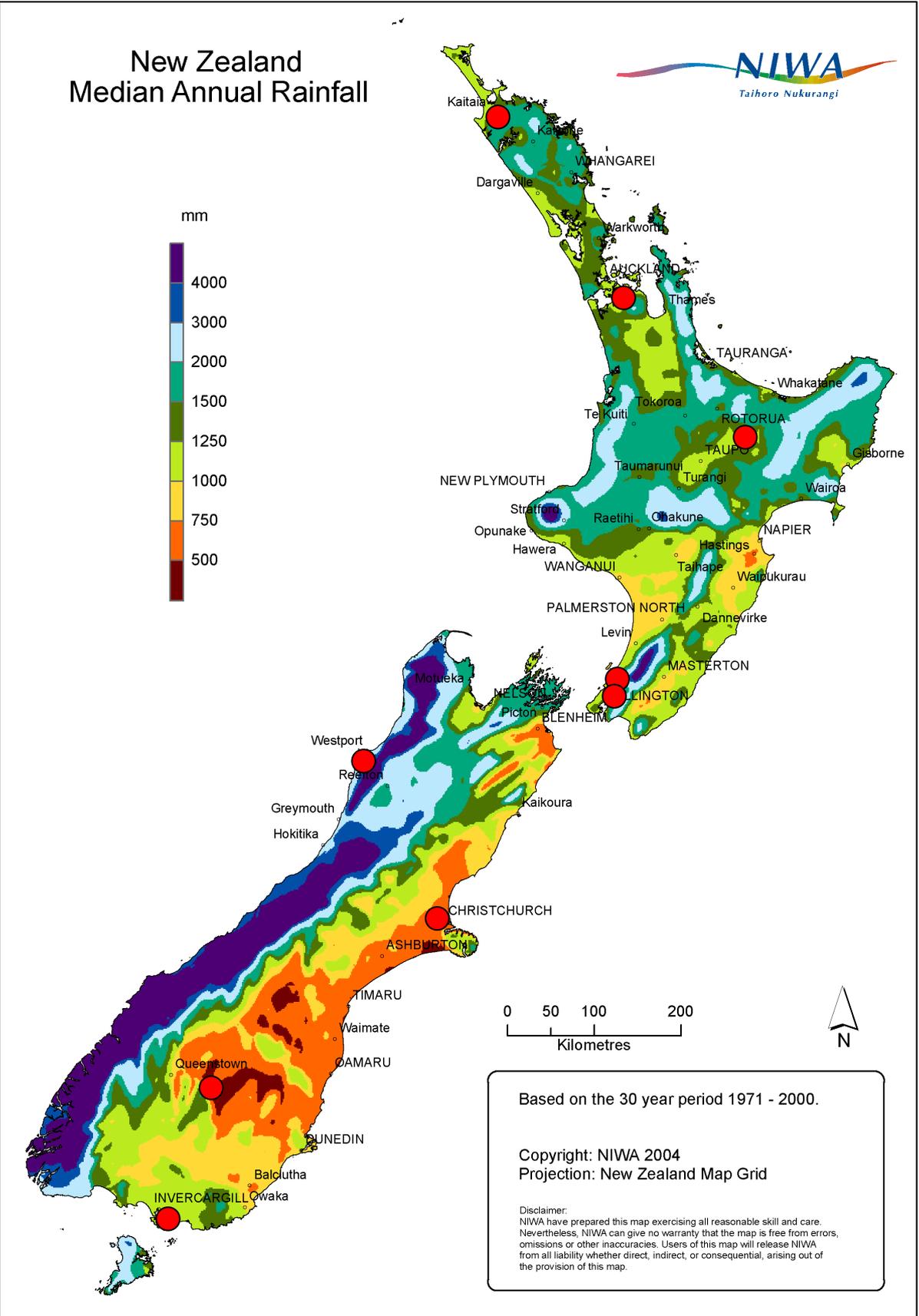


Figure 4. Median annual rainfall map provided by NIWA

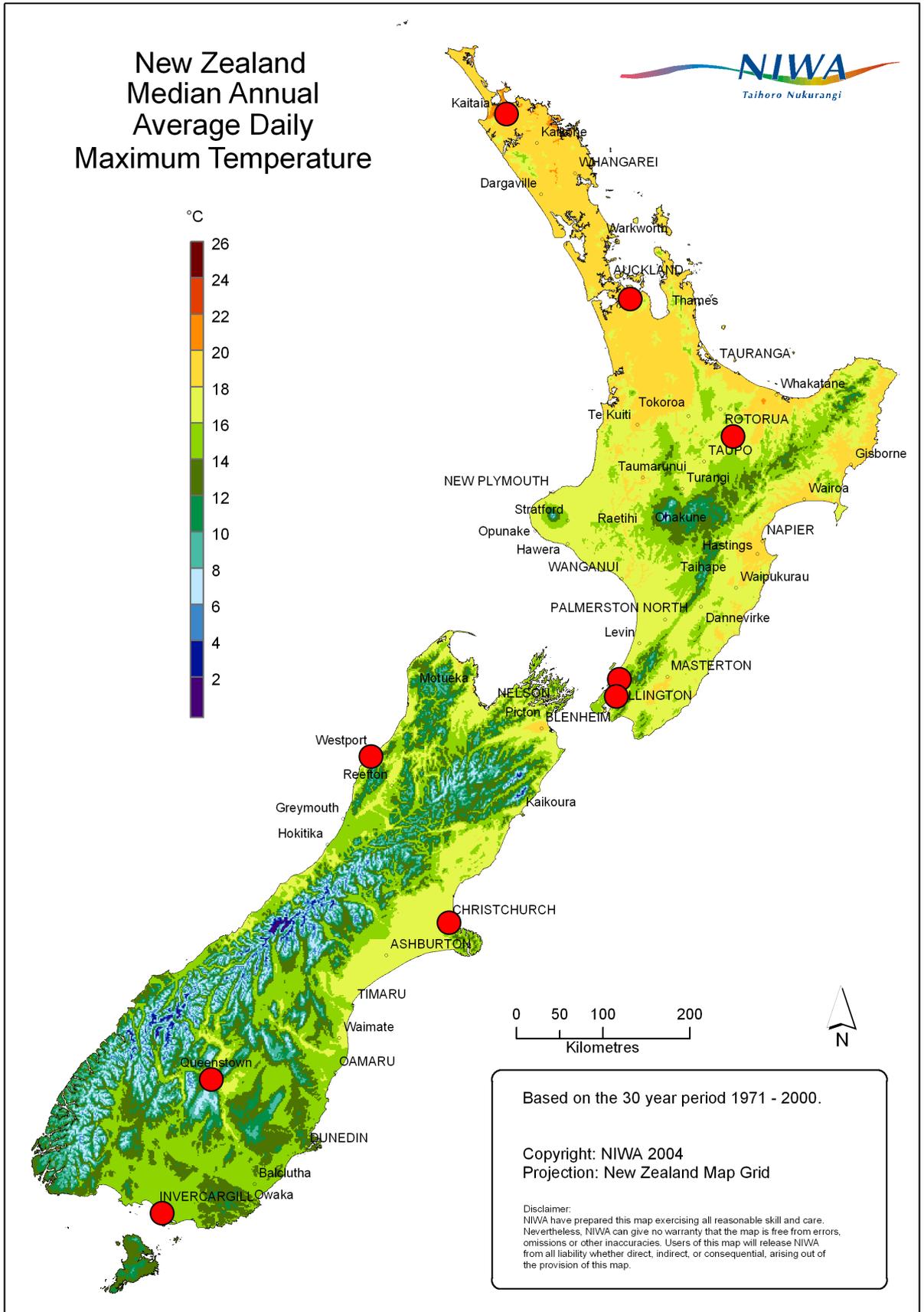


Figure 5. Median annual average daily maximum temperature map provided by NIWA

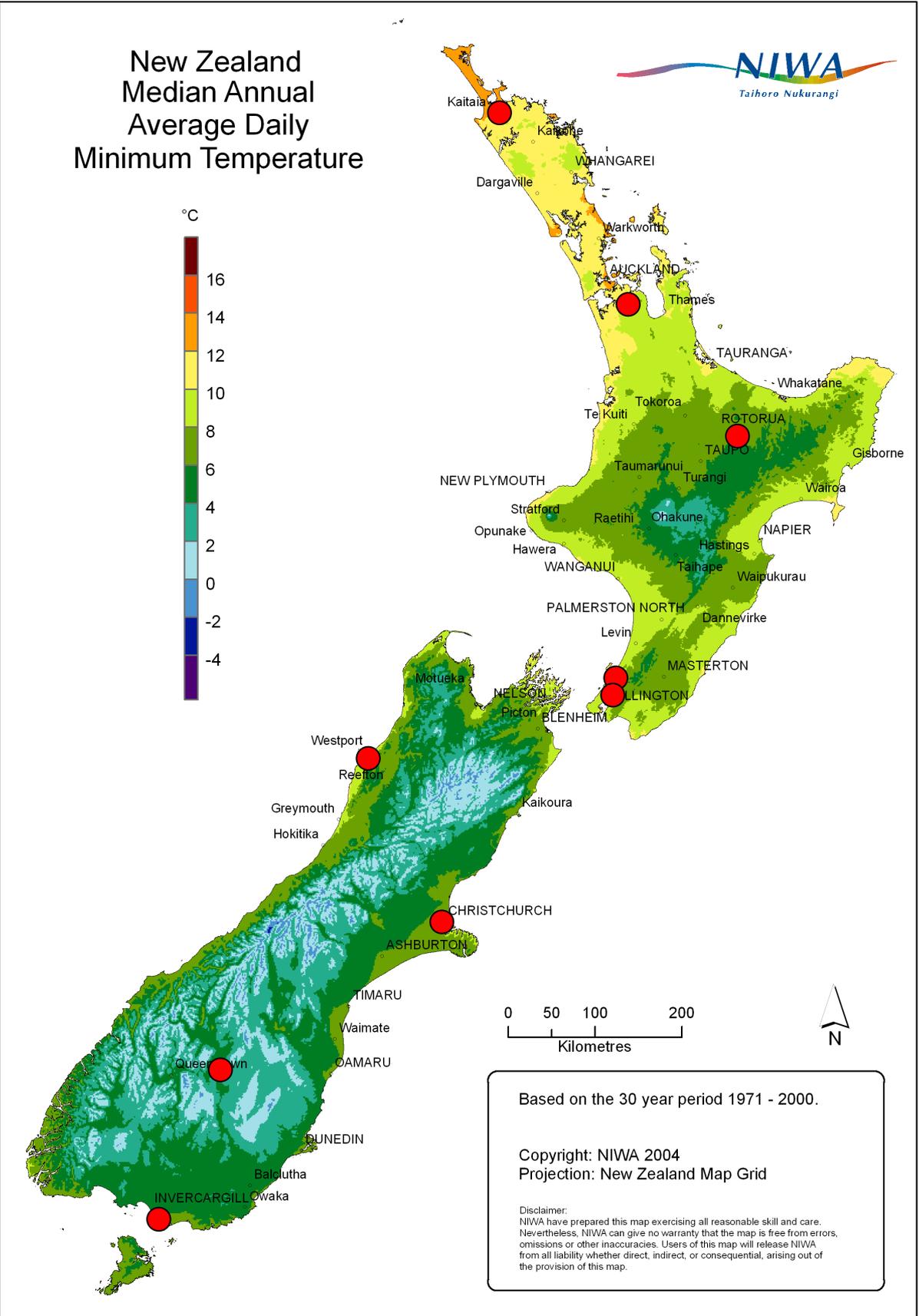


Figure 6. Median annual minimum daily maximum temperature map provided by NIWA

Samples of the plastics were exposed as non-stressed sheets, and an identical set of plastics were set up in an aluminium tension rig under a 1% strain to simulate the stress encountered by building plastics in certain situations.

The commercial plastic pipes were also exposed on each of the sites, in addition to the plastics sheets. The pipe products were placed under stress by use of a restraining chain mechanism for the uPVC pipes (see Figure 7) and by securely bolting the samples in the case of the PE pipe.

Exposure racks were constructed to allow exposure of the samples at 45° to the horizontal facing the equator, as prescribed in ASTM G7 Clause 4.2.2. However, rack construction varied from the manner of construction described by ASTM G7 Clause 5.2 in that stainless steel screws were used to secure the corners of the samples. This construction method could prevent expansion and contraction of the samples and will need to be considered in interpretation of the results obtained.

A typical arrangement of the samples during exposure is shown in Figure 7. The un-stressed plastic sheet samples fill the three rows on the right of the sample rack. On the left side are the multiple aluminium stress racks with each of the polymer sheets held under tension. The PE and uPVC pipe products can also be seen at the top and bottom of the rack respectively.



Figure 7. BRANZ exposure rack configuration

A more compact rack design was employed for the additional sites. These contained the sample types used in the original sites (sheets from the same batches of materials were used), but a reduced number of samples were exposed. The un-stressed plastic sheet samples fill the top three rows on the typical sample rack shown in Figure 8. Below these, in the centre, is the aluminium stress rack with each of the un-reinforced polymer sheets held under tension. The uPVC and PE pipe products can also be seen at the bottom of the rack.



Figure 8. Exposure rack configuration used on the additional exposure sites

In each exposure location the exposure racks were aligned with magnetic north, i.e. facing the equator, to maximise solar radiation exposure (ASTM G7).

Samples were collected from each of the exposure sites on an annual basis. Sample collection occurred towards the end of summer. Initially pairs of each polymer type, pairs of aluminium stress racks and pipe samples of each type were collected to maximise the reliability of the subsequent analysis. However, in 2006 when sampling the additional exposures sites, only pairs of un-stressed samples were collected. Finally, in 2007 single samples were collected to allow for a continuation of the programme into subsequent years.

It should be noted that control samples were retained and stored in a climate controlled environment at 23°C and 50% RH for the entire duration of the outdoor tests.

3. EXPERIMENTAL PROCEDURES

3.1 Mechanical testing

The compressive strength of the proprietary uPVC pipe products were tested as-received. Compressive testing along the lengths of the uPVC pipes and of the uPVC injection moulded 90° joint pieces was completed. These tests were believed to be most representative of the in-service failure mechanism for spouting products.

For compressive testing, sections 250 mm long were used for the white uPVC pipes and the injection moulded joint pieces were tested as a whole. The samples were then conditioned at 23°C and 50% RH for 48 hours.

Post-conditioning, the test pieces were subjected to compression testing. The maximum compressive load was determined at a cross-head rate of 20 mm/min.

The proprietary white uPVC pipe and the black medium density polyethylene pipes were tested for tensile strength along the pipe direction.

Test coupons (55 mm x 250 mm) were cut from the uPVC pipe samples. Test coupons (45 mm x 250 mm) were cut from the PE pipe samples. Four coupons were taken from each. The samples were then conditioned at 23°C and 50% RH for 48 hours.

Post-conditioning, the test pieces were subjected to tensile strength testing. The tensile strength was determined over a gauge length of 100 mm with a cross-head rate of 10 mm/min.

Testing was carried out on a calibrated Instron Universal Testing Machine with a 10kN load cell. Testing of a sheet sample in progress is shown in Figure 9.

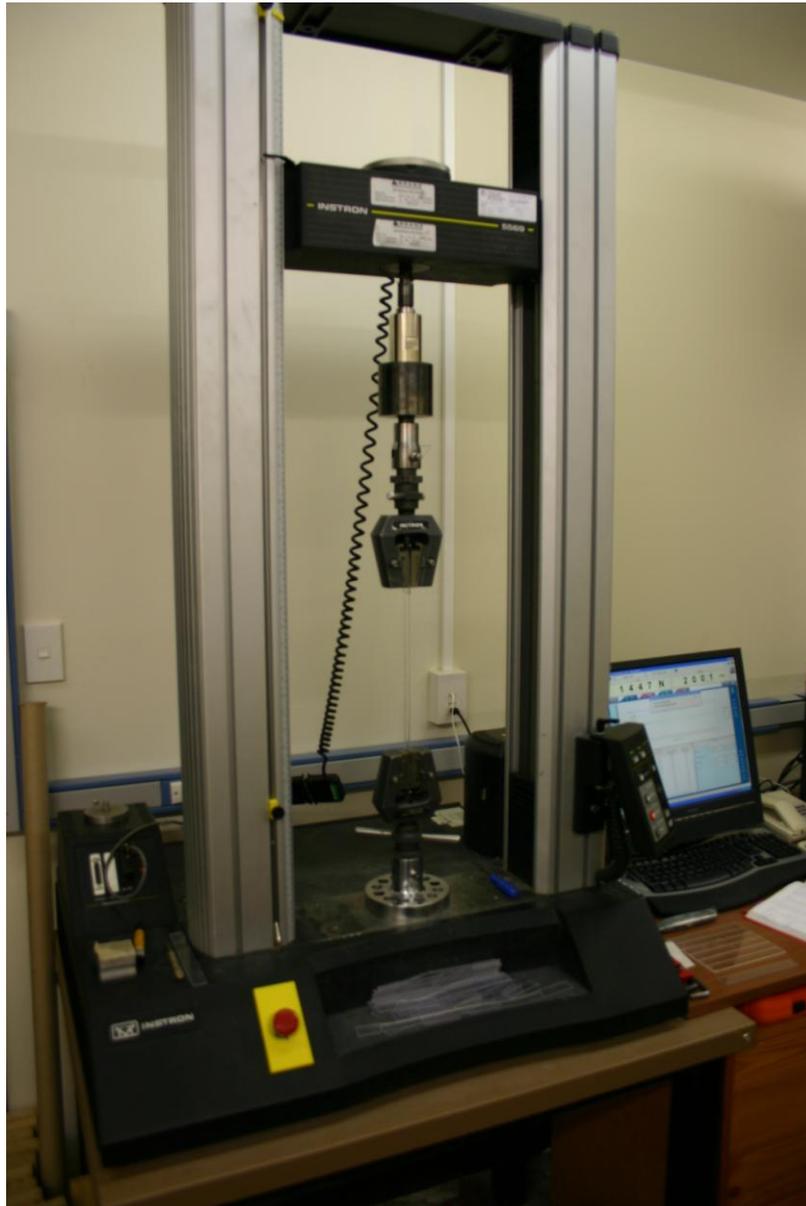


Figure 9. Tensile property testing

The as-received mechanical properties of the polymeric sheet materials were also tested for all the samples listed in Table 2.

Tensile testing was selected as it was decided that this would most effectively examine the effects of surface degradation on the mechanical properties of the polymeric materials.

Test coupons (20 mm x 165 mm) were cut from the machine and cross-direction of the sheet samples. Five coupons were taken from each direction. The samples were then conditioned at 23°C and 50% RH for 48 hours.

Post-conditioning, the test pieces were subjected to tensile strength testing. The tensile strength was determined over a gauge length of 100 mm with a cross-head rate of 15 mm/min.

Testing was carried out on a calibrated Instron Universal Testing Machine with a 10kN load cell.

Linear regression models were used to explore the relationship of the tensile strength to the factors of exposure time, applied stress, test direction and location. An initial screening process was used first to determine if a particular variable affected the tensile, and only those showing a statistically significant effect were included in the models.

3.2 Colour measurement

The CIELab colour space is an internationally accepted model used as a standard to define colour within the industry. CIE stands for “Commission Internationale de l’Eclairage”, an international group of colour scientists whose standards make it possible to accurately communicate colour information. The three-dimensional colour space model designates ‘L’ for the lightness axis, ‘a’ for the red-green axis and ‘b’ for the yellow-blue axis.

Colour measurements were made on the control and exposed samples using a Minolta Chroma Meter CR-200b colour meter. The exposed samples were measured in the as-received state without any wiping or washing to remove surface deposits. Values for the CIELab colour space parameters (L, a and b) were recorded for each specimen. Comparison to the unexposed control sample then allowed derivation of CIELab ΔE , the colour shift.

It should be noted that colour shift, ΔE , of 0.6 is perceptible by most people.

3.3 Surface gloss measurement

Surface gloss measurements were made on the control and exposed samples. The exposed samples were measured in the as-received state without any wiping or washing to remove surface deposits.

Measurements were made using a Rhopoint Novogloss gloss meter using a measurement angle of 85°. Six measurements were made across each sample, and a mean and standard deviation (SD) were then calculated.

3.4 Sensitivity spectra

The principal component of sunlight that causes damage to polymeric materials is ultraviolet light (UV). A typical intensity spectrum of incoming UV radiation is shown in Figure 10.

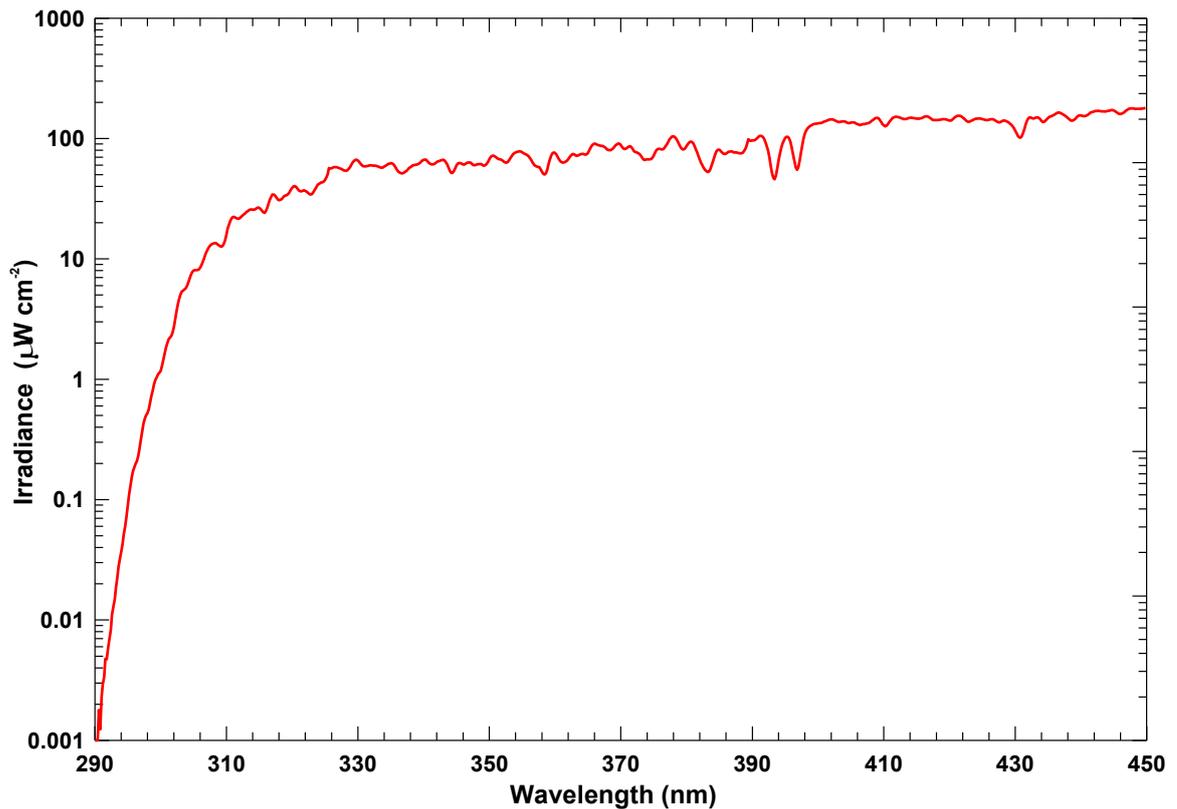


Figure 10. Typical spectra of the UV region of New Zealand sunlight (NIWA 1991)

The UV is the most energetic part of sunlight and does the most damage, even though it comprises only about 5% of light reaching the earth's surface.

Different polymers are most sensitive to damage from different wavelengths of UV radiation, known as the activation spectra (Andrady 1997, Andrady 2002, Andrady 2003), as detailed in Table 3 and shown schematically in Figure 11.

Table 3. Reported activation spectra for polymers for change of different properties on exposure to UV radiation

PC	281–290* 308–330*	yellowness
PE	308–326*	strength
PET	290–315†	strength
PMMA	290–315*	strength
PP	360–380‡	strength
uPVC	300–318*	yellowness

* Andrady 1997

† Andrady 2002

‡ Andrady 2003

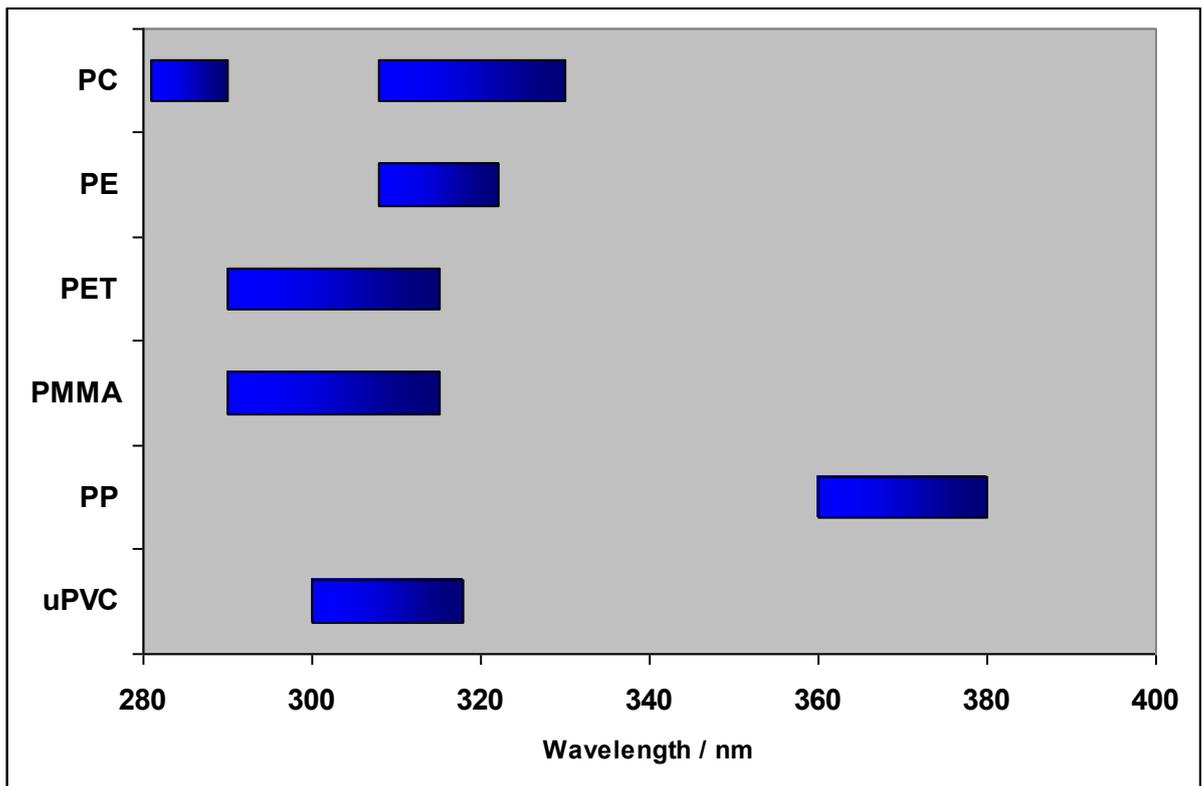


Figure 11. Reported activation spectra for polymers on exposure to UV radiation

The potential for a polymer to degrade due to incident radiation is controlled by the ability of the material to absorb photons of suitable energy and by the availability of photochemical pathways to allow chemical reactions using the absorbed energy (Andrady 1997). Only radiation absorbed by a system is effective in producing chemical changes. Polymers exhibit marked different wavelength sensitivity in their photo-degradation behaviour since different polymer types consist of different chemical structures. Additionally, photons of different wavelengths have different energies, photon energy increasing with decreasing wavelength.

The incident solar intensity spectra is monitored on an ongoing basis at stations spread across New Zealand by NIWA. The data collected is used to provide information on UV Index, UVI, by weighting the raw data to the sensitivity of human skin as discussed in Section 2.2.

The raw solar spectra data from across the NIWA monitoring network was weighted according to the activation wavelength ranges given in Table 2 for each of the exposed polymers. This allowed the derivation of maps showing the dose of the most harmful UV radiation each polymer would receive per year of outdoor exposure. It also allowed precise calculation of this dose for each of the exposure sites in the study.

The mechanical property data for each of the polymers was assessed against the cumulative radiation dose at each exposure site. This process allowed the identification of a maximum radiation dose before the polymer became mechanically non-viable.

As a final step, where appropriate, the maximum radiation dose results were used to generate maps of predicted lifetime for the polymers.

4. RESULTS AND DISCUSSION

4.1 Polymeric materials

No significant quantities of UV stabilisers were found in the PE or PP sheet by Nuclear Magnetic Resonance (NMR) Spectroscopy on extracts taken from the material. NMR analysis of extracts from the PP materials showed that it contained primary and secondary anti-oxidants: sterically hindered phenolic antioxidant (Irganox 1076) ~0.12 % weight/weight (w/w); hydrolytically stable phosphite stabiliser (Irgafos 168) ~0.18 % w/w. The addition of these antioxidants is intended to reduce the degradation of the material during melt processing to minimise the concentration of chromophoric moieties in the finished sheet.

The rutile titanium dioxide concentrations in the white uPVC materials were determined by Inductively Coupled Plasma – Atomic Emission Spectroscopy. The white uPVC pipe was found to contain 4.2% w/w, while the white uPVC sheet contained 5.4% w/w.

The carbon black concentrations in the black PE materials were determined by first using a Setaram TAG 24 Thermal Analyser to heat each sample to 900°C in a nitrogen atmosphere, then by determining weight loss in air by thermogravimetric analysis (TGA). The second, TGA, heating determined the weight change on oxidation resulting from the degradation of the carbon black. The PE pipe was found to contain 1.9% w/w, while the black PE sheet contained 1.7% w/w.

4.2 Mechanical properties

4.2.1 Initial properties

The mechanical properties of the pipe materials for exposure on the initial four sites were determined when the samples were received (in 2001). The mechanical property results obtained, including SDs about the mean, are shown in Table 4.

Table 4. Mechanical properties of unexposed pipe samples

Sample name	Thickness / mm	Tensile strength (MPa)	SD (MPa)	Max compression load (N)	SD (MPa)
PE pipe	3.5	11.0	0.2	3026	57
uPVC pipe	1.8	39.4	1.1	18600	650
uPVC 90° joints	1.8	–	–	2765	290

The mechanical properties of the materials for exposure on the initial four sites were determined when the samples were received (in 2001). These samples were rechecked after four years of storage (in 2005) in a climate controlled environment at 23°C, 50% RH prior to samples being placed on the five further exposure sites.

The mechanical property results in the machine and cross-direction were found to be the same and so the results obtained for the machine direction are shown in Table 5.

Table 5. Mechanical properties of unexposed samples

Sample name	Thickness / mm	2001	SD (MPa)	2005	SD (MPa)
		Tensile strength (MPa)		Tensile strength (MPa)	
PE	2	11.8	0.4	12.3	0.2
PE	3	11.8	0.2	12.5	0.1
PE black	3	10.5	0.3	10.7	0.4
PP	3	30.9	0.2	31.4	0.7
uPVC	2	49.3	0.6	44.6	0.3

4.2.2 Exposed pipe samples

Statistical analysis of the results from compressive testing of the black PE and white uPVC proprietary pipe products showed that no significant change had occurred after four years of exposure. No change in tensile strength was observed for PE. Meanwhile, for uPVC, the tensile strength increased by about 15% per year from the years 2002 to 2004. This result had a very high statistical significance. No differences in tensile strength were found between the exposure site locations. It is believed that the tensile strength increases resulted from the thermal cycling of the samples. This has allowed the stress in the samples, resulting from the extrusion product process, to be relaxed. Effectively the samples were annealed during the exposure, a process well known to improve the properties of polymeric materials (Grellman 2001).

The retention of properties by these materials is not unexpected, since the formulations of the products have been developed and refined to deliver service-lives in excess of 15 years under New Zealand conditions (Davis 1983).

After four years the pipe samples included on the exposure racks were all used, and so the examination of longer-term mechanical property retention of black PE and white uPVC became focussed upon the sheet samples that remained in place at each exposure location.

4.2.3 Exposed sheet samples – six years

4.2.3.1 PP 2 mm clear

Figure 12 presents the tensile strength results for the un-stressed 2 mm PP from the original exposure sites.

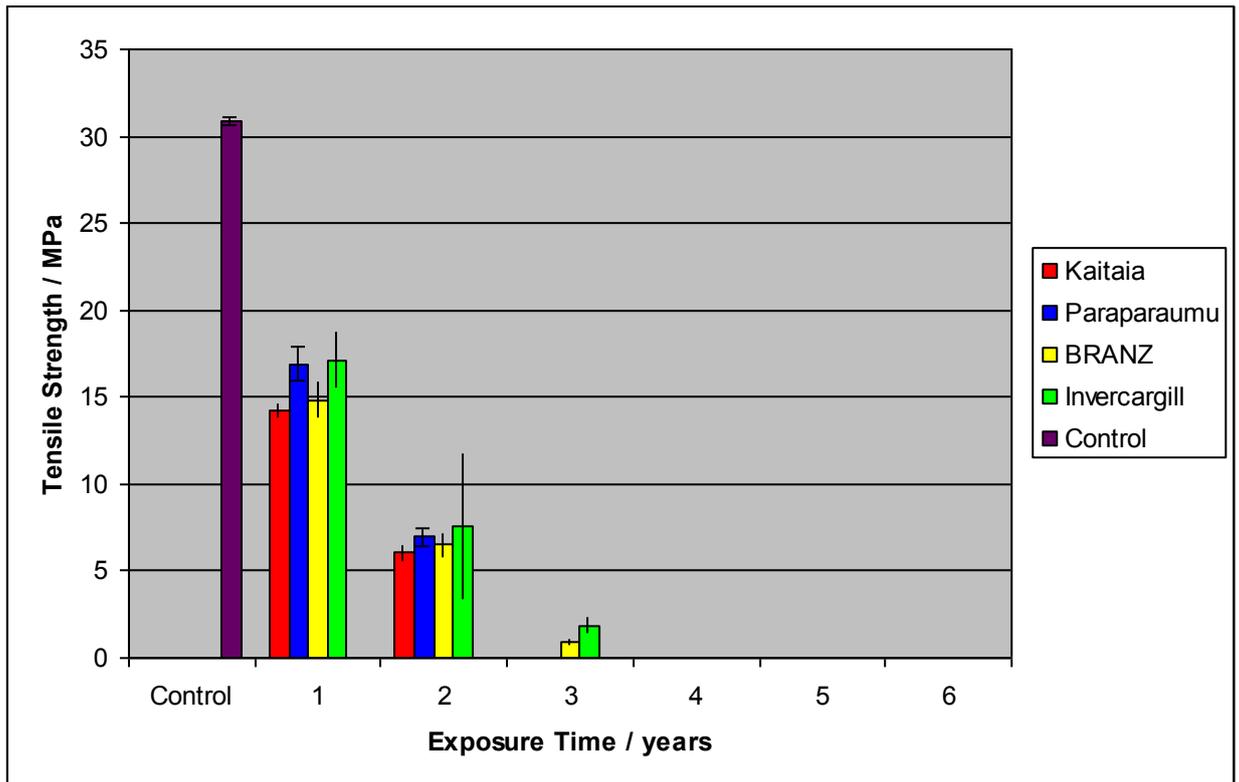


Figure 12. Tensile strength of un-stressed 2 mm PP sheet as a function of time and location

The clear polypropylene samples have shown the most rapid decline in surface, colour and mechanical properties, despite the inclusion of antioxidants in the formulation. However, PP is well known to photo-oxidise faster than other polyolefins (Davis 1983).

Statistical analysis of the clear 2 mm PP samples showed strong effects of exposure time, smaller effects of location, and a weak effect of direction. No statistically significant effect for stressing of the samples was found. Samples exposed at the Kaitaia site had lower strength than at the BRANZ site, while samples at the Paraparaumu and Invercargill sites had a higher strength. The weak effect of direction manifested in that when tested in the cross-direction tensile strength was uniformly higher by 1.1 ± 0.7 MPa.

Over 50% of tensile strength had been lost in the first year of exposure. This observation is in line with results and trends reported by other workers (Manson 1976, Davis 1983) and this rapid degradation has been clearly attributed to reactions with oxygen (Winslow 1967). It is also well known that embrittlement is typically a precursor to visible changes (Winslow 1967).

By the end of three years of exposure the materials had undergone extensive micro-cracking, were visibly completely degraded, and had lost all mechanical strength as is clear from Figure 12 and as exemplified by the photo in Figure 13. After four years no intact samples were found on any of the original exposure sites.



Figure 13. Typical appearance of the PP sheet after three years of outdoor exposure

Microscopic examination of the surface of the PP material allowed visualisation of the individual micro-cracks as shown in Figure 14.

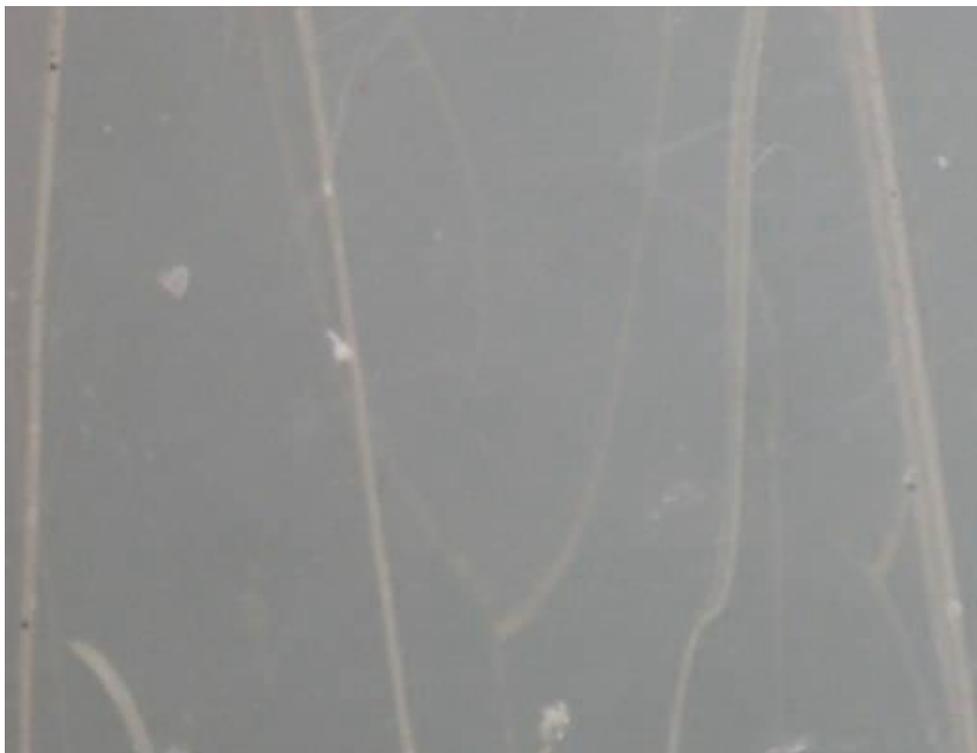


Figure 14. Optical microscope image of micro-cracks in PP sheet after three years of exposure

When viewed from the sheet edge the extent of the penetration of the cracks into the material and the explanation for the loss of strength was clear (see Figure 15).



Figure 15. Optical microscope image of PP sheet edge showing penetration of the microcracks into the sheet after three years of exposure

4.2.3.2 PE clear

The tensile strength results for the un-stressed 2 mm clear PE from the original exposure sites are shown in Figure 16.

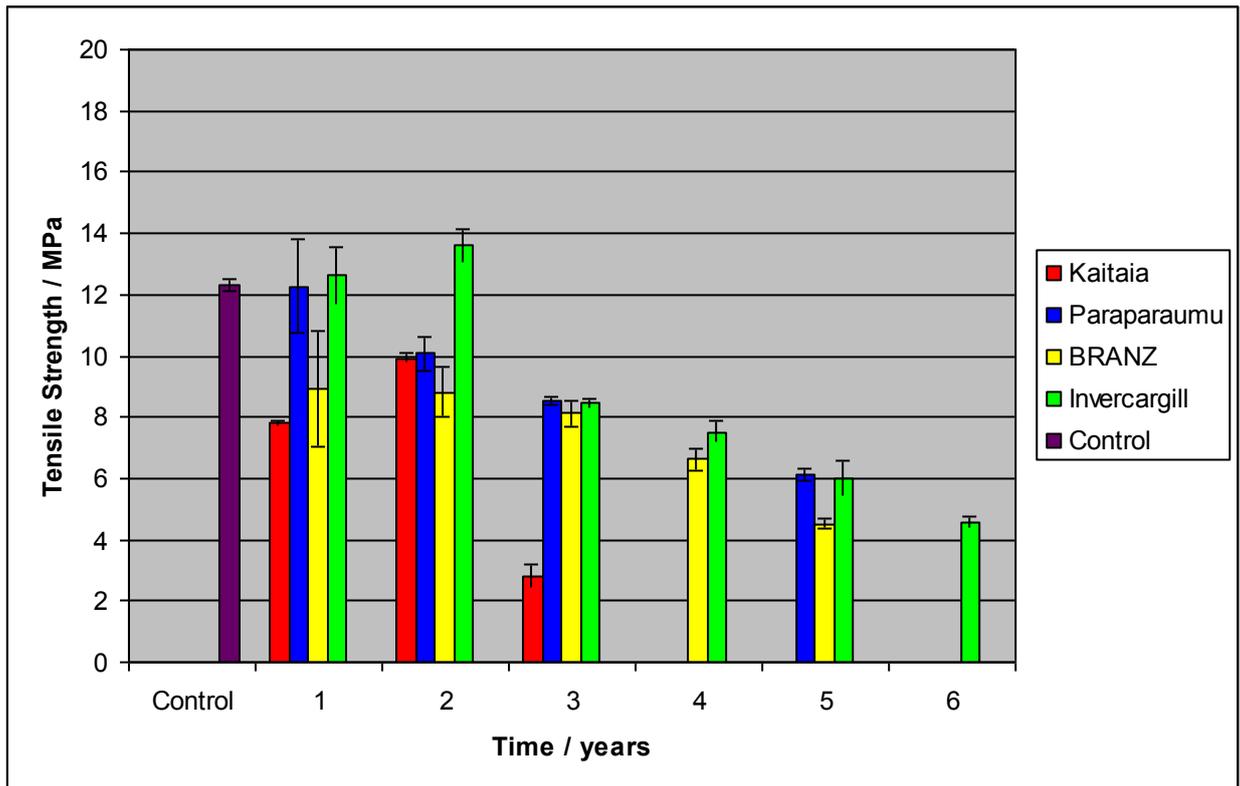


Figure 16. Tensile strength of un-stressed 2 mm PE sheet as a function of time and location

Statistical analysis of the clear 2 mm PE data showed strong effects for exposure time and for location, and a weak effect of direction and no effect of stress. The strength decreased with exposure time. This result is in line with results found by other workers (Manson 1976). Samples in the Kaitaia site had a strength on average 4 ± 0.4 MPa lower than the BRANZ site samples. Samples at the Invercargill and Paraparaumu sites were slightly stronger on average than those at the BRANZ site. Strength in the cross-direction was 0.7 ± 0.4 MPa higher.

Statistical analysis of the data for clear 3 mm PE samples showed similar effects to the clear 2 mm PE samples. There were strong effects of exposure time and location, and effects for both stress and direction. Un-stressed material was on average 0.7 ± 0.3 MPa stronger. Strength in the cross-direction was 1.1 ± 0.4 MPa higher.

The mechanisms of photo-oxidation of PE are well understood (Bolland 1948, Bolland 1949, Bateman 1954) and it is known that the ease of photo-oxidation increases in the order HDPE, LDPE and PP (Davis 1983). All un-pigmented, and therefore UV transparent, polyolefin materials are well known to lose strength rapidly during outdoor exposure (Davis 1983).

The clear polyethylene samples lost the majority of their mechanical strength due to micro-cracking. These micro-cracks will rapidly compromise the integrity of the sheet and after four years of exposure fewer samples remained intact for collection. The rate of degradation of the PE sheet materials is as expected, considering that the material does not contain any UV stabilisers.

Surface micro-cracks in a PE sheet are shown in Figure 17.

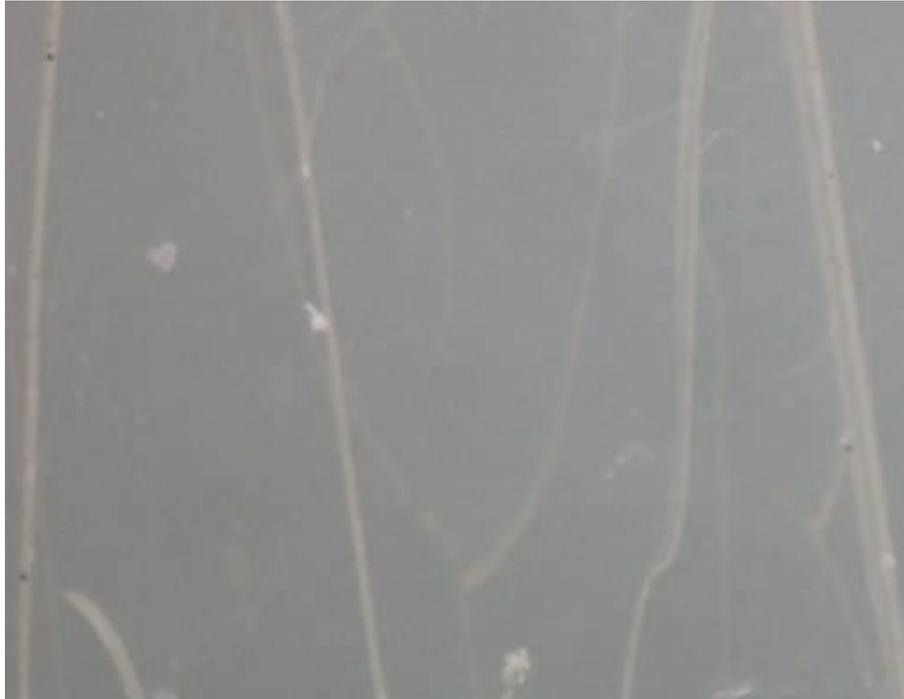


Figure 17. Optical microscope image of micro-cracks in PE sheet after three years of exposure

The optical microscope image shown in Figure 17 is the same scale as that for PP shown in Figure 14. It exemplifies that the micro-cracks in the PE, made visible using blue dye, are further apart than for the PP sheet. However, the cracks in the PE were found, with time, to propagate deeper into the sheet and this is demonstrated in Figure 18 below.

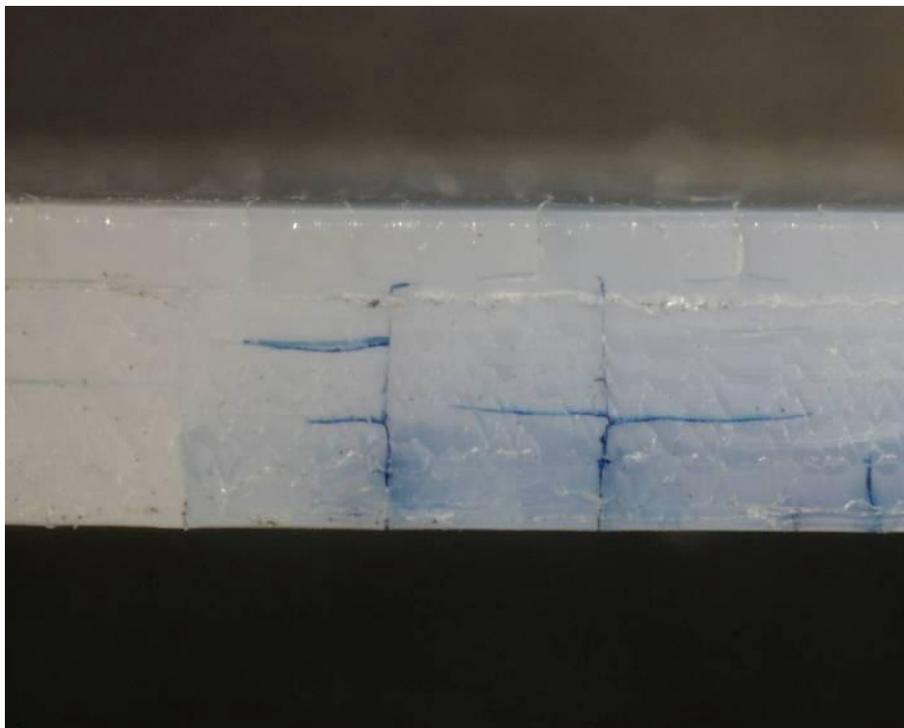


Figure 18. Optical microscope image of PE sheet edge showing penetration of the micro-cracks into the sheet after three years of exposure (dye has been used to make the cracks easier to see)

4.2.3.3 PE 3 mm black

The tensile strength results for the un-stressed 3 mm black PE from the original exposure sites are shown in Figure 19.

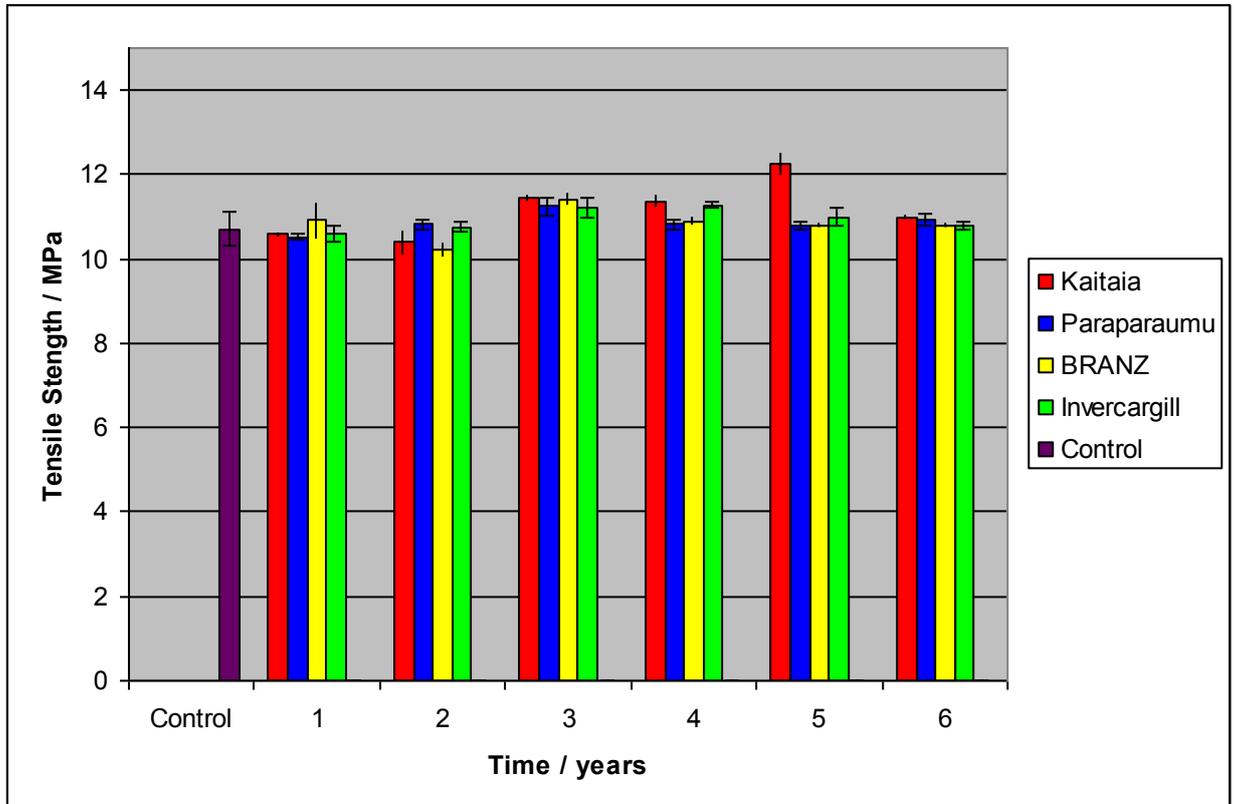


Figure 19. Tensile strength of un-stressed 3 mm black PE sheet as a function of time and location

The tensile strength data for black PE showed a significant effect of exposure time, with strength increasing up to Year 3 then decreasing. There was weak evidence of a direction effect by 0.1 ± 0.07 MPa in the cross-direction, but no statistically significant effect for stress or location.

Publications by other authors have indicated that correctly formulated and pigmented PE can have a life of 20–30 years, dependent on climate (Gilroy 1979). However, the sample surfaces studied here exhibited extensive, very fine, micro-cracking as shown in Figure 20. Again this image is to the same scale as Figure 14 and Figure 17.



Figure 20. Optical microscope image of micro-cracks in black PE sheet

It is believed that the carbon black pigment has limited the size of these micro-cracks. Carbon black is a very effective stabiliser for PE. Typical additions, in the range 2–4% by weight, result in both light screening and antioxidant effects (Wypych 1990).

While white pigments reflect incoming radiation, coloured pigments absorb selective wavelengths. This affects their influence on the material's surface layers. Carbon black is highly UV absorbing, is capable of giving excellent UV opacity in very thin layers, and hence effectively limits UV damage to the very surface of the material (Davis 1983). The carbon black particles also have highly condensed aromatic ring structures and impurities at their surfaces that endow radical scavenging and antioxidant abilities (Scott 1965, Liu 2002). These mechanisms will tend to restrict the micro-cracking to the very surface of the material and prevent the extensive cracks seen in the more transparent polyolefin (PE and PP) samples. When viewed from the sheet edge (see Figure 21), it is clear that the extent of the penetration of the cracks into the sheet was small.

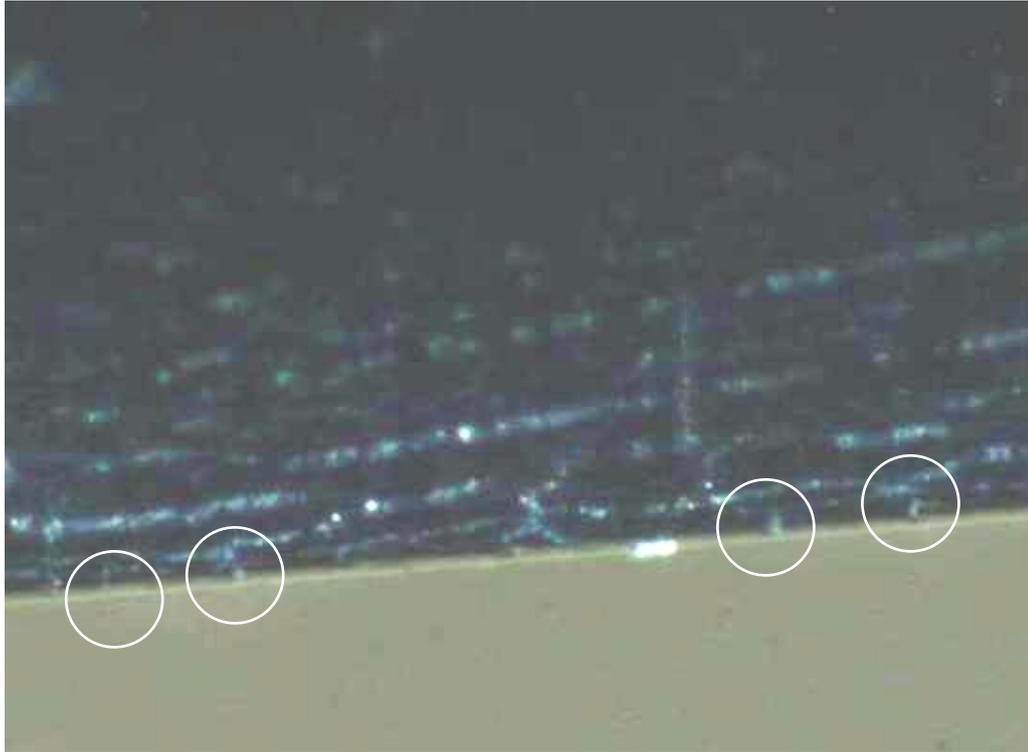


Figure 21. Optical microscope image of black PE sheet edge showing the limited penetration of the micro-cracks into the sheet after three years of exposure (some of the micro-cracks present are circled for clarity)

These shallow, but numerous, cracks will not compromise the mechanical properties of the black PE sheet in the same way as the larger cracks seen in the clear samples. It is also evident, from the strength retention of the exposed samples, that the fine cracks are too small to initiate crack propagation when the samples are placed under tension.

4.2.3.4 uPVC 2 mm white

The tensile strength results for the un-stressed 2 mm white uPVC from the original exposure sites are shown in Figure 22.

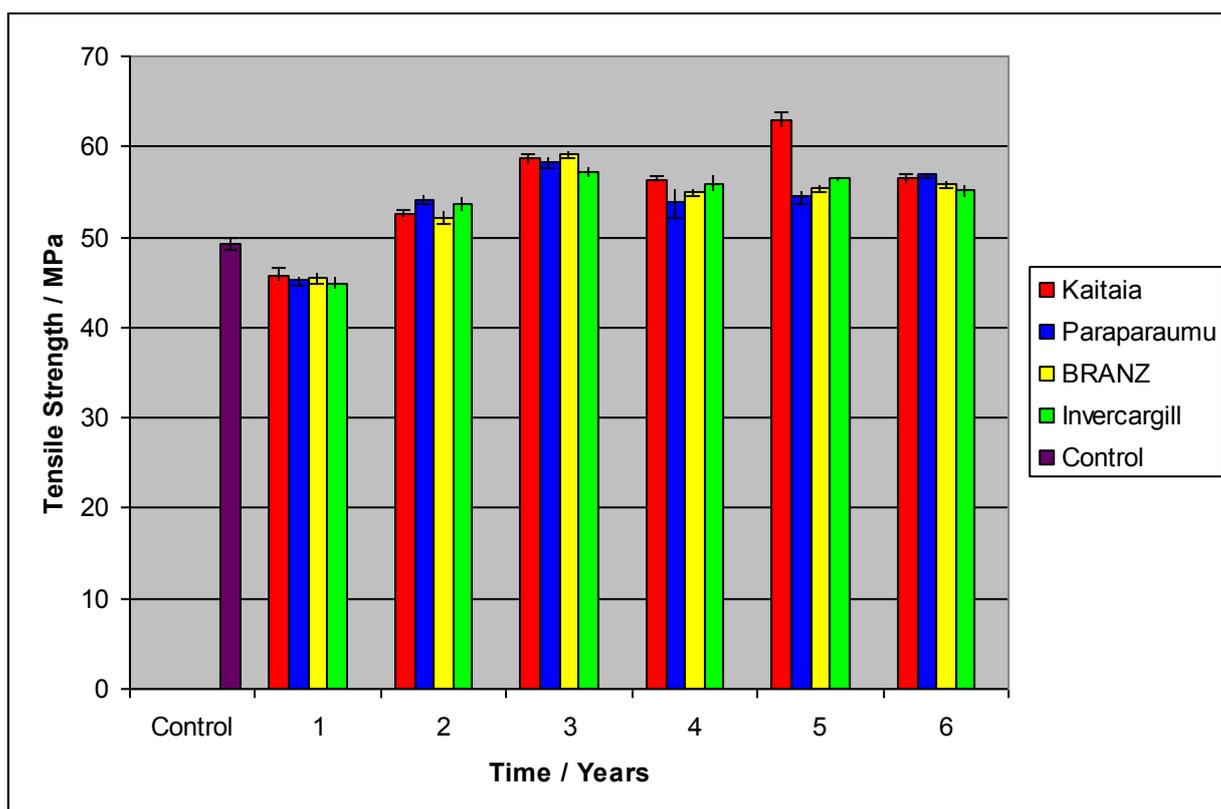


Figure 22. Tensile strength of un-stressed 2 mm white uPVC sheet as a function of time and location

Statistical analysis of the tensile strength data for white uPVC found no effect of location, but statistically significant effects were found for exposure time, stress and direction. The tensile strength varied with the exposure time, increasing for the first three years, then decreasing. This effect has been reported by other workers for the tensile strength of uPVC following three years of natural exposure (Tsurue 1981). Un-stressed samples had an average strength 1.6 ± 0.9 MPa higher than stressed samples. Samples tested in the cross-direction were on average -4.6 ± 1.0 MPa lower strength. The main effect was clearly the exposure time.

As discussed for the black PE samples, it is believed that the increase in tensile strength for the first three years of exposure is a result of the thermal cycling of the samples. This has allowed the stress in the samples, resulting from the extrusion product process, to be relaxed. Effectively the samples have been annealed during the exposure.

While it is true that the white pigment used in the uPVC studied here will reflect incoming radiation. In any event, the effects of weathering are restricted to a depth of only about $200 \mu\text{m}$ (Andrady 2003). Therefore, the retention of properties by these materials is not unexpected, since the formulations of uPVC products have been developed and refined to deliver service-lives in excess of 15 years under New Zealand conditions (Davis 1983).

The role of the rutile titanium dioxide (TiO_2) pigment used in these uPVC samples is discussed in greater detail later in this report in connection with the colour changes observed for these samples.

4.2.4 Discussion of mechanical properties – six years of exposure

All of the sheet samples showed a non-linear change in strength with exposure time. White uPVC and black PE showed an initial increase in strength in the first year or two,

then a gradual decline. The clear PE and PP samples showed decreasing strength from Year 2 onwards. This was expected, since neither material contained UV stabilisers.

Location was only a statistically significant variable for the clear polyolefin sheet products. This is believed to be because the opaque materials stop UV radiation from penetrating the surface, so only the surface is damaged (Davis 1983).

The effects of test direction and stress were usually relatively small. In most cases the materials were stronger in the cross-direction, the exception being white uPVC. It is possible that this is the result of the choice of fixing method that did not allow movement induced by thermal expansion. In all cases un-stressed material had higher strength than stressed material, by 3–8% of initial strength, depending on the material type.

The variability in the effects from stress is believed to show that the approach used in this study has been unsuccessful in applying a reproducible stress to the exposed polymer samples. The variability of the applied stress has resulted in a lack of reproducibility in the resulting tensile strength changes. For this reason, it is not possible to conclude if the application of stress has had any effect upon the strength retention of the exposed polymer samples.

4.2.5 Exposed sheet samples – two years

4.2.5.1 PE and PP clear

The % tensile strength retention for the polyolefins after two years of exposure on the five recently established exposure sites, compared to results after the same exposure time on the original sites, is shown in Figure 23.

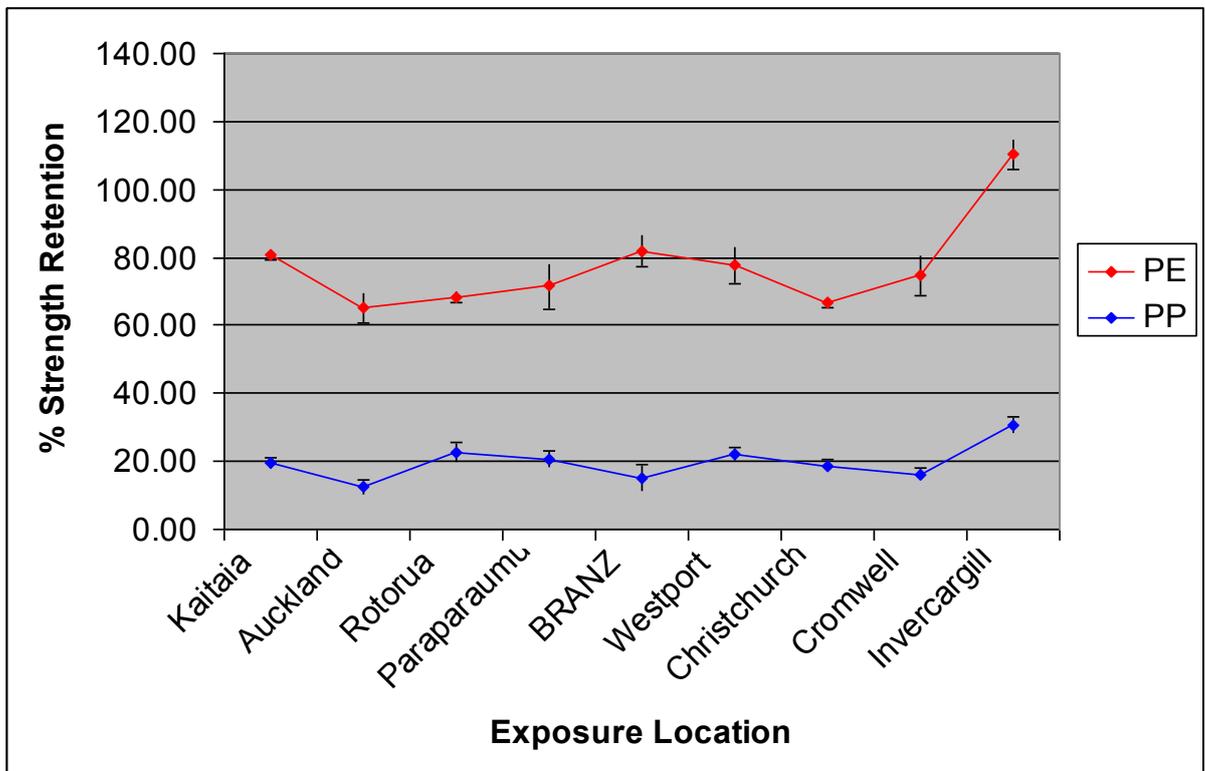


Figure 23. % tensile strength retention of un-stressed 2 mm PE and PP sheet after two years of exposure as a function of location

When comparing these data it appears that the strength retention at Invercargill is perhaps higher than those found elsewhere. However, when this result is

contextualised by reference to the properties in the cross-direction and for stressed sheets, it is apparent that the results across the length of the country are actually very consistent. It is also apparent in Figure 12 and Figure 16 that this trend persists until the materials are completely degraded.

4.2.5.2 PE black and uPVC white

As expected, the black PE and white uPVC samples retained tensile strength at all new sites after two years of exposure and even showed slight strength increases for the reasons already discussed in Section 4.2.3.

4.2.5.3 Glazing materials

The % tensile strength retention for the clear PC, PET and PMMA samples, after two years of exposure on all exposure sites, is shown in Figure 24.

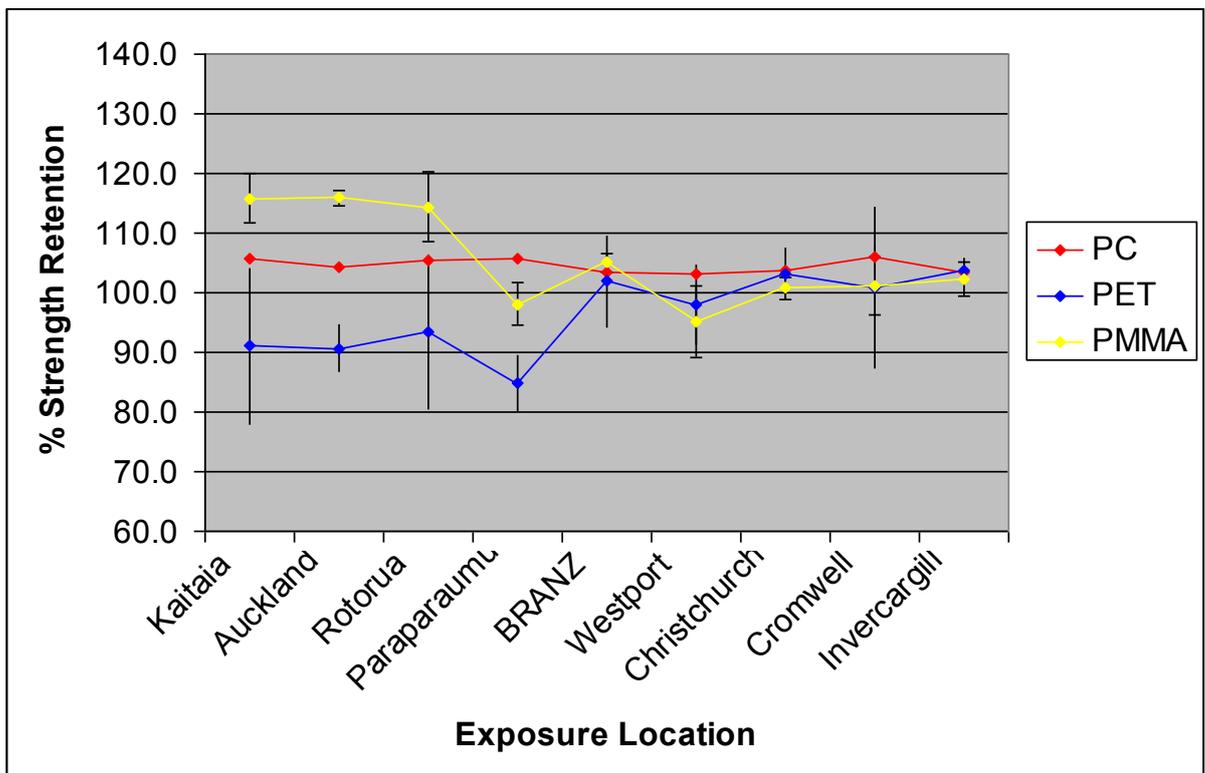


Figure 24. % tensile strength retention of un-stressed PC, PET and PMMA sheet after two years of exposure as a function of location

The strength retention results shown in Figure 24 appear relatively consistent across the length of the country for each of the materials. This is as expected as these materials are typically used in glazing applications, where a service-life of greater than two years might reasonably be expected (Sharman 1989).

It is possible that the properties of the PET are starting to change in the higher radiation environment of the most northern sites, although it is not possible to confirm this hypothesis at this point in the sample exposure. Further work is required and more research on these materials is already underway, funded by Building Research.

4.3 Colour measurements

Colour measurements were made at three positions distributed across the surface of the exposed samples. Samples that did not contain any pigment were backed with the Minolta white colour reference tile while the measurement was made.

Colour measurements were completed on all the exposed materials.

The colour shifts found for the clear polyolefin materials tracked the mechanical property changes already reported. This is as expected given the findings of other workers (Winslow 1967).

The pigmented materials (black PE and white uPVC) gave more interesting results and those reported in the following sections are the mean results for sheets sampled and measured for each of the exposure sites.

4.3.1 Colour measurements on black PE

Colour shift, ΔE , data obtained for black PE from the original exposure sites, as the years passed, is shown in Figure 25.

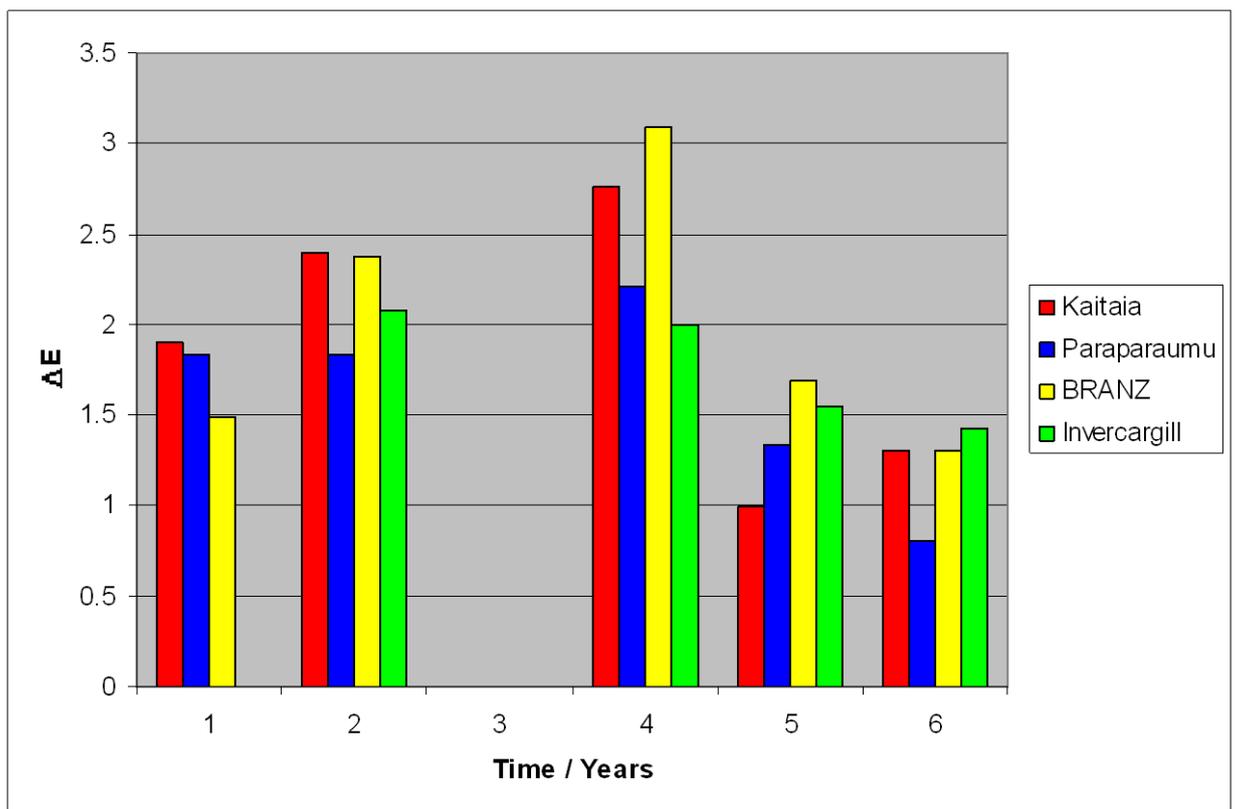


Figure 25. Colour shift, ΔE , data for black PE on the four original exposure sites

The colour shift, ΔE , data obtained for black PE for the all exposure sites over the first two years of exposure is shown in Figure 26.

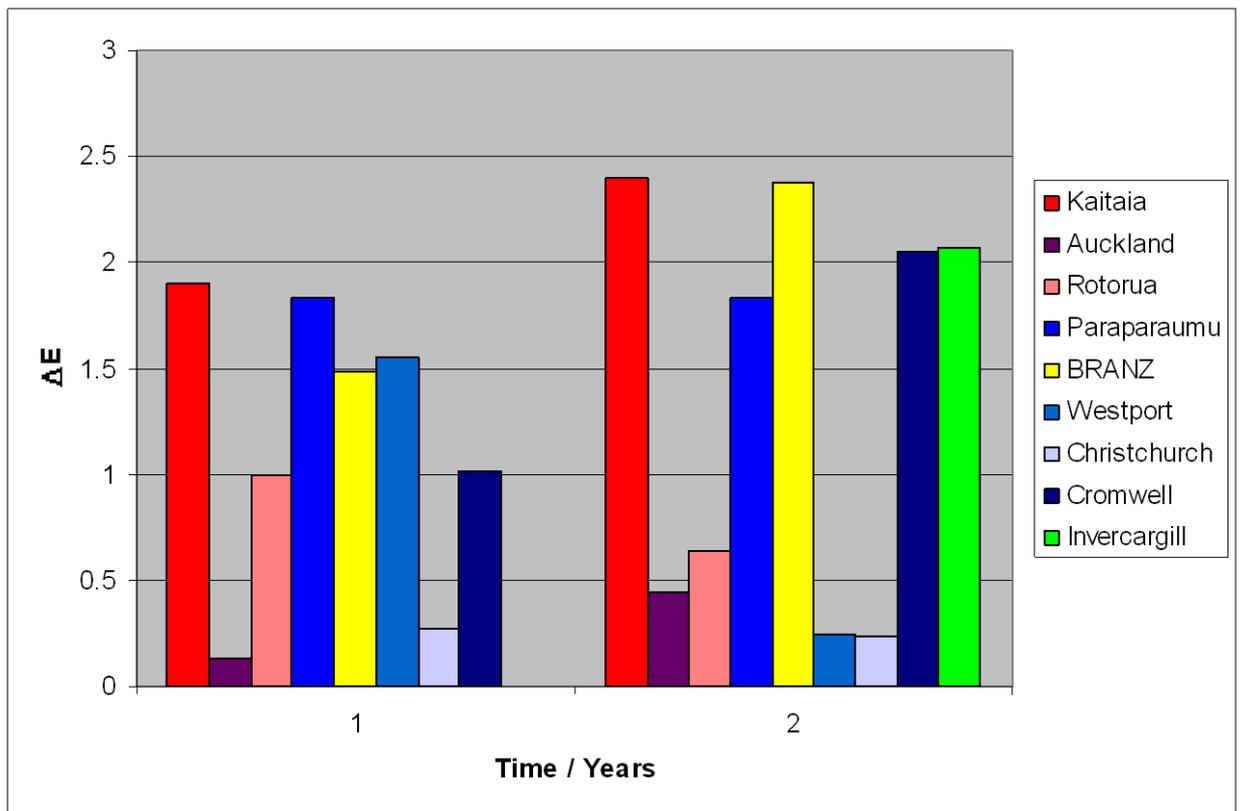


Figure 26. Colour shift, ΔE , data for black PE on all exposure sites during the first two years of exposure

The magnitude of the colour changes observed for the black PE samples are small, and indicate that these materials have satisfactorily retained their colour during the exposure to date. This is as expected given the level of incorporation, and inherent properties, of carbon black as already discussed in Section 4.2.3.3.

However, it is also clear for the black PE that markedly different trends exist when comparing the colour shifts for the first two years of exposure on the original four exposure sites (over years 2001 to 2003) with exposure on the later sites (over years 2005 to 2007).

Additionally a marked change of colour back towards the control sample colour is also apparent in Figure 25 between Years 4 and 5 at most of the original exposure sites.

These observations reinforce the well-known assertion that outdoor weathering results cannot be directly compared for different years. This is a result of the expected inconsistencies in hours of sunshine, temperature and rainfall that are an obvious feature of variations in the weather over the years.

4.3.2 Colour measurements on white uPVC

Colour shift, ΔE , data obtained for white uPVC from the original exposure sites, as the years passed, is shown in Figure 27.

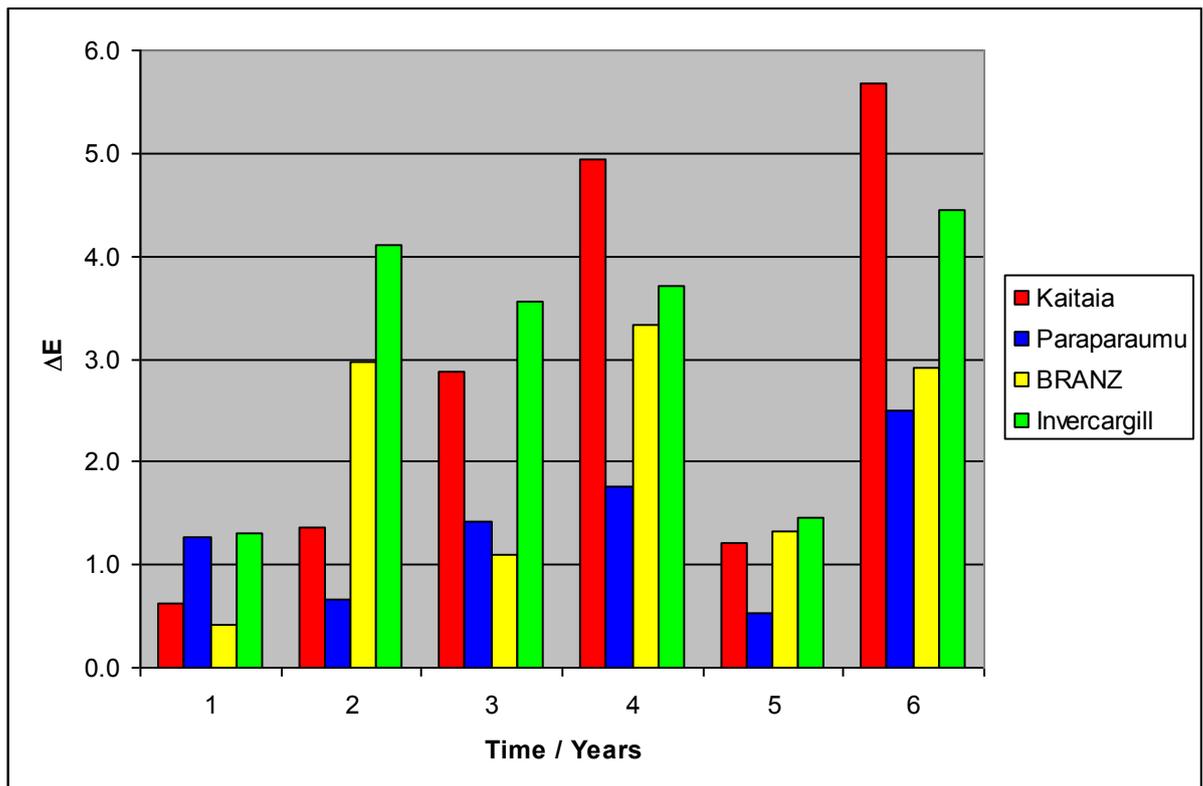


Figure 27. Colour shift, ΔE , data for white uPVC on the four original exposure sites

The magnitude of the colour changes observed for the white uPVC samples on the original sites is relatively small, and indicates that these materials have satisfactorily retained their colour during the exposure to date.

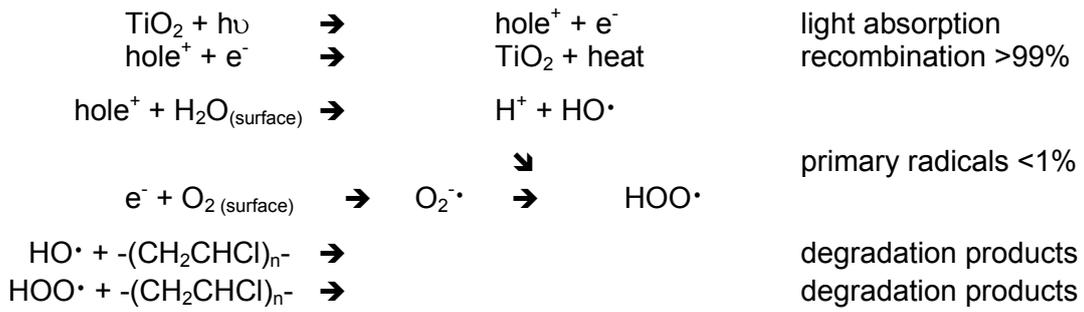
The fact that the white uPVC samples at the Paraparaumu site consistently show lower colour shifts is believed to be due to loss of material from the sample surface because of abrasion by wind-blown sand. The Paraparaumu exposure site is less than 500 m from the beach.

Generally, for the other samples, the trends of colour shift for the white uPVC materials are believed to be a consequence of the presence of TiO_2 pigment.

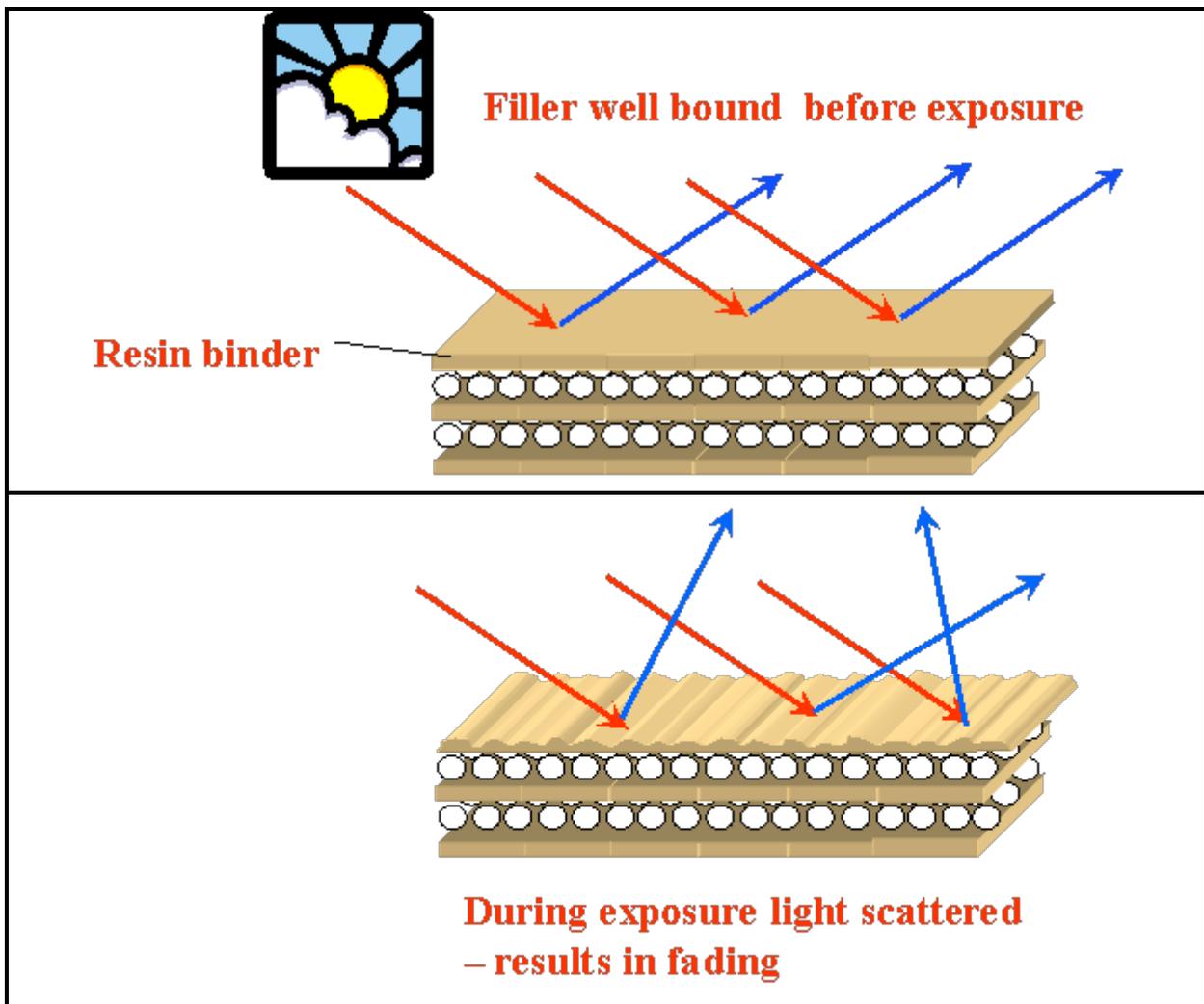
The role of TiO_2 in the pigment formulation, or as an additive in its own right, is (Archema 2005):

- UV light absorption to protect the resin from direct degradation
- visible light scattering to increase opacity and hide yellowing
- photo-catalytic degradation resulting in gloss loss, colour fade and chalking.

The absorption of light by TiO_2 results in dissociation to release an electron as detailed in the equations below. The free electron usually recombines to reform TiO_2 , but it can react with water or oxygen present in the uPVC to form reactive species. These in turn attack the uPVC as shown in the last two equations (Archema 2005).



This attack on the uPVC manifests as loss of material adjacent to the pigment particles. This phenomenon is described as chalking and a schematic of this mechanism is shown in Figure 28. An example electron microscope image for a chalked uPVC surface showing the degradation of the resin and exposure of the filler and pigments is shown in Figure 29.



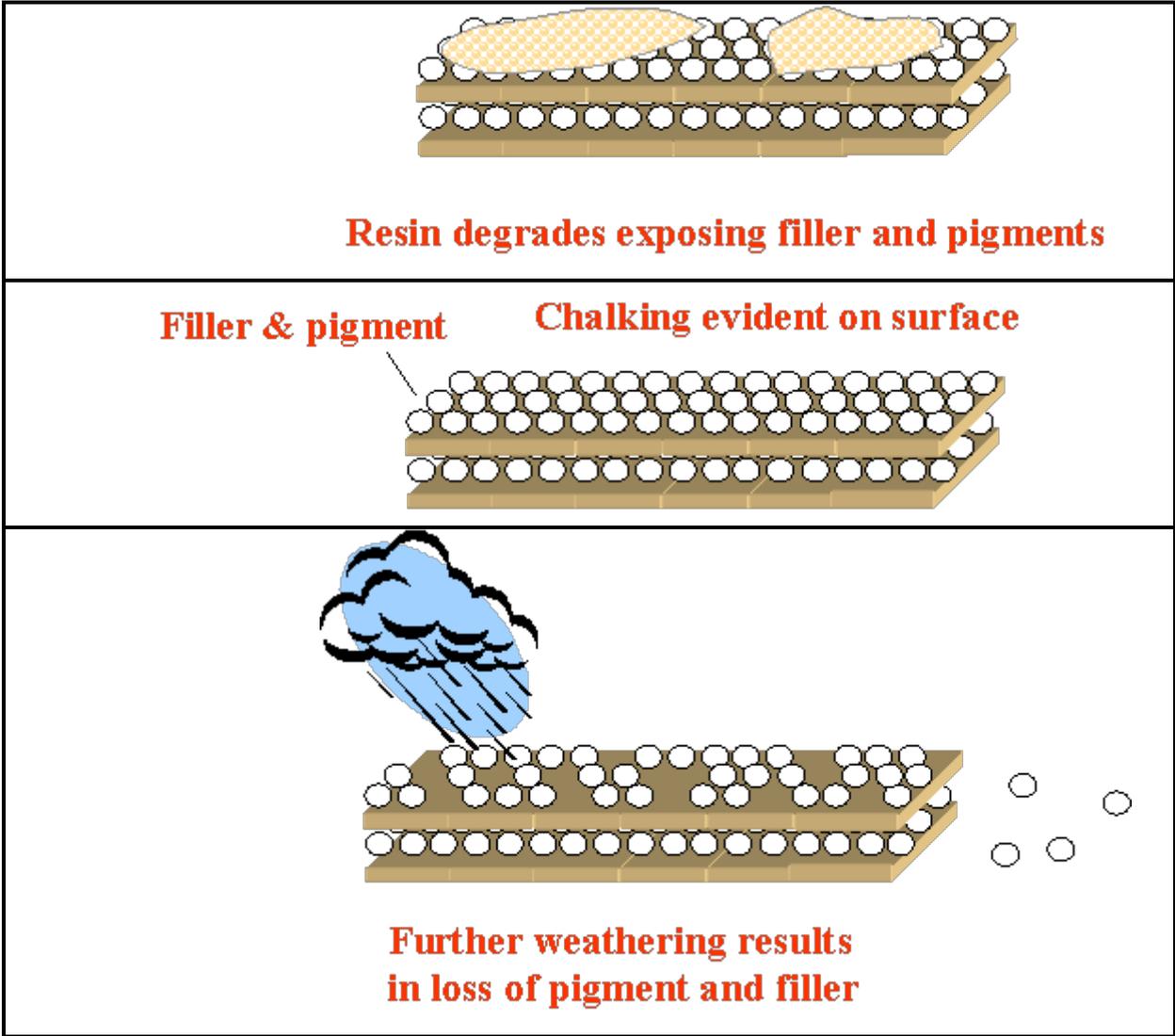


Figure 28. Schematic of the uPVC chalking mechanism

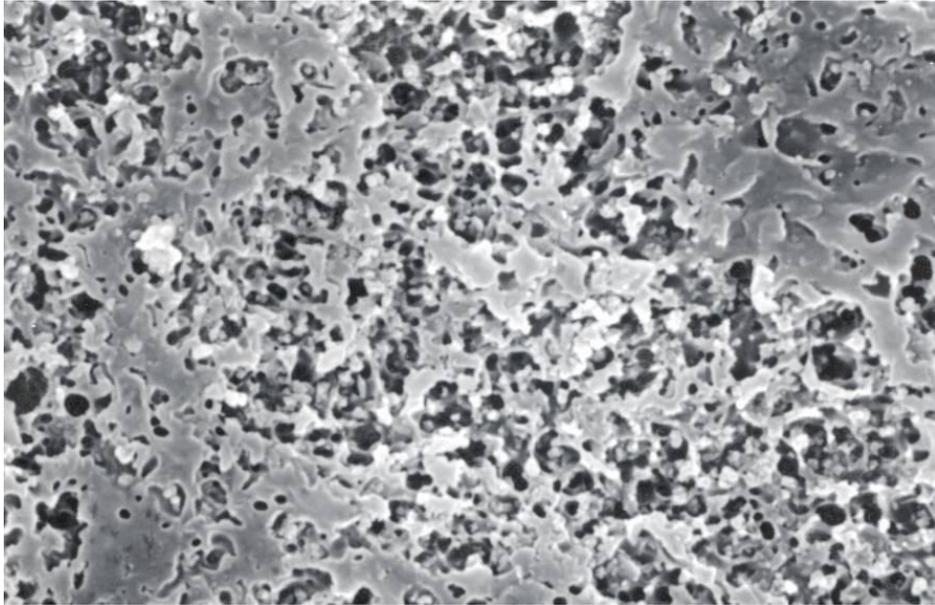


Figure 29. Electron microscope image showing uPVC chalking

Onset of the chalking mechanism is characterised by a gradual increase of colour shift as the surface resin degrades, followed by a relatively rapid reduction as the resin and pigment are lost and a fresh resin surface is exposed. This trend is clear in Figure 27 between the fourth and fifth years for the exposed samples. Photographs of uPVC samples collected in the fourth and fifth years exemplifying this are shown in Figure 30 and Figure 31.



Figure 30. uPVC sample from the Kaitaia exposure site collected in 2005 – the bottom of the sample was covered by the stress rack clamp during exposure and is markedly lighter than the exposed area of the sample



Figure 31. uPVC sample from the Kaitaia exposure site collected in 2006 – the bottom of the sample, covered by the stress rack clamp during exposure, is now much more similar in appearance to the exposed area of the sample

It is clear in Figure 31, when compared to Figure 30, that the colour difference between the bottom of the sample (that was covered by the stress rack clamp during exposure) and the exposed top of the sample has dramatically reduced. This is believed to be a result of the onset of the uPVC chalking.

The results obtained after two years of exposure on the five recent exposure sites, compared to results after the same exposure time on the original sites, are shown in Figure 32.

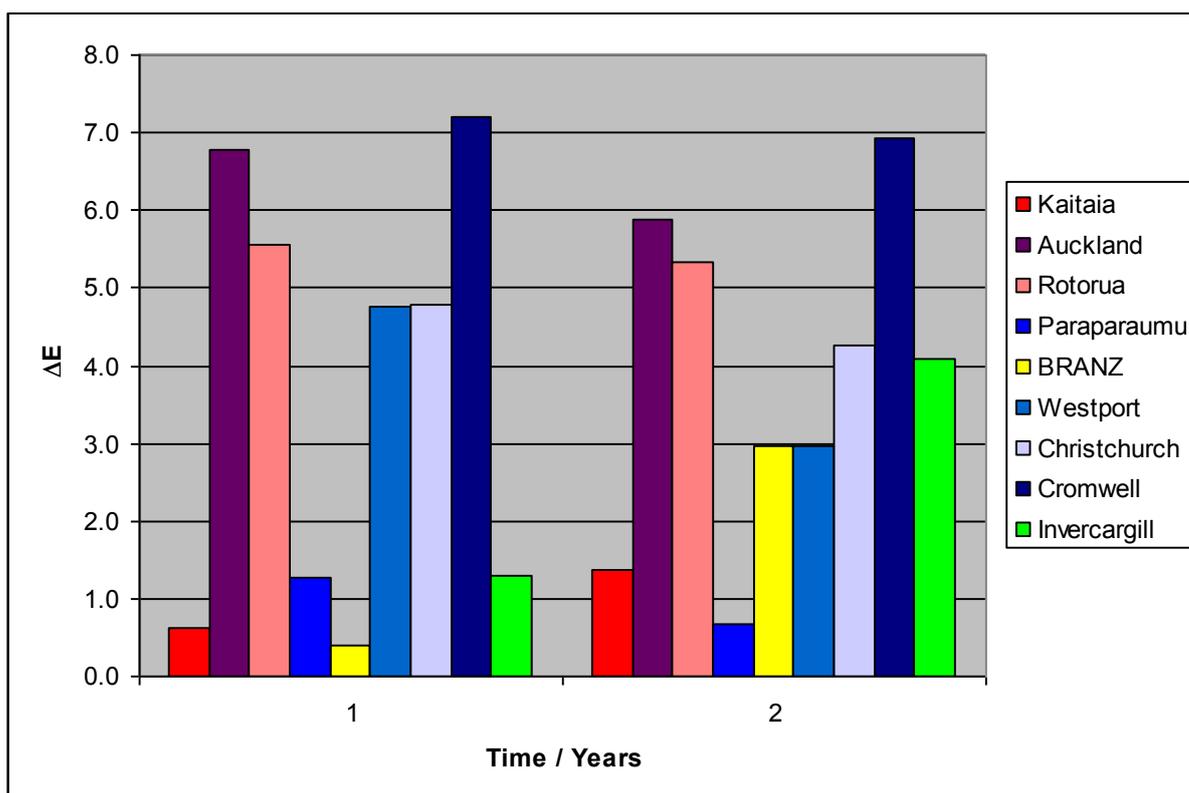


Figure 32. Colour shift, ΔE , data for white uPVC on all exposure sites after two years of exposure

It is clear for the white uPVC that radically different trends exist when comparing the colour shifts after two years of exposure on the original four exposure sites (over years 2001 to 2003) with exposure on the later sites (over years 2005 to 2007).

Concurrently a step change of colour shift is also very apparent in Figure 27 (between Years 4 and 5 and Years 5 and 6 at most of the original exposure sites).

It is possible that the increase in colour shift between Years 5 and 6, at the original exposure sites, is a consequence of further yellowing following the exposure of a fresh resin surface by the chalking effect. However, another possible explanation for these observations is differences in the cumulative radiation dose over the time-frame 2001 to 2003 compared to 2005 to 2007. This possibility will be explored further in relation to polymer solar radiation sensitivity in Section 5 of this report.

4.4 Surface gloss measurements

Surface gloss measurement sensitively probes the surface morphology and structure of flat materials. The gloss meter illuminates the material surface at a defined angle (85° was used for this study), collects the light that reflects from the surface and derives a dimensionless gloss value from this. Highly polished, flat surfaces are highly reflective and have a gloss value of over 90. Matt surfaces have much lower values. A typical interior silk finish acrylic emulsion paint surface has a gloss value of approximately 10.

Surface gloss measurement is effective in detecting early signs of material surface degradation that may not manifest in material colour or mechanical properties changes. In the context of this study, it is therefore of particular interest with respect to the materials that have not shown any significant change in other properties e.g. black PE, white uPVC and PMMA.

4.4.1 Gloss results for PE samples

The surface gloss data obtained for clear PE from the original exposure sites, as the years passed, is shown in Figure 33.

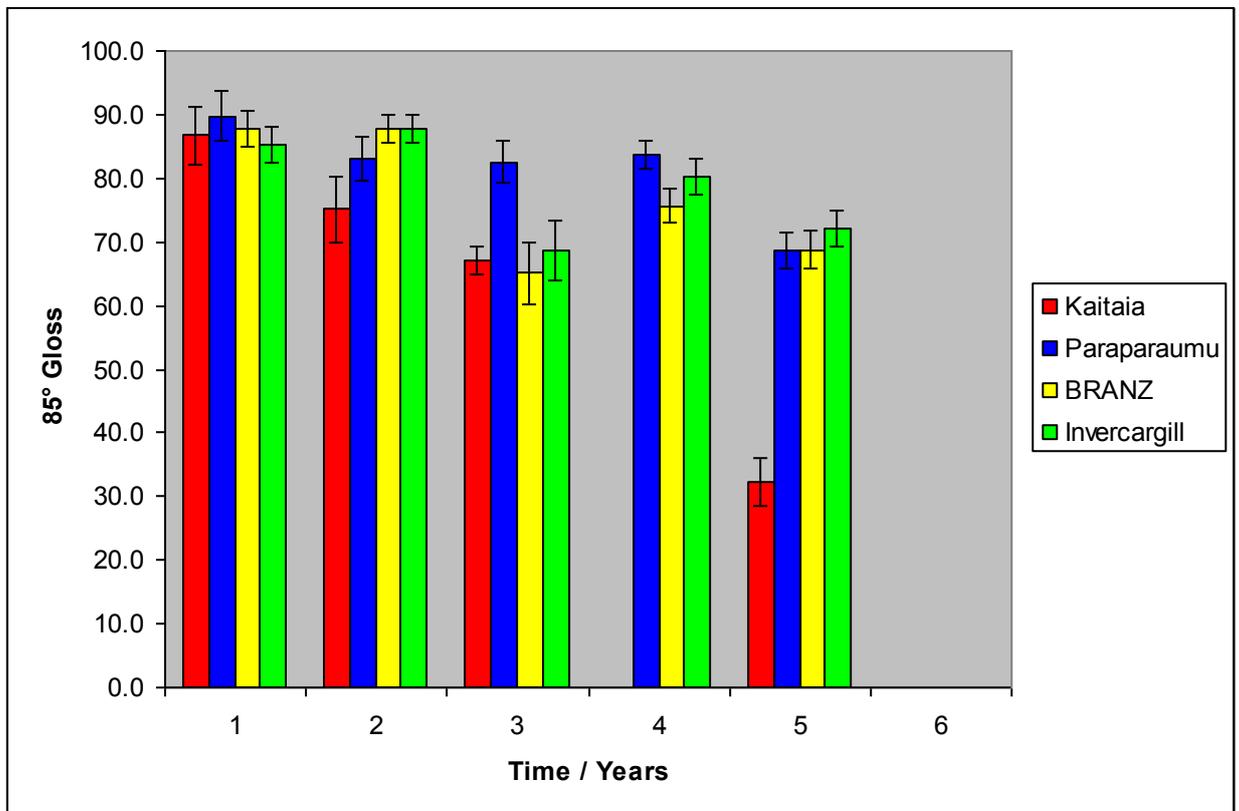


Figure 33. Surface gloss data for clear PE on the four original exposure sites

A result for four years of exposure at Kaitaia is not reported since the row of samples scheduled for collection in 2005 was completely degraded.

The trend towards higher gloss reduction (implying more micro-cracking at the surface) in Kaitaia is as expected and also seems to support the interpretation of the clear PE mechanical property trends in Section 4.2.3.2. The lag of the gloss reduction behind the mechanical property changes agrees with observations by other workers (Winslow 1967).

4.4.2 Gloss results for black PE samples

The surface gloss data obtained for black PE from the original exposure sites, as the years passed, is shown in Figure 34.

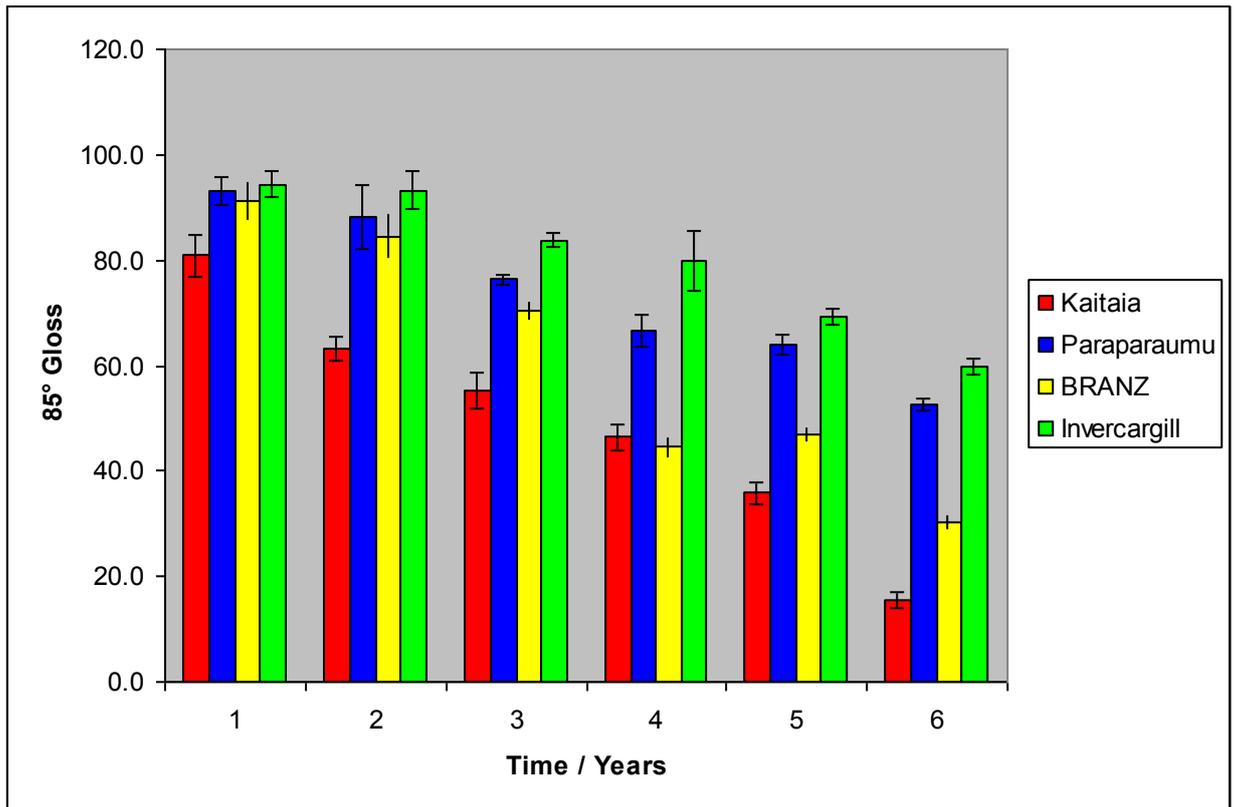


Figure 34. Surface gloss data for black PE on the four original exposure sites

This loss of surface gloss is clearly differentiated between the original exposure sites and is believed to be due to differences in harmful radiation dose and the resulting progression of surface micro-cracking described in Section 4.2.3.

However, these clear trends do not lend themselves to any simple analysis to act as a predictor for material life expectancy, since there is no correlation between gloss loss and the mechanical properties for these samples.

The gloss data obtained for black PE for the five recent exposure sites, and the results obtained for the first two years of exposure on the original sites, are shown in Figure 35.

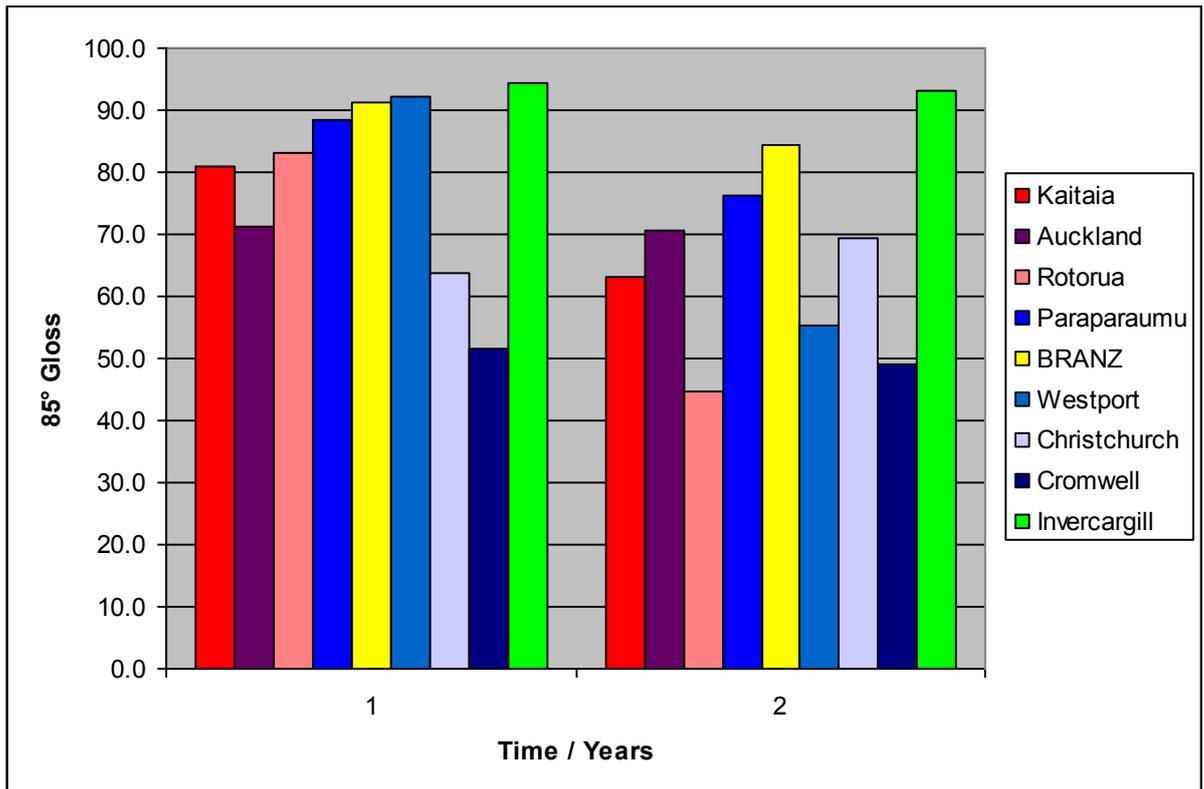


Figure 35. Surface gloss data for black PE on the five recent exposure sites

There is some agreement in the trends that exist when comparing the gloss data after two years of exposure on the original four exposure sites (over years 2001 to 2003) with exposure on the later sites (over years 2005 to 2007). However, it is clear that these weathering results cannot be reliably directly compared for different years as noted by other workers (Pickett 2005)

The behaviour of these black PE samples will be monitored as the exposure progresses as part of further research funded by Building Research.

4.4.3 Gloss results for white uPVC samples

The surface gloss data obtained for white uPVC from the original exposure sites is shown in Figure 36.

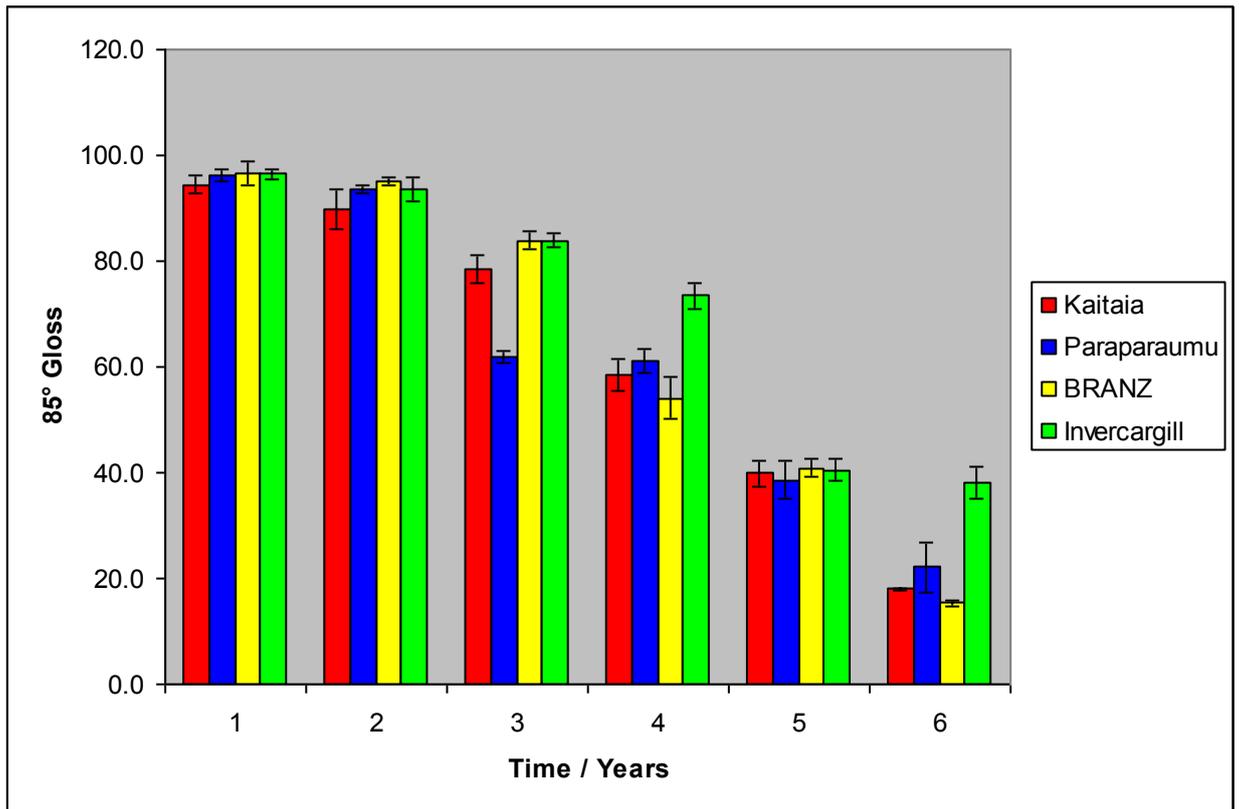


Figure 36. Surface gloss data for white uPVC on the four original exposure sites

The faster drop in surface gloss of the white uPVC samples at the Paraparaumu exposure site is believed to be due to the proximity of the site to the beach and the effects of wind-blown sand as already discussed in Section 4.3.2.

The reduction of surface gloss of the samples from the other sites is believed to be the result of the uPVC chalking as explained in Section 4.3.2. It is apparent that the chalking mechanism does not commence, to any significant extent, until the samples have been exposed for more than two years.

The samples at Invercargill are believed to show little change since they were removed before the summer of 2006/07 due to maintenance of the building on which the racks were positioned.

The gloss data obtained for uPVC for the five recent exposure sites, and the results obtained for the first two years of exposure on the original sites, are shown in Figure 37.

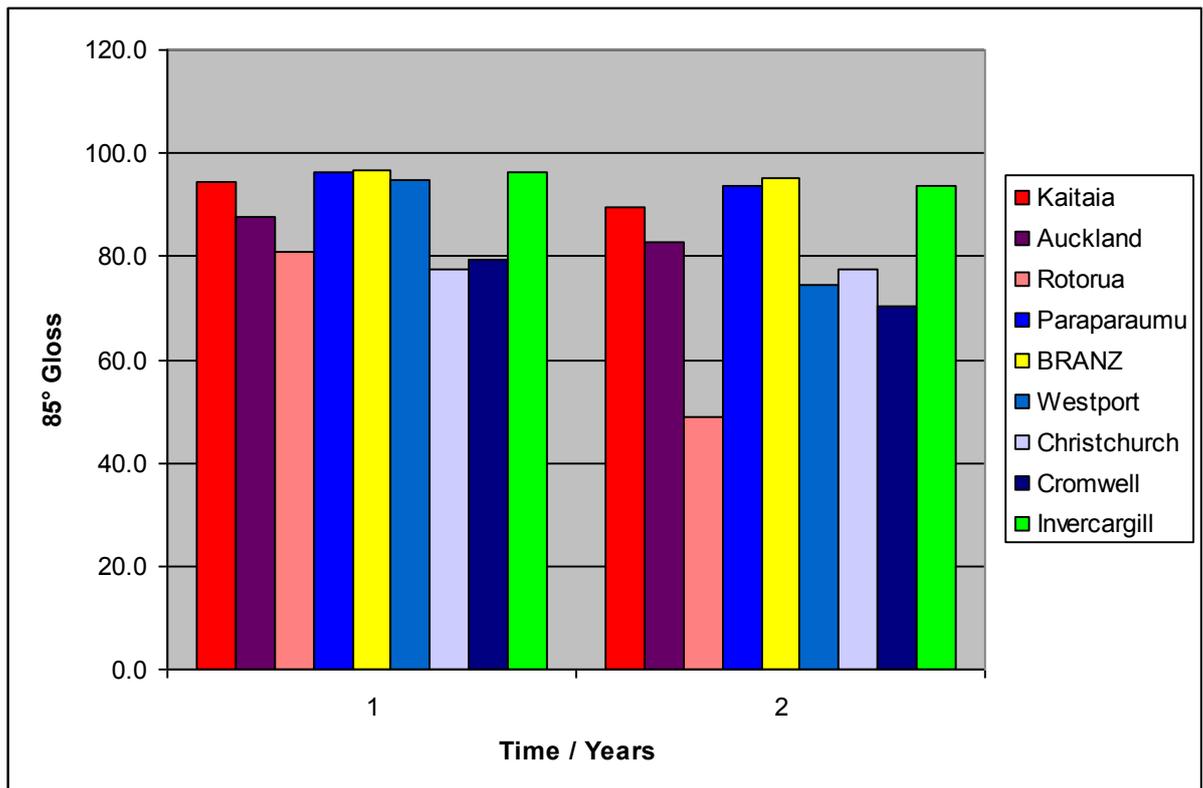


Figure 37. Surface gloss data for white uPVC on the five later exposure sites

There is some agreement in the trends that exist when comparing the gloss data after two years of exposure on the original four exposure sites (over years 2001 to 2003) with exposure on the later sites (over years 2005 to 2007). The low gloss results after two years of exposure for the new exposure sites can be mainly attributed to surface dirt. When this was cleaned off the surface glosses were in excess of 90 units for all the new sites. These relatively high gloss values indicate that the samples have not begun to chalk to any significant extent, as determined for the original exposure sites after two years of exposure.

5. CLIMATE DATA

NIWA was able to apply a weighting to their broadband radiation data records according to the activation wavelength (Table 3) for each of the exposed polymers.

5.1 Sensitivity maps

Maps of New Zealand were then derived from the weighted data showing the expected annual dose of the most harmful UV radiation (in mega-Joules per square metre, MJ/m²) each polymer would receive. Examples of these maps for each of the polymers studied are shown in Figure 38 through Figure 42.

Total polycarbonate (281-290nm , 308-330nm) dose

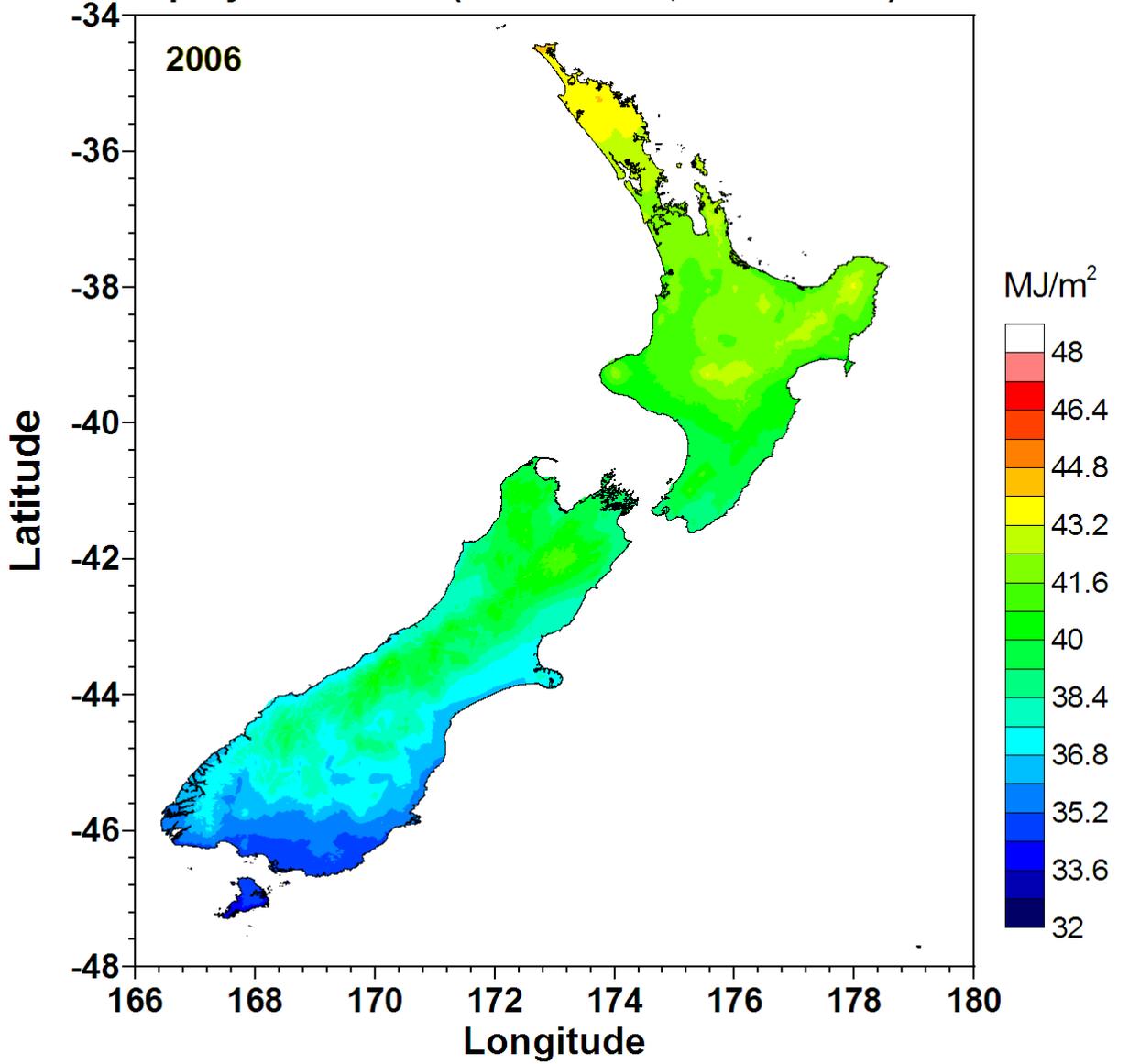


Figure 38. PC energy dose map based on NIWA 2006 broadband radiation data

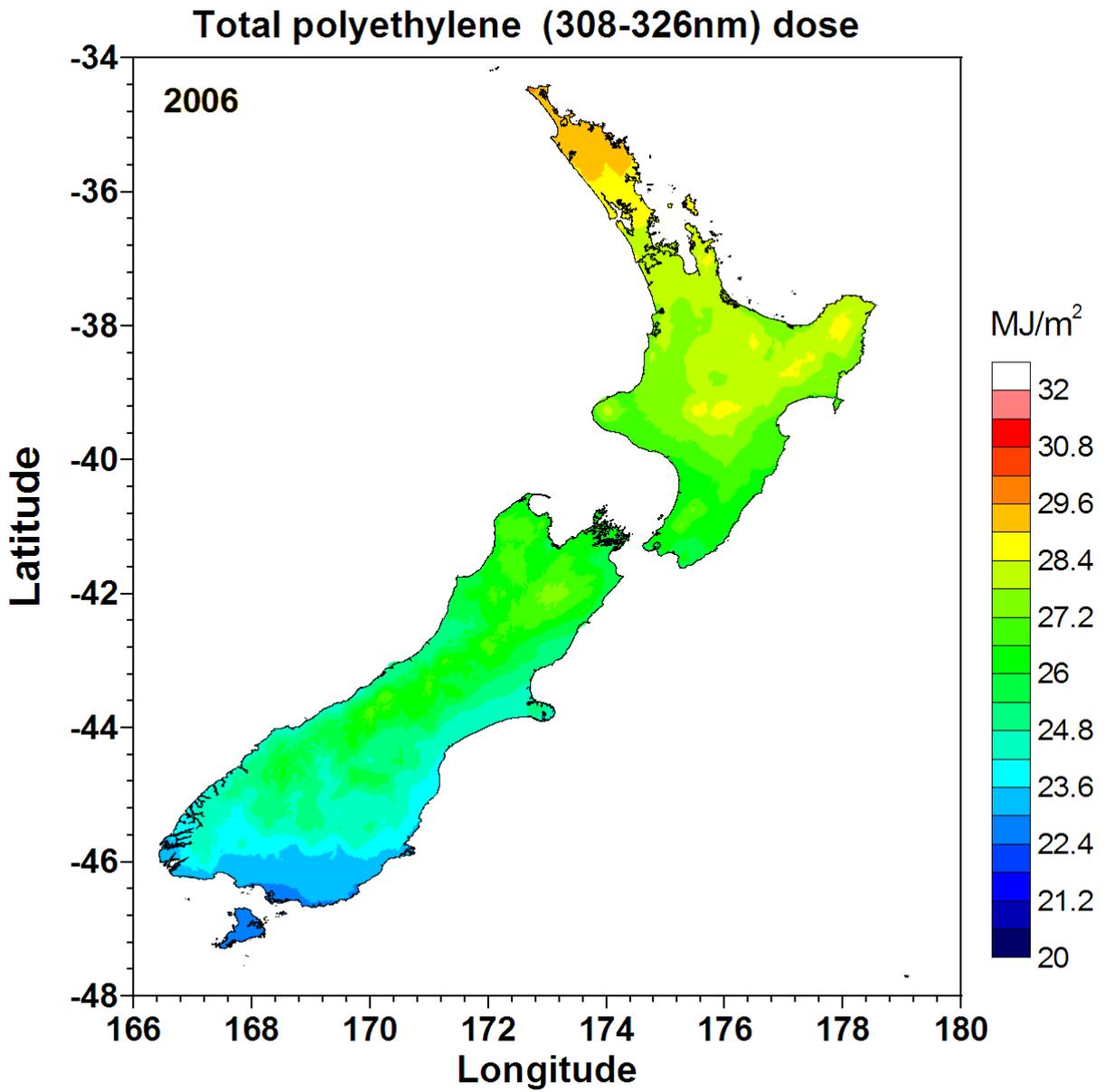


Figure 39. PE energy dose map based on NIWA 2006 broadband radiation data

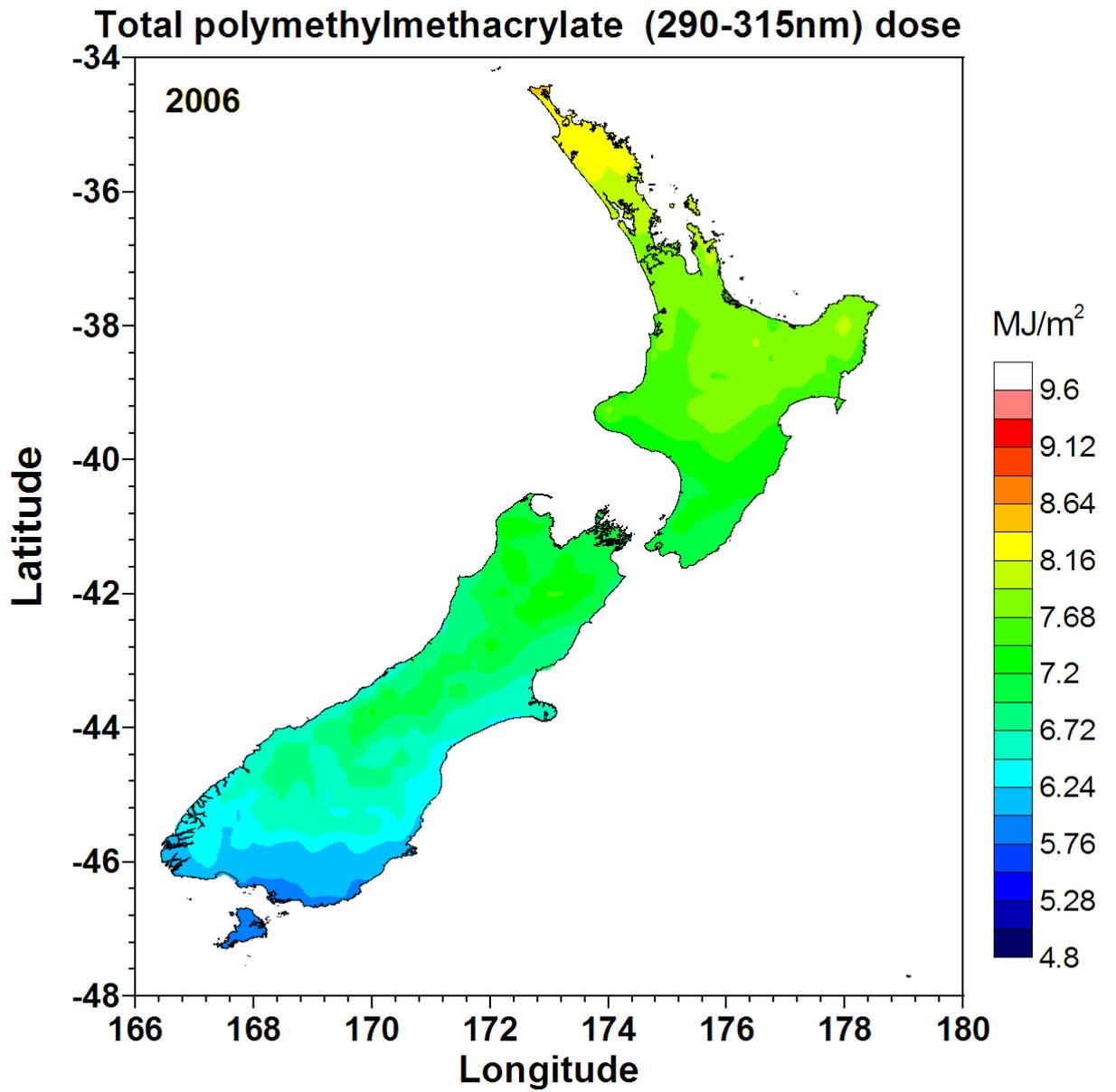


Figure 40. PMMA energy dose map based on NIWA 2006 broadband radiation data

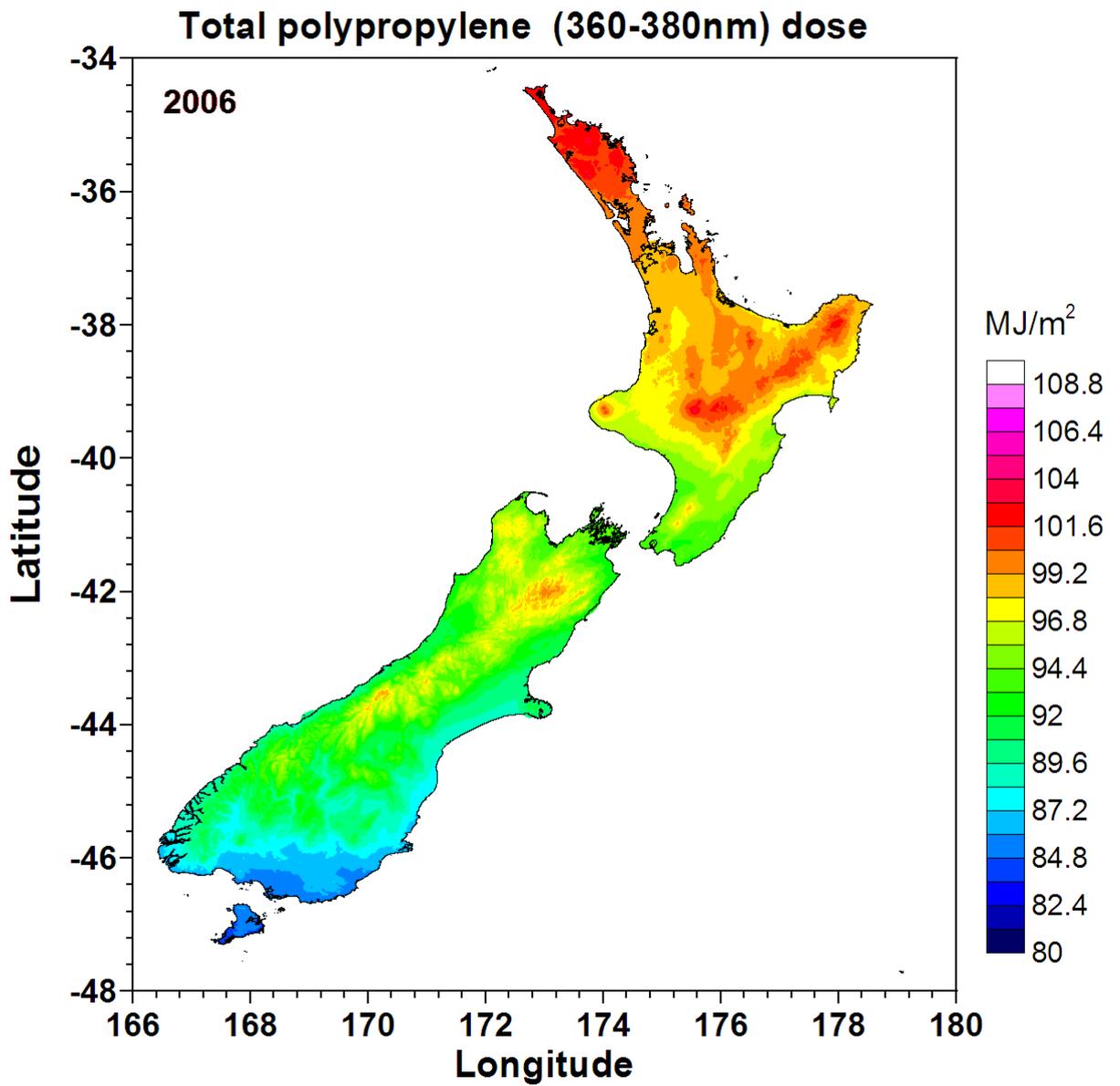


Figure 41. PP energy dose map based on NIWA 2006 broadband radiation data

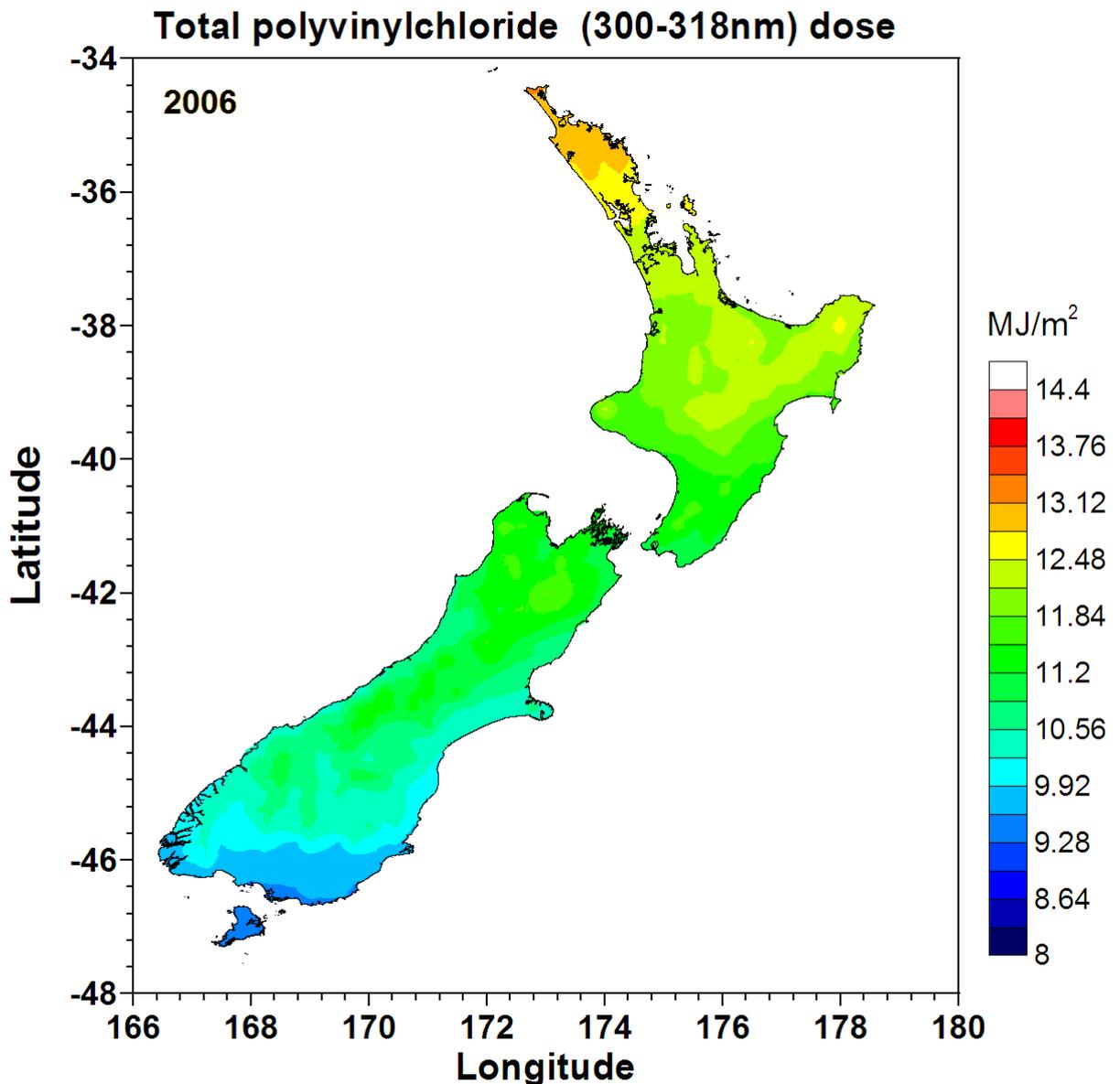


Figure 42. uPVC energy dose map based on NIWA 2006 broadband radiation data

It is immediately clear, by comparison of the maps above, that over a year outdoors the different polymer types will receive widely varying doses of UV radiation that is most likely to damage them.

The received dose is both a function of the width of the wavelength band, across which the polymer is susceptible, and the amount of energy within that band that is incident. For example, PP receives a far higher dose of harmful radiation per annum than the other polymers studied because its activation spectra lies in the range 360–380 nm where there is more light energy (see Figure 10).

The uPVC energy dose maps were examined to look for an explanation of the differences in sample colour and gloss change between the original exposure sites in the years 2001–2003 and the more recent exposure sites in the years 2005–2007 (see Sections 4.3.2 and 4.4.3). The results for each site from 2001–2007 are shown in Table 6.

Table 6. uPVC energy dose map based on NIWA 2001, 2002, 2005 and 2006 broadband radiation data

Years	Year Exposure Ending	Annual Harmful Radiation Dose for uPVC / MJ/m ²								
		Kaitaia	Auckland	Rotorua	Paraparaumu	BRANZ	Westport	Christchurch	Cromwell	Invercargill
1	2002	11.0	-	-	9.3	9.1	-	-	-	8.3
2	2003	11.2	-	-	9.7	9.5	-	-	-	8.4
3	2004	11.0	-	-	9.4	8.9	-	-	-	8.3
4	2005	11.6	-	-	9.8	9.9	-	-	-	8.0
5	2006	11.5	11.3	10.8	9.7	9.5	10.0	9.5	9.5	8.5
6	2007	11.2	8.4	10.8	9.6	9.4	9.7	9.8	9.8	3.0 *

* The radiation dose for Invercargill in 2007 is low since samples were removed from the site in November 2006. This was due to maintenance of the building on which the exposure racks were placed.

It is clear from Table 6 that there are no great differences in the harmful radiation doses experienced by uPVC samples at the original sites during 2001–2003 and that experienced by the uPVC samples at the new sites during 2005–2007. This result for uPVC will be echoed for the other polymer types, since the dose each polymer received is derived directly from the total radiation experienced at each exposure site.

Therefore, harmful radiation dose alone does not account for the results found for the as-recovered samples presented in Figure 26, Figure 32 or Figure 37.

Established theory for uPVC weathering (see Section 4.2.3) suggests that if surface gloss remains relatively constant then a colour change of the samples can occur because degraded resin remains in place at the surface. It is apparent that the samples at all sites have not begun to chalk to any significant extent after two years of exposure as the surface gloss results are uniformly high (see Figure 37). The behaviour of these white uPVC materials will be monitored as the exposure progresses as part of further research funded by Building Research.

5.2 Sensitivity fitting

Application of the weighting to NIWA’s broadband radiation data records, according to the activation wavelength (Table 2), also allowed precise calculation of the cumulative dose at each of the exposure sites for each of the exposed polymers in the study.

It was then possible to plot the change of tensile strength of the PE and PP sheets (shown in Figure 12 and Figure 16) against the cumulative harmful radiation dose at each of the original four exposure sites. The resulting plots are shown in Figure 43 and Figure 44. The data for the PE and PP are then combined in Figure 45.

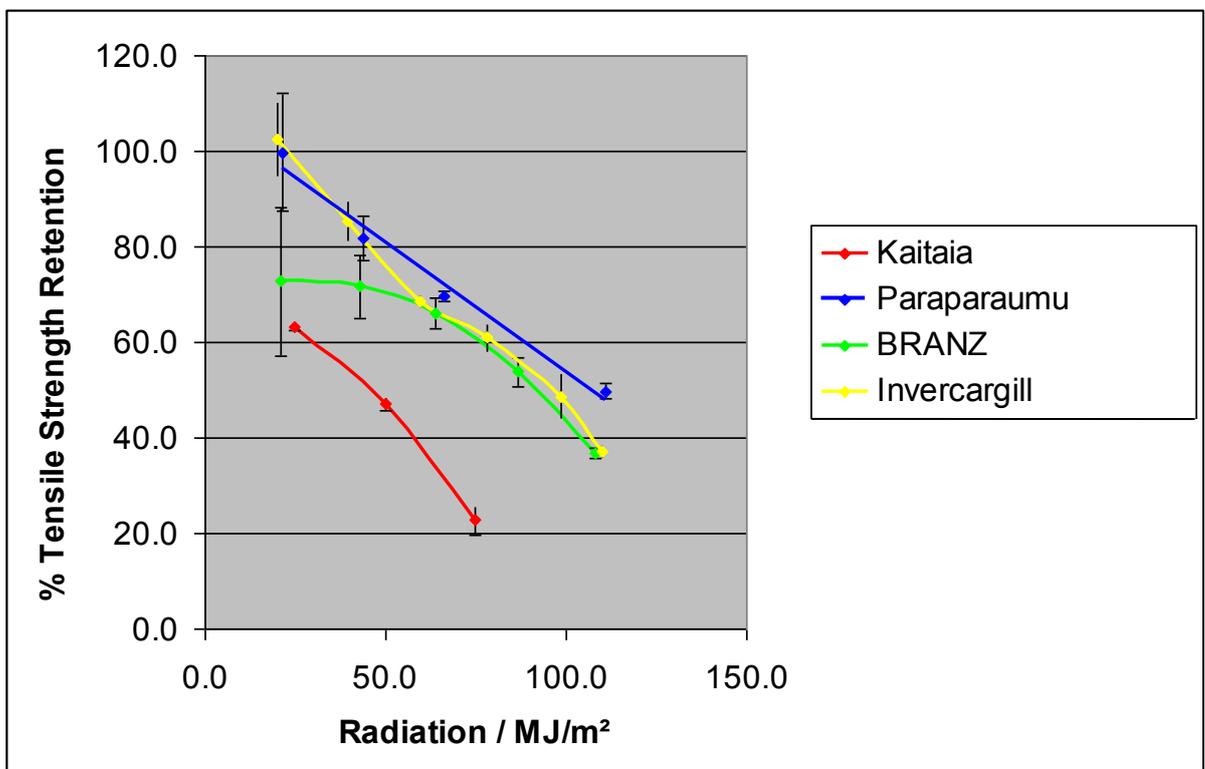


Figure 43. PE tensile strength retention as a function of cumulative harmful radiation dose

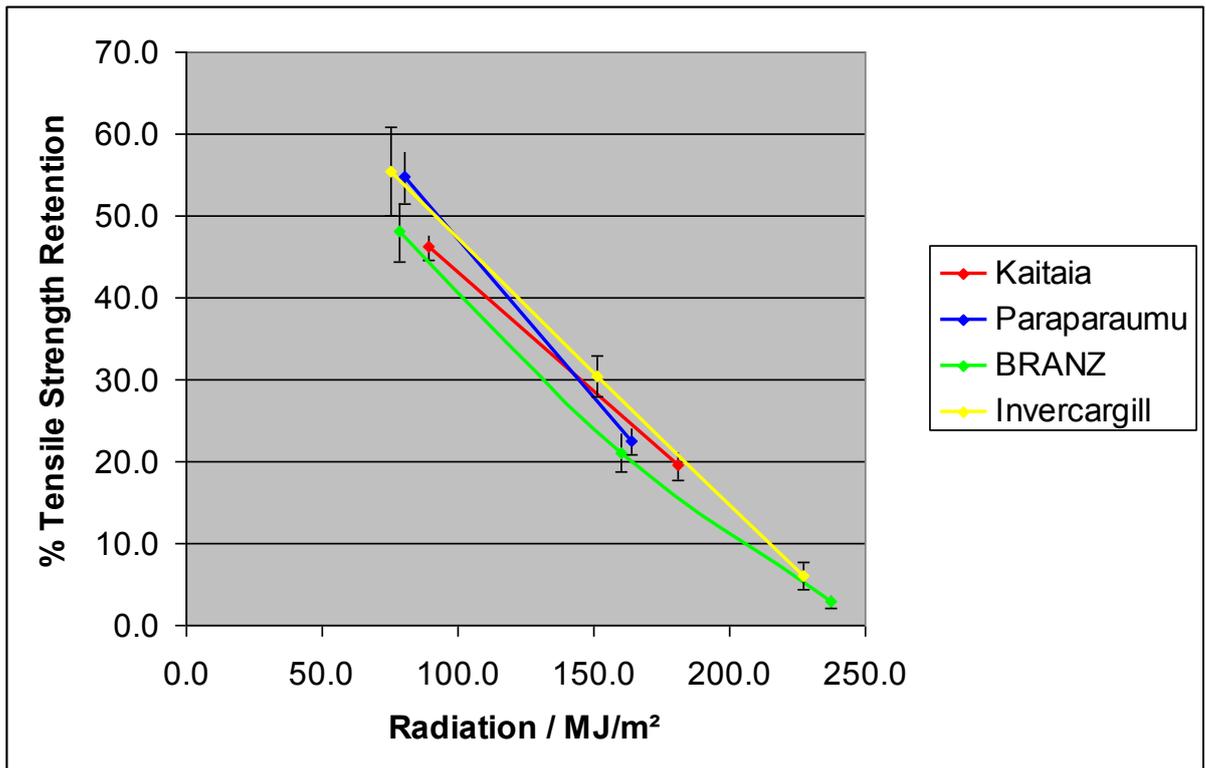


Figure 44. PP tensile strength retention as a function of cumulative harmful radiation dose

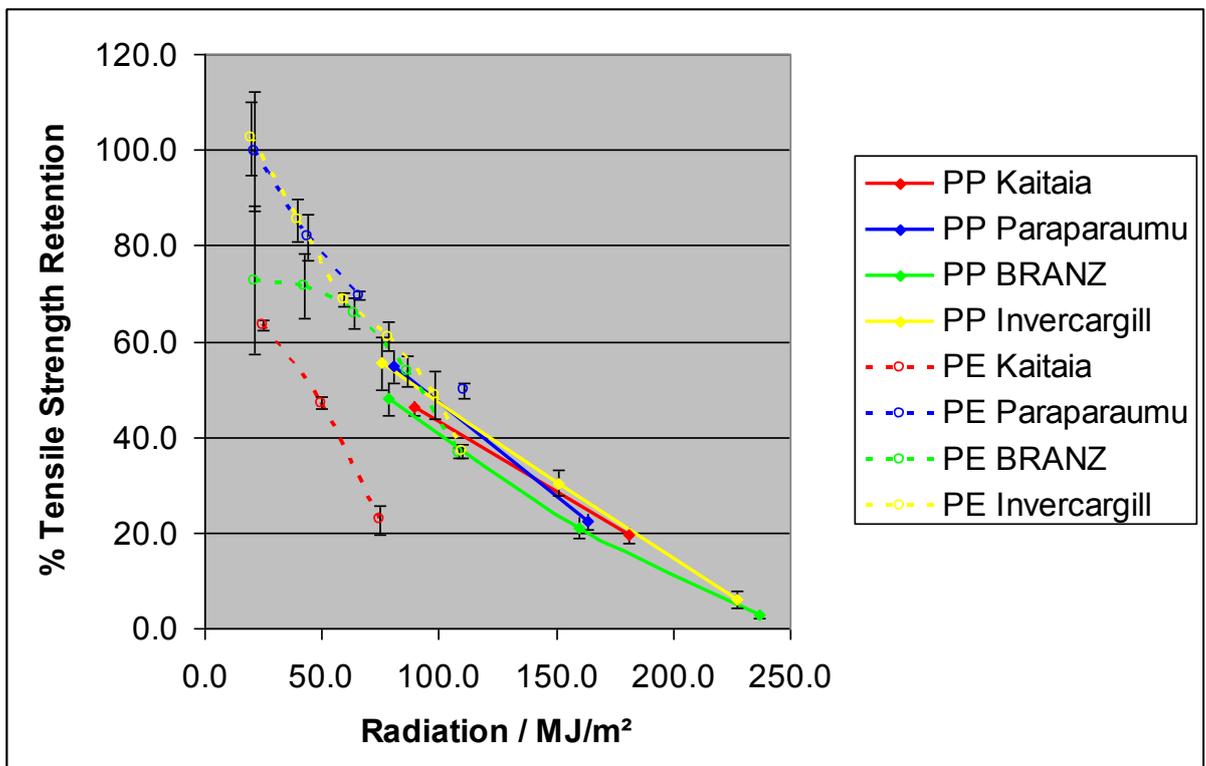


Figure 45. Combined tensile strength retention as a function of cumulative harmful radiation dose for PE and PP

It can be seen in Figure 45 that there is generally a good correlation between the cumulative harmful radiation dose for PE and PP and the change in tensile strength.

The PE samples show increased material degradation at Kaitaia compared to the other sites, as already discussed in Section 4.2.3. It is believed likely that this results from a coupling between radiation dose and temperature as proposed by other workers (Winslow 1972, Hirt 1967).

The strength results for PE at the other sites show closer agreement as a result of plotting against a cumulative harmful radiation dose and this explains the differences in strength noted for different locations in Sections 4.2.3.1 and 4.2.3.2.

These plots also allow the identification of a cumulative maximum radiation dose after which the polyolefins become mechanically non-viable. This is discussed further in Section 6.

This approach is, in some ways, analogous to that adopted by other workers to predict the degree of carbonyl content of exposed LDPE film materials as a function of estimated solar UV radiation exposure (Winslow 1972, Hirt 1967). This work is, perhaps, superior to these previous approaches in that it is not clear if the effect of auto-catalytic carbonyl production was not considered in this earlier work and as a result estimated and measured figures do not fully coincide. By monitoring and fitting the strength of the exposed samples any additional degradation effects, such as auto-catalytic effects, will be encompassed within the material lifetime prediction.

The black PE and white uPVC materials did not lose mechanical strength over the first six years of exposure, so analogous plots against cumulative harmful radiation dose at each of the exposure sites are not useful. However, it is instructive to plot the surface gloss of these materials against the cumulative harmful radiation dose as shown in Figure 46 and Figure 47.

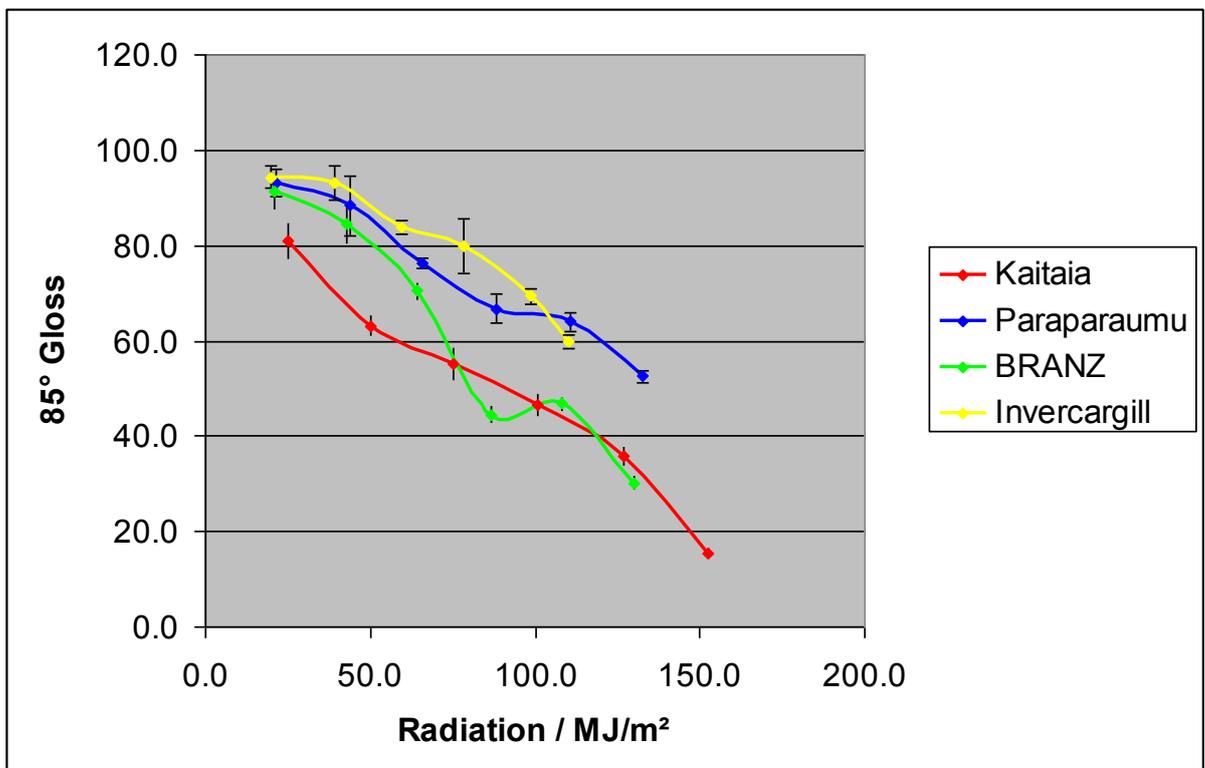


Figure 46. Black PE gloss data as a function of cumulative harmful radiation dose

The results for black PE demonstrate a reasonable agreement between the amount of harmful radiation to which the samples are exposed and the reduction of surface gloss, believed to be a result of micro-cracking of the sheet surface (Sections 4.2.3 and

4.4.2). The clarification of the trend towards higher gloss reduction per unit harmful incident radiation (implying more micro-cracking at the surface) in Kaitaia also seems to support the interpretation of the clear and black PE mechanical property trends in Section 4.2.3.

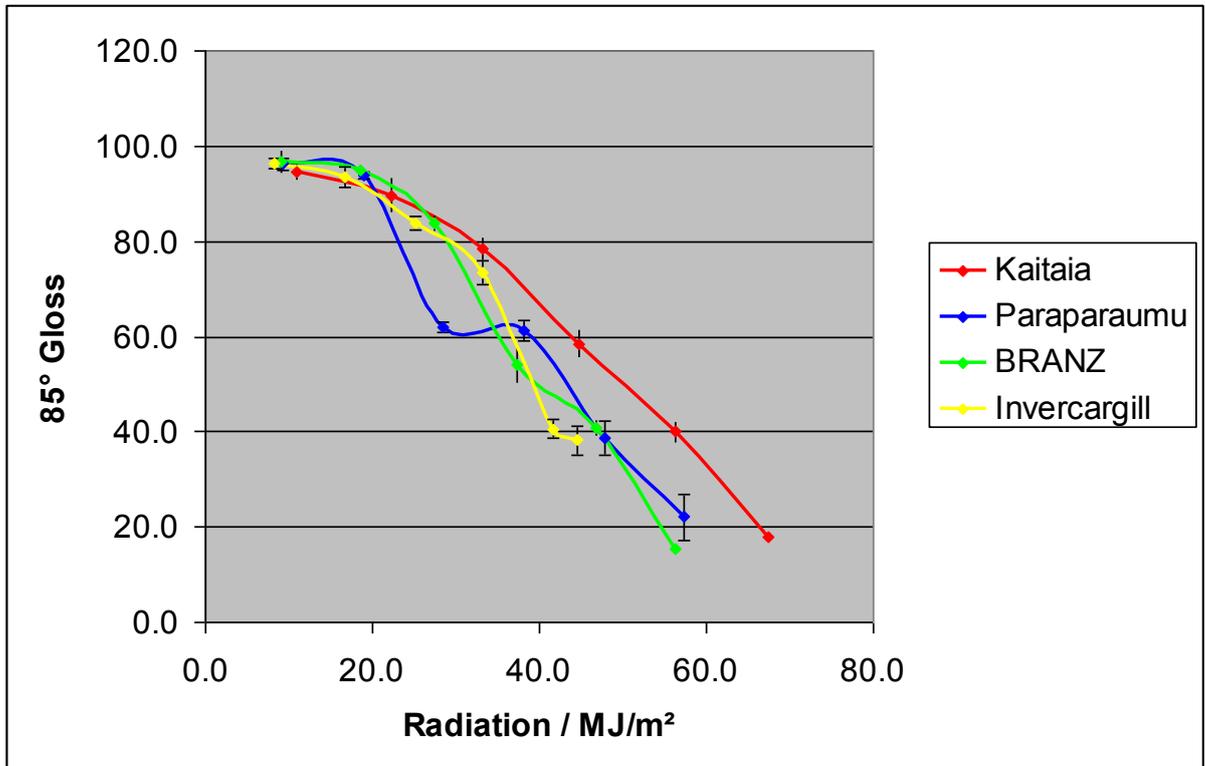


Figure 47. uPVC gloss data as a function of cumulative harmful radiation dose

The results for white uPVC also demonstrate a reasonable agreement between the harmful radiation exposure and the surface gloss of the samples. The plot demonstrates that samples are higher gloss at Kaitaia compared to the other three original sites when exposed to the same dose of harmful radiation. This may be a result of the orientation of the racks at Kaitaia which results in the prevailing winds blowing across the faces of the samples. This will quickly remove any exposed filler or pigment to reveal the fresh, more glossy, underlying resin.

6. DURABILITY MAPS

As a final step in the analysis the maximum radiation dose results for the rapidly degraded, non-UV stabilised, polyolefins were used to generate maps of predicted lifetime for these unstabilised, clear, materials.

For the purposes of lifetime mapping it seemed reasonable to select a percentage tensile strength retention as the point when the polymer sheets were no longer viable. 50% tensile strength retention was chosen as a reasonable figure.

Examination of the polyolefin tensile strength data, as a function of the effective dose of harmful radiation (Figure 45), led to the conclusion that both the 2 mm PE and PP were following the same trend line and it was clear that 50% tensile strength remained after an effective dose of 75 MJ/ m².

Subsequently, it was noticed that it seems likely that the white uPVC samples will also have reached an equilibrium (low) gloss level after an effective dose of 75 MJ/m² (see

Figure 47). Further research, funded by Building Research, will confirm this observation.

6.1 Polyethylene

The predicted lifetime for the non-UV stabilised PE sheet used in this study is shown in Figure 48. The map was derived by taking a worst case harmful radiation dose for PE (radiation of wavelengths 308–326 nm – see Table 3) for the year 2006 by examination of data from each of the NIWA’s broadband monitoring sites across New Zealand. An extrapolation was then made to produce the map showing how many years it would take to reach a cumulative harmful radiation dose for PE of 75 MJ/m², based upon data from each of NIWA’s broadband monitoring sites across New Zealand.

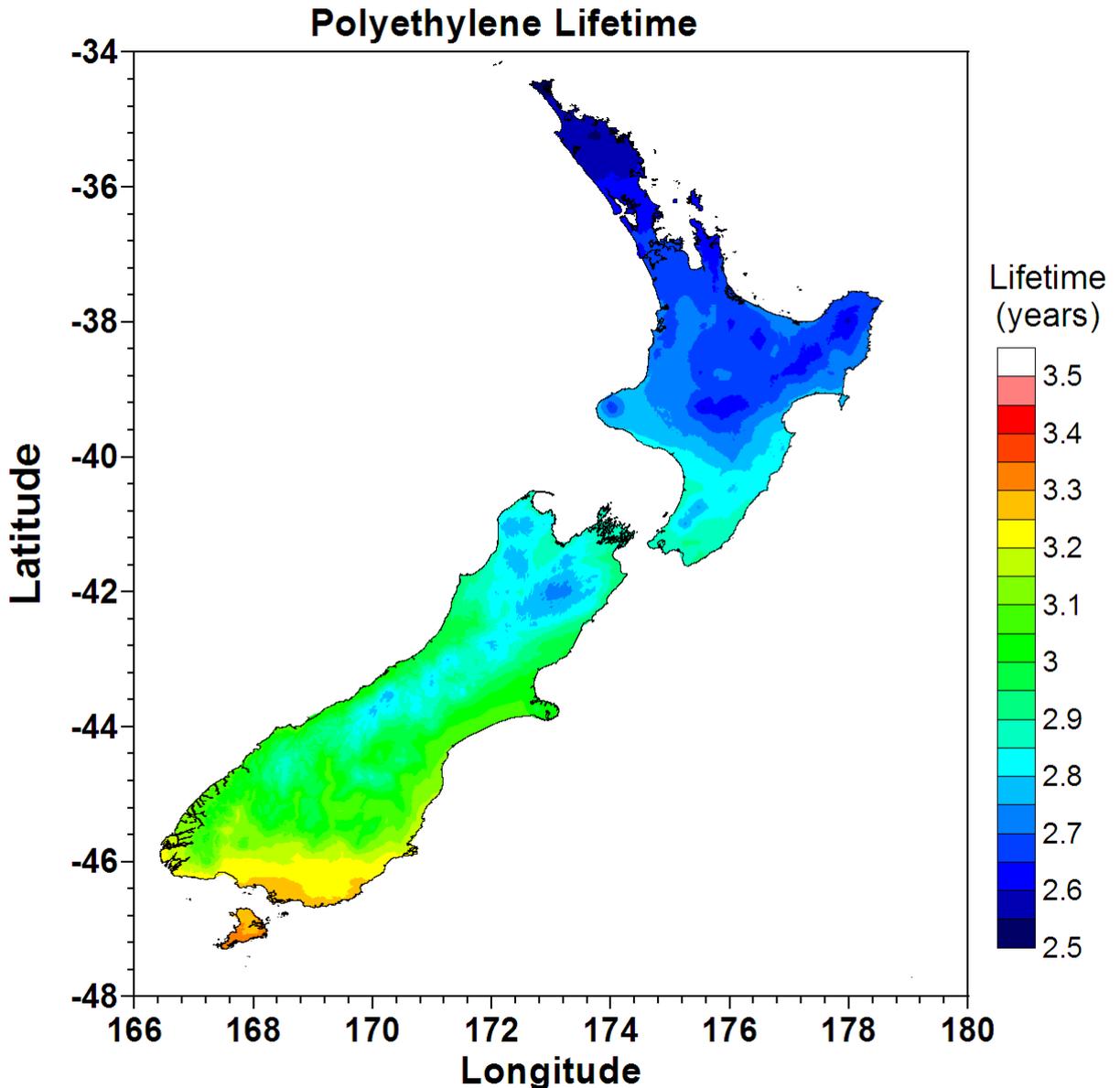


Figure 48. Predicted lifetime for the PE sheet used in this study derived using NIWA 2006 broadband radiation data

The map in Figure 48 gives an expected timescale for clear 2 mm PE to lose 50% of its tensile strength. It should be noted that this lifetime map is only likely to apply to clear, non-UV stabilised, PE sheet. PE materials containing pigments and / or UV stabilisers could be expected to have a longer lifetime in the New Zealand environment.

6.2 Polypropylene

The predicted lifetime for the non-UV stabilised PP sheet used in this study is shown in Figure 49. The map was derived as described above by taking a worst case harmful radiation dose for PP (radiation of wavelengths 360–380 nm – see Table 3).

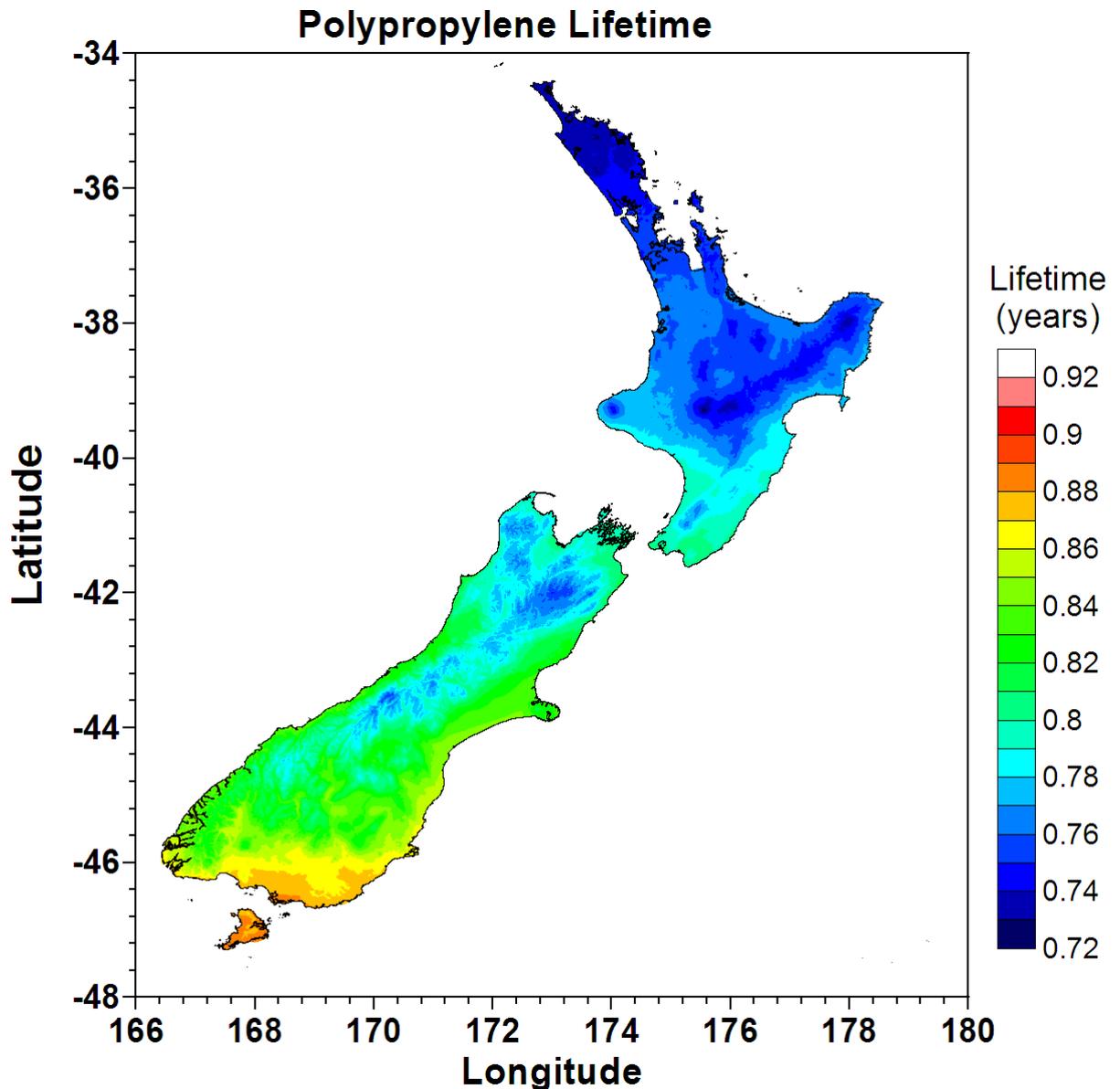


Figure 49. Predicted lifetime for the PP sheet used in this study derived using NIWA 2006 broadband radiation data

The map in Figure 49 gives an expected timescale for clear 2 mm PP to lose 50% of its tensile strength. It should be noted that this lifetime map is only likely to apply to clear, non-UV, stabilised, PP sheet. PP materials containing pigments and / or UV stabilisers could be expected to have a longer lifetime in the New Zealand environment.

6.3 Other polymers

It is clear, from Sections 4.2.3.3 to 4.2.3.4 and Sections 4.2.5.2 to 4.2.5.3, that the black PE, white uPVC and glazing materials samples have not as yet started to lose any significant mechanical strength. As such, it is not yet possible to reliably predict a lifetime for outdoor exposure for any of these materials.

7. CONCLUSIONS

The experimental programme completed as part of this project has confirmed the susceptibility of the main polymers used in the construction industry to surface and mechanical property degradation in the New Zealand environment.

The predicted lifetime maps generated for non-UV stabilised, clear, polyolefin materials demonstrate that there are significant effects on service life from the different climatic conditions across the country. It was also found that the products are not durable for any considerable time in the New Zealand environment. In fact, their predictable loss of mechanical strength and surface property changes make them ideal control materials for studies of other developmental materials or for quantification of accelerated aging methods.

The rapid failure of the non-UV stabilised, clear, polyolefin materials results almost entirely from degradation by UV radiation. The durability of the PE and PP samples exposed are clearly insufficient to give them any significant service life in the NZ environment. In fact, it is seen as highly unlikely that clear polyolefin materials will meet the NZBC B2 Clause 2.3.1(c) requirement of five years durable life when exposed outside in NZ. Polyolefin materials containing pigments and / or UV stabilisers could be expected to have a longer lifetime in the New Zealand environment. Polyolefin products for outdoor use should be carefully formulated, in close consultation with the material and additives manufacturers. The performance of the resulting formulations should also be systematically examined, under representative conditions, to ensure acceptable performance prior to sale.

Some interesting trends have emerged when comparing these clear polyolefins to a pigmented equivalent, concerning the connection between crack initiation at the surface, dependencies of crack dimensions on formulation and effects on material mechanical performance.

The addition of carbon black to PE is well known to increase stability to UV exposure. The exposed sheet samples tested here contained 1.7% w/w carbon black. These results indicate that this level of addition is sufficient to expect thick sheet materials will meet the NZBC B2 Clause 2.3.1(c) requirement of five years durable life when exposed outside in NZ. This is, of course, on the proviso that the base resin and other additives types and concentrations are fit-for-purpose.

As expected the pigmentation of uPVC, using rutile TiO₂, has also been found to yield good results resisting UV exposure. The exposed sheet samples tested here contained 5.4% w/w rutile TiO₂. These results indicate that this level of addition is sufficient to expect thick sheet materials will meet the NZBC B2 Clause 2.3.1(c) requirement of five years durable life when exposed outside in NZ. This is, of course, on the proviso that the base resin and other additives types and concentrations are fit-for-purpose.

Although the experimental work presented here has found the expected trends, it has only developed an initial predictive model and mappings of the performance of the rapidly degraded polyolefin materials in the New Zealand environment.

Durability mapping for more stable polymer types, and those containing effective UV stabilisers, will be more complicated. Extension of the work presented here to these materials, where the trends will inherently be less predictable, will require further testing work and access to polymeric materials that have been exposed for longer periods of time. It is fortunate that a selection of black PE and white uPVC samples exist on the BRANZ exposure site awaiting analysis.

8. FUTURE WORK

In order to either validate or reduce the apparent growth of sustainability arguments against the use of polymeric materials in construction, further refinement of the initial predictive model presented here for the determination of the functional lifetime in the New Zealand environment for polymeric materials is required.

Further development work would draw together, and attempt to establish a correlation between, already existing natural and accelerated exposure data for key polymer types (such as uPVC, carbon black-filled PE) to deliver an improvement in the reliability of the understanding of durability issues for polymeric materials.

It is envisaged that a further step would be to examine the effect of UV stabiliser concentration in unpigmented polyolefins and other materials.

The potential of developing highly accelerated exposure tests should also be investigated. This would be achieved by exposing each polymer type to only the most harmful wavelengths of radiation, as defined by the sensitivity spectrum. This would lead to the determination of an effective dose, per critical performance parameter, for each polymer type.

Ideally, any test methodology would have the capacity to determine property degradation rates as a function of composition and application over short exposure periods. It should also be capable of considering environmental conditions in a flexible manner, which would include both current architectural design and future best practice for optimum durability performance. These goals could be achieved through the development of verification techniques that varied as a function of structural environment.

If warranted, the conclusions of the work would also lead to a development or revision of standards and, with the support of the polymer producers, an increase in creative solutions available within the market place.

Any future programme of work in this area should not only examine existing polymeric materials technologies, but also encompass the increasing range of polymer materials and systems that are not derived from fossil fuels. These include recycled resins, bio-polymer resins and natural fibre reinforcements, such as flax.

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