

The Influence Of Rain And Humidity On The Lifetime Of Transparent Polymeric Roof Materials

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Summary: PMMA and PC undergo photochemical ageing leading to a gradual loss of material transparency and appearance during service life which is desired to reach 50 years or more. Available artificial weathering test methods are unable to distinguish materials in terms of the speed of ageing in outdoor use as roof materials. In order to design an appropriate accelerated or time compressed test method the “Worst Case” scenario of the respective climatic conditions must be found. Therefore, samples of PMMA and PC were exposed to artificial weathering tests using different climatic conditions in terms of relative humidity and surface wetness. In case of PMMA it was found that water accelerates the photo degradation enormously. The fastest ageing occurred when liquid water and UV radiation acted simultaneously on the sample surface and the PMMA reached its highest water content during weathering. In the case of PC it was found that both vapour and liquid water speed up the photoageing, similarly to PMMA. But differently from PMMA the “Worst Case” scenario for PC proved to be weathering conditions with high relative humidity. A test method has to be able to run artificial weathering under the different moisture conditions which can occur in the field.

Keywords: Polymeric roofings, poly(methyl methacrylate), Polycarbonate, photodegradation, weatherability

1 INTRODUCTION

Transparent polymeric materials are increasingly used in the place of glass for transparent applications in the building sector because they are lightweight, tough, easily formed into complex shapes and transmit light well. However plastics are more susceptible to degradation by weathering than the traditionally used glass; notably to the combined effects of ultraviolet light, heat and moisture. A large range of plastics glazing is available ranging from highly photo stable materials that are commonly used without photostabilisers to poorly photo stable polymers that require extensive protection against the destructive weather conditions. Applications such as roof materials usually require a lifetime of several decades. Therefore, accelerated or time-compressed artificial weathering tests are used to assess the weatherability of plastics glazing or combinations of plastics glazing. Nowadays, the favoured method to design an appropriate test is the so-called “Test-tailoring”. This means that each kind of plastic glazing needs its specially designed weathering tests. Test-tailoring requires the knowledge of the “Worst case” scenario of the weather periods occurring in the field, characterising the combination of environmental factors that most accelerate the photodegradation for the concerned plastics glazing. Today’s standardised artificial weathering tests for plastics are performed mostly too dry and do not meet the “Worst case” scenario of most types of plastics glazing consuming a lot of time without showing the typical degradation phenomena. Therefore, our work is directed at the influence of water (vapour or liquid) during weathering on two widely used materials for plastics glazing (PMMA and PC). A good example of the use of PMMA glazing over about thirty years is the roof of the renowned Munich Olympic stadium. The roof plates had to be replaced completely in the last few years because they reached the end of their lifetime. The commonly observed failure mode in PMMA is the gradual development of crazes. Because the PMMA used was stretched in two axis the crazes developed in a horizontal direction leading to a scale-like splitting-off of material from the surface. The result of this degradation phenomenon was an unacceptable loss of light transparency. But none of the standardised artificial weathering tests used commonly for evaluating the material quality could cause this phenomenon in the laboratory. Therefore, the great variation in lifetime of the plates that was observed during the last three decades in the environment could not have been predicted. A special phenomenon that could be observed on the roof plates in the field led to the suspicion that moisture conditions had accelerated the deterioration of the PMMA. Figure 1 shows an almost 25 year old highly damaged roof plate. The almost clear surface

parts which can be seen near the metallic disks or frames needed for fixing the plates were mostly warmer than the other parts in clear nights and therefore, affected by dew for shorter periods and less intensely. Lehmann (1997) describes the frequent changes of wetting and drying as the most likely cause for the damage of the weathered roofing site. But the contribution of water to the loss of fastness by photodegradation cannot be discarded. Finding experimental evidence for this presumption was one aim of this work.

The contribution of humidity to the photodegradation of polycarbonate is controversial. In artificial weathering studies, Pryde (1985) reported that pre-hydrolysis of polycarbonate accelerated photo-induced discoloration when compared to dry samples. However, the presence of high humidity levels during exposure to UV was reported to have an opposite effect, decreasing the rate of photo-induced yellowing according to Factor and Chu (1980) and Pryde (1984). While Tjandraatmadja et al (1999) reported that under moderate humidity (42%) the rate of yellowing underwent an acceleration stage in the early stages of degradation, but as exposure progressed dry samples experienced more intense yellowing. On the other hand, high humidity seems to favour the rate of photo-oxidation in polycarbonate according to researchers, such as Clark and Munro (1984) and Rivaton et al (1986). In context with developments to improve the relatively bad scratch resistance of PC by covering it with appropriate hard coats, more knowledge about the behaviour of the basic PC sheet material at extreme weather conditions is necessary. Further clarification of the influence of water on the photodegradation of PC due to the differences in the existing opinions was the other aim of this work.

2 EXPERIMENTAL

2.1 Materials

Two types of PMMA and four types of PC were evaluated. All of them were commercially available sheet materials. The identification of the samples is shown in Table 1.

Table 1: Identification and features of the glazing examined

| Sample | Type | Thickness | Property |
|--------|------------------|-----------|--|
| PMMA 1 | GS 215 stretched | 4 mm | Uncoloured |
| PMMA 2 | GS 816 stretched | 4 mm | Light brown coloured |
| PC-1 | Lexan | 1 mm | Only basic stabilisation |
| PC-2 | Indoor | 3 mm | Only basic stabilisation |
| PC-3 | APEC HT | 3 mm | Only basic stabilisation, optical quality, |
| PC-4 | Longlife | 3 mm | Both sides co-extruded with highly stabilised PC films |

2.2 Methods

Artificial weathering was performed using a commercially available fluorescent UV lamp weathering device, model "Global UV Test" in combination with a special box which allowed to expose specimens to three different moisture conditions at equal temperature at the same time and in the same weathering chamber. The conditions are characterised in Table 2.

Table 2. The three different weathering conditions

| Short term | dry | humid | wet |
|--------------------|--------------|---------------|--|
| Climatic condition | 50°C; 13% RH | 50°C; 98 % RH | 50°C; steady under a 5 mm sheet of water |

The test ran under constant conditions. The specimens were subjected to continuous UV radiation (39 W/m^2). Spectral radiation distribution was performed according to ISO 4892-3: 1994 (no UV output below the normal solar cut-off of 290 nm). The "Global UV Test" equipment enables the application of the test under defined and reproducible weathering conditions, which is a requirement for good repeatability and reproducibility. The temperatures of the panels were constant to $\pm 1\text{K}$. Periodically specimens were taken out of the weathering device and their properties (listed in Table 3) were determined.

Table 3. Examinations of the weathered specimens

| Glazing | Property | Measuring technique |
|---------|--|--|
| PMMA | appearance | Visual (unarmed eye) |
| PC | Exposure up to first occurring of crazes | Visual (unarmed eye) |
| PC | Spectral transmission | Carl Zeiss – DMC 25 |
| PC | Haze | Gardiner Pivotal Sphere UX-10 |
| PC | Gloss 60° | BYK Gardner Tri Gloss meter |
| PC | Colour | BYK Gardner Color guide, sphere 65/10° (white tile background) |
| PC | Surface image | LAIKA macroscope M420/ DC200 |
| PC | Surface profile | WYKO white light interferometer |
| PC | SEM | Phillips XL30 at 2 kV |
| PC | Chemical change | Bruker FTIR |
| PC | Acid resistance | ADF test of the BAM |

3 THE EFFECT OF WEATHERING

3.1 PMMA

After certain exposure periods specimens of each material were taken out of the weathering device, dried at normal room conditions and photographed all using a scanner. The weathering was finished after 130 days and the last specimens were dried in vacuum to determine the water content. Weathered specimens of PMMA 1 are shown in Figure 2. As can be seen in Figure 2 the test duration that is necessary for the first occurring of scales clearly depends on the climatic conditions. No visible deterioration could be found after weathering under dry conditions. The joint action of UV radiation and liquid water proved to be the “worst case” for PMMA. In this case the steady wetness of the surface led to the highest water content in the polymer. An environment with high relative humidity showed a slower deterioration obviously because of the lower reachable water content in the polymer. No difference could be found in the behaviour of the two PMMA qualities.

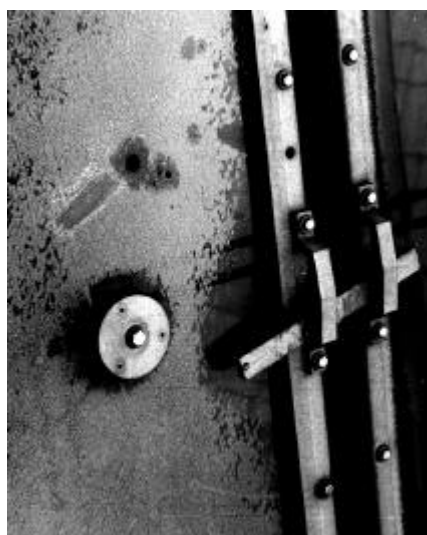


Figure 1. Image of damage of a 25 years old roof plate made from PMMA 1

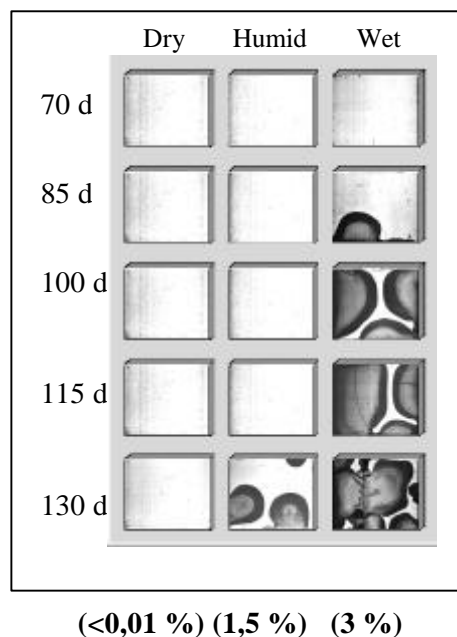


Figure 2. Image of damage of PMMA 1 after exposure in dependence on the test conditions (from left to right) and the test duration from top to bottom. In brackets the water content after 130 days of exposure

3.2 Polycarbonate

3.2.1 Spectral transmission

One of the characteristic traits of polycarbonate photodegradation is yellowing.

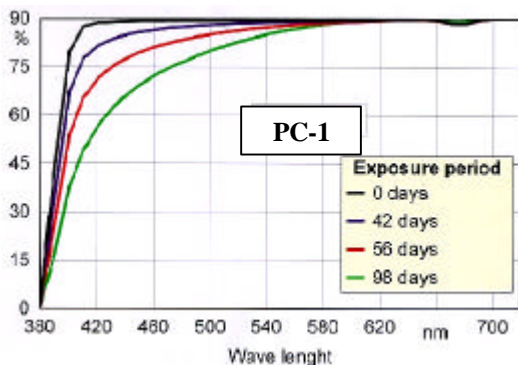


Figure 3. Spectral Transmission of PC1 at wet weathering conditions in dependence of the exposure period

The behaviour of PC-1 shown in Figure 3 is a typical example of the change of the spectral transmission of PC due to the weathering. The most evident variation could be found at the 400 nm shoulder resulting in yellowing. The transmission curves for the other test conditions and for the other samples are very similar. They differ only in speed and intensity of decrease of the 400 nm value. In the same context, the yellow/ blue chromaticity factor b^* shifting in the yellow range predominates significantly in the results of the colour change measurement in accordance to CIE $L^*a^*b^*$ coordinates. Therefore, in the discussion concerning colour the influence of the weathering conditions on yellowing is presented using the factor b^* only.

3.2.2 Colour change

As can be seen in Figure 4, all of the four PC samples are yellowing progressed at different rates during different stages of exposure.

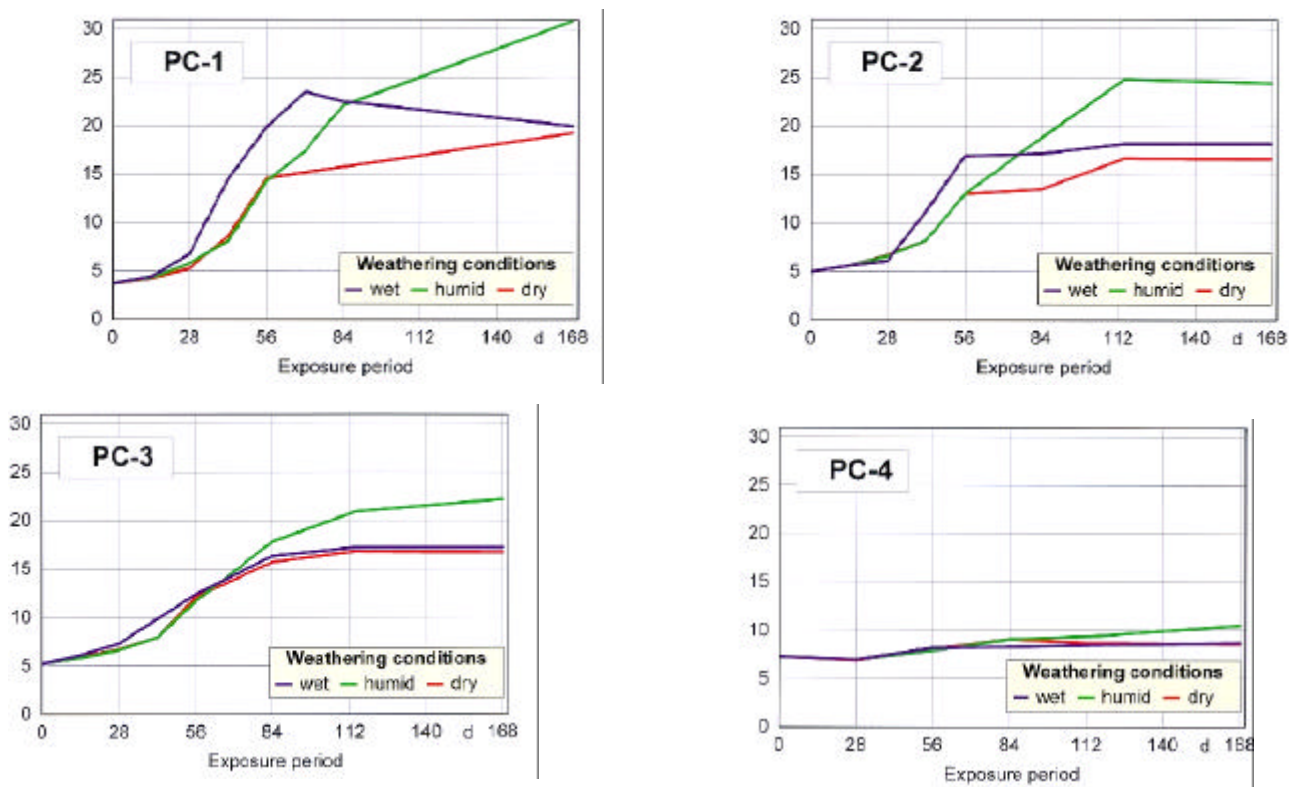


Figure 4. Yellowing of polycarbonate upon exposure

The increase in yellowing was not significant during the first 30 days of exposure. This could be due to the combined action of UV stabilisers present in the sheets' formulation and the induction period required for the concentration of yellow

polyconjugated species to cause noticeable color changes. After the initial period the rate of yellowing increased at an accelerated pace between 50 and 80 days of exposure, after which it slowed down again at an apparent plateau. The rate of increase was dependent on the characteristics of each sample. PC-4 (Long life) experienced the least variation with exposure, hence it could be assumed to undergo the least photodegradation. It displayed less than 20% change for “Wet” and “Dry” conditions and a maximum change of 43.8% for the “Humid” one. In comparison the other types of polycarbonate displayed increases in yellowness ranging from 220 - 325% (PC-3), 230-400% (PC-2) and 420-735% (PC-1). Hence the better stabilisation system in the PC-4 samples protected them effectively from the effect of UV. PC-1 and PC-2 (both indoor quality) samples were the most susceptible to photodegradation as would be expected, since both would contain less stabilisers being indoor type materials. Moisture had a detrimental effect to the yellowing process. Samples exposed to UV and covered permanently with a water film (wet) yellowed at a faster pace than the other samples during the acceleration stage. However the yellowness values (b^*) reached similar values as the samples degraded at 13%RH(dry) after prolonged exposure (>100 days). Whilst, the samples photodegraded at 98% RH displayed the most intense yellowness (b^*).

3.2.3 Development of crazes

Crazes are another typical feature of photodegradation of polycarbonate. Figure 5 presents the WYKO-profiles of several surface sections of weathered PC-1 specimens showing the variety of weathering-caused alterations of the surface morphology:

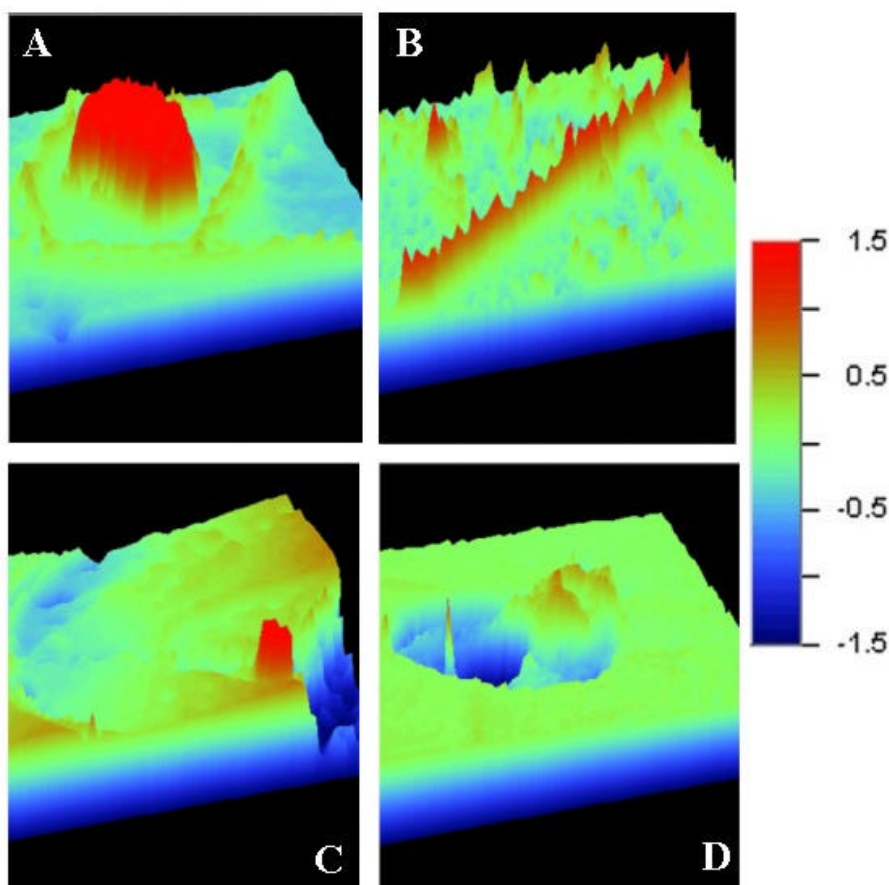


Figure 5. Typical details of the surface profile of differently weathered specimens of PC-1
 (A: 56 days, wet - 60 x 45 μm ; B: 84 days, wet – 220 x 300 μm , C: 84 days, humid – 60 x 45 μm ; D: 84 days, humid – 190 x 250 μm ; height in μm)

Blisters up to 1.5 μm in height surrounded by crazes up to 0.5 μm in height and up to 15 μm in width (see profile A). Crazes up to more than 1.5 μm in height (see profile B). Caves and holes down to deeper than 1.5 μm signalling loss of material (see profiles C and D). These features were distributed irregularly across the sample surface. But in general crazes dominated in comparison to other features. Therefore, only the development of crazes was used to discuss the weathering-related changes of

surface morphology in the further discussion. In contrast to the literature, crazes were risings predominantly and fissures beside the risings appeared only secondarily as can be seen in the SEM photos in Figure 6. It was found that the development of crazes ran in close agreement to the change of colour characterised by the following arguments which were derived from the images of 2 mm wide surface areas of the differently weathered specimens in Figures 7 and 8: First: Visibility and density of crazes increased with increasing exposure period. Second: The dry-weathered specimens did not show any crazes in general. Comparing the specimens weathered at moist conditions crazing is stronger on the humid-weathered specimens than on the wet-weathered ones after 168 days of weathering particularly in case of PC-1. Third: In comparison of the different PC samples, PC-1 showed the strongest crazing and PC-4 had not shown any crazes after 168 days. Fourth: Crazes first occurred during weathering under wet conditions (see also Table 4).

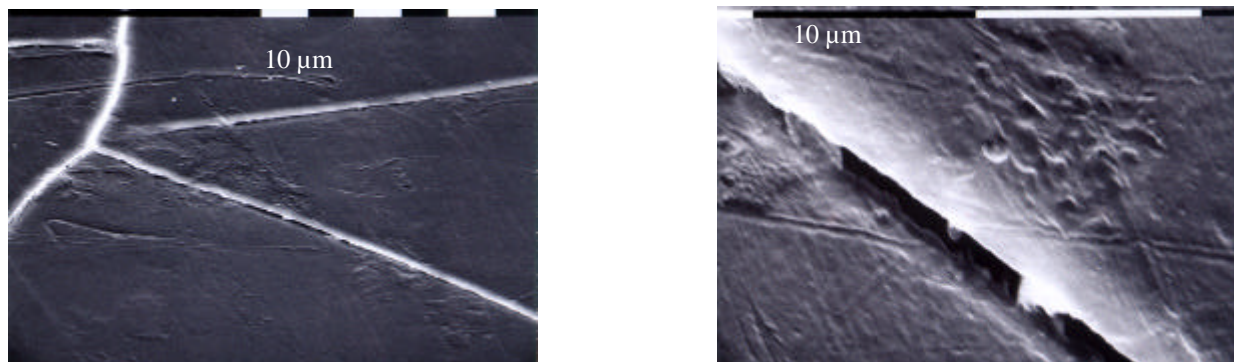


Figure 6. SEM image of a section of the 56 days wet-weathered specimen of PC-1 in different magnification

Table 4. Exposure period up to the first occurrence of crazes identifiable by the unarmred eye

| Sample: | PC-1 | | | PC-2 | | | PC-3 | | |
|---------------------------------------|------|-------|-----|------|-------|-----|------|-------|-----|
| Weathering condition | Dry | Humid | Wet | Dry | Humid | Wet | Dry | Humid | Wet |
| Exposure period for crazing (in days) | >168 | 56 | 42 | >168 | 56 | 42 | >168 | 70 | 42 |

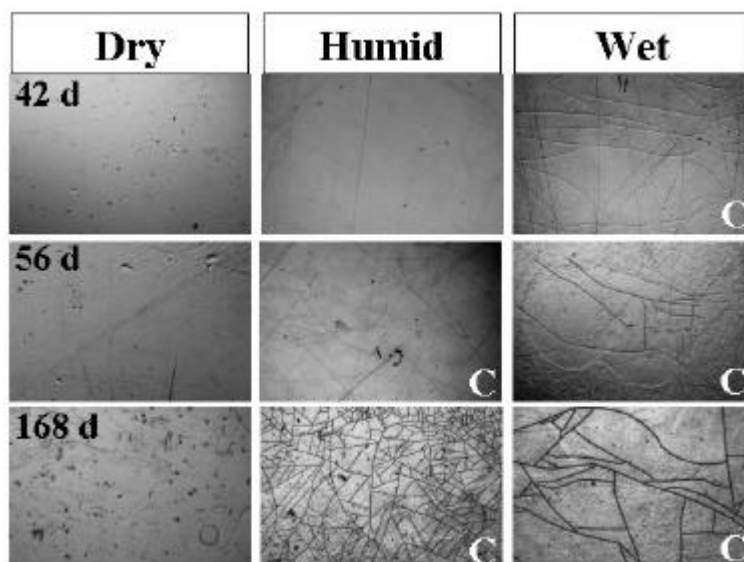


Figure 7. Crazing of PC-1 in dependence on weathering conditions and exposure period (width of the section: 2 mm, C means: Crazes can be spotted by unarmred eye)

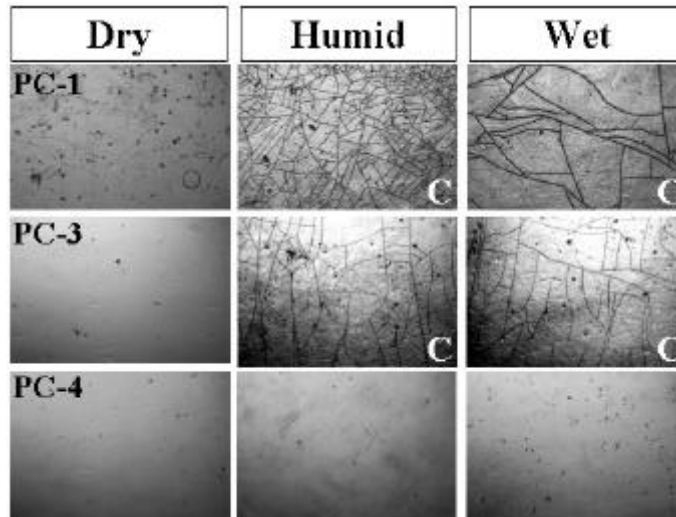


Figure 8. Crazing after 168 days in dependence on weathering conditions and type of PC

3.2.4 Changes in Gloss and Haze

Surface deterioration was reflected by gloss readings. As the roughness of the surface increased, more light scattering took place, reducing the gloss readings for the specimens. Haze, which measures the light scattered by the polymer, both internally and on the surface, increased almost linearly with exposure for all samples. All samples behaved similarly. Sample PC-1 best showed the influence of moisture (see Figure 9). It exemplifies the typical behaviour of all four samples, i.e. that changes in gloss and haze seemed to be independent of the moisture levels during the initial 50 days of exposure. Similarly to changes in colour or intensity of crazing, the samples that were exposed to dry conditions experienced a significantly slower change in gloss and haze than the humid or wet exposed ones with further weathering. In contrast to the phenomenon observed in yellowing and crazing, wet conditions resulted in stronger deterioration than humid conditions in terms of gloss and haze. Sample PC-4 which did not show any significant changes in yellowing and surface morphology due to moisture conditions during 168 days of exposure revealed its first ageing effects by small changes in gloss and haze at humid and dry conditions (see Figure 10).

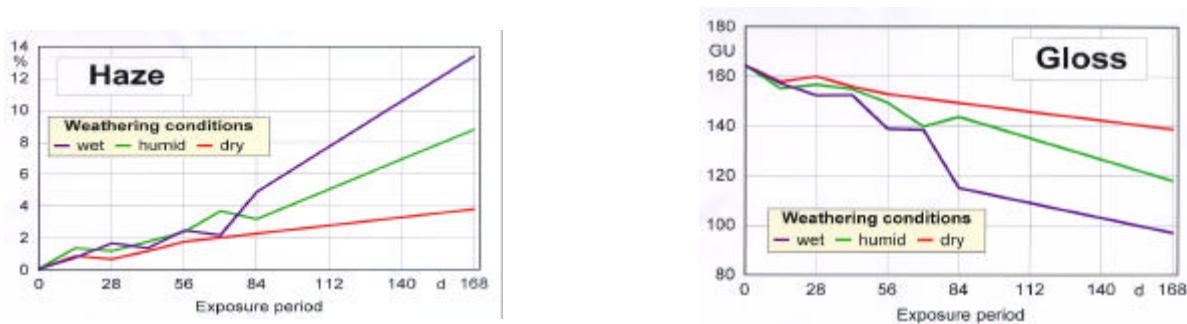


Figure 9. Haze and gloss of PC-1 upon weathering depending on the weathering conditions

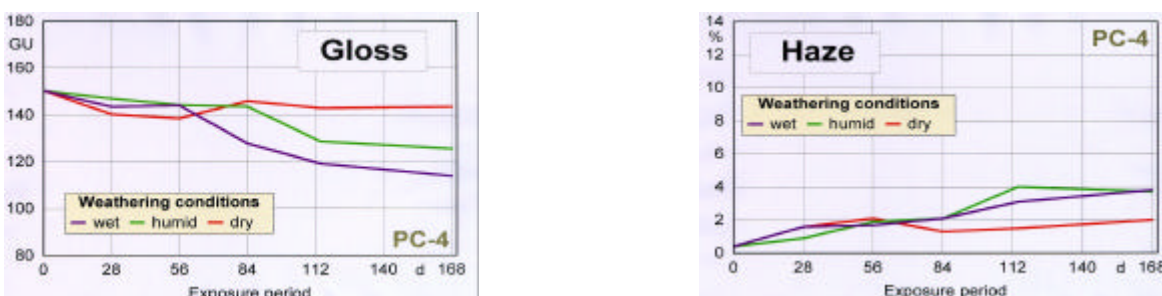


Figure 10. Gloss and haze of PC-4 upon weathering depending on the weathering conditions

3.2.5 Change in acid resistance

Acidic atmospheric precipitation like acid rain, dew and fog are products of the modern industrial society and an essential climatic factor that can accelerate the photodegradation of polymers. Roof materials used in highly industrialised or heavy traffic areas must also have sufficient resistance against the action of acidic precipitation. To assess the resistance of plastics glazing to acidic precipitation it is usual to test whether attacks by acidic deposition result in changes in appearance.

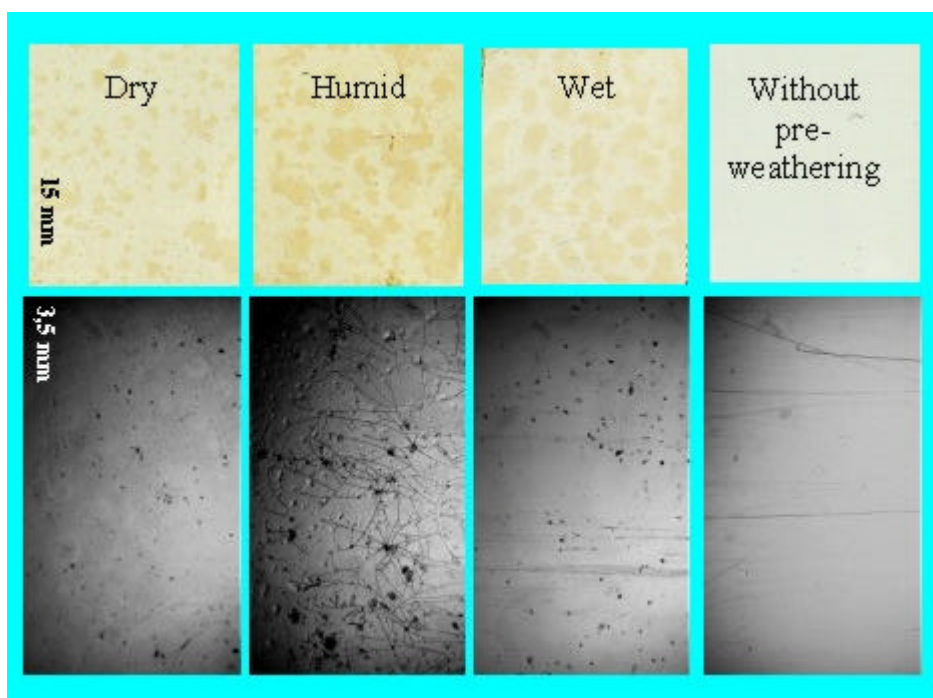


Figure 11. Influence of the weathering conditions on the acid etch resistance of PC-4 (colour and surface image after 168 days of pre-weathering plus 5 ADF cycles in comparison to an un-weathered specimens after 5 ADF cycles)

The Acid Dew and Fog test (ADF test in short) as described by Schulz (1999) was used to determine this material property. Because the specimens of sample PC-4 did not show any crazes or essential yellowing after 168 days of weathering under dry, humid as well as wet conditions yet, they were selected and subjected to the ADF test together with an un-weathered specimen. Figure 11 shows colour and surface images of these specimens after this test. In contrast to the unweathered specimen, the acid deposition (a solution of sulphuric, nitric and hydrochloric acid diluted to pH 1.5) which was sprayed on the specimen surface once a day caused varied strong yellowing on all of the three pre-weathered specimens and crazing on the humid weathered one, revealing that weathering had decreased the good initial acid etch resistance of polycarbonate differently with a strong and clear dependence on the weathering conditions. High relative humidity combined with high temperature proved clearly to represent the “worst case” scenario in this regard. According to this conclusion crazes could also be found on specimens of PC-4 that were exposed outdoors in Jacksonville, Florida. The Jacksonville harbour area is known to combine humid warm climate with frequent occurrence of acid rain and dew. On the other hand practical experiences with PC longlife proved that natural exposure at the temperate European climate characterised by lower absolute humidity and temperature did not generate any visible damage. Examples for the good durability are the more than ten years old roofs of the “BayArena” sporting stadium in Leverkusen and the main station in Krefeld, Germany. Long service life of PC-4 can also be expected under dry hot conditions.

3.3 Chemical changes

The deterioration experienced by the polycarbonate samples is the result of chemical changes due to photodegradation and physical processes. The photo-degradation reactions, Photo-Fries and photo-oxidation, are triggered whenever a sample is exposed to UV in air, and degradation is evidenced unless enough UV stabilisers are used in its formulation (Factor 1996, Rivaton 1995). These reactions result in chain scission and crosslinking, generate yellow species responsible for colour changes, form oxidised species (eg. alcohols, acids, esters, etc) (Factor et al 1987), alter molecular weight, etc. In summary they change the chemical and physical composition of the degraded layer. The extent of such photoreactions is limited by the depth of penetration of UV radiation into the polymer, which varies according to the source of radiation, material, exposure time, etc (Factor and Chu 1980).

Figure 12 compares the IR-spectra of PC-1 samples aged for 168 days under the different moisture conditions (Wet, Dry and Humid) with the control sample (without weathering). As highlighted in the hatched square the peaks in the carbonyl region

(1600-1800 cm^{-1}) differed for each condition. At dry conditions the peak at 1775 cm^{-1} decreased in intensity and a shoulder of new peaks from 1770 to 1600 cm^{-1} was developed. This indicates the presence of -C=O from new photo-oxidised species, for example ketones, carboxylic acids, aromatic esters, which can absorb in that range. The other samples show a much smaller shoulder in that region, although the wet-weathered specimen had a larger shoulder than the humid-weathered one. This would suggest that the surface layer experienced more oxidation in the order Dry>Wet>Humid. Such observations confirm that moisture interferes with the photo-oxidation of polycarbonate.

3.4 The contribution of moisture to photodegradation of polycarbonate

Moisture aggravated the physical changes initiated by photodegradation. For example, the onset of crazing contributed markedly to the alteration of optical properties: It coincided with the rapid increase in haze, reduction of light transmission and gloss. Furthermore, moisture also interfered with the rate of the photodegradation reactions. The acceleration observed during yellowing suggests that moisture aided in the formation of yellow species. The exact mechanism is not yet known. There are two possibilities, moisture might favour the mobility of free radicals within the degraded layer and the transfer of products, or it could react with free radicals slowing down the photo-oxidation reaction. The results prove that the first possibility seems to be predominant. Additionally, moisture levels could also affect the rate of photo oxidation by limiting the diffusion of oxygen into the polymer. Another possibility is that stabilisers could have leached out of the polymer due to moisture. If loss of stabilisers took place then it would contribute to a lower resistance to oxidation in a wet environment compared to a humid one. In summary, the rate of degradation is a complex process that could be influenced by a number of factors, including loss of stabilisers, oxygen availability and mobility of free radicals in presence of moisture.

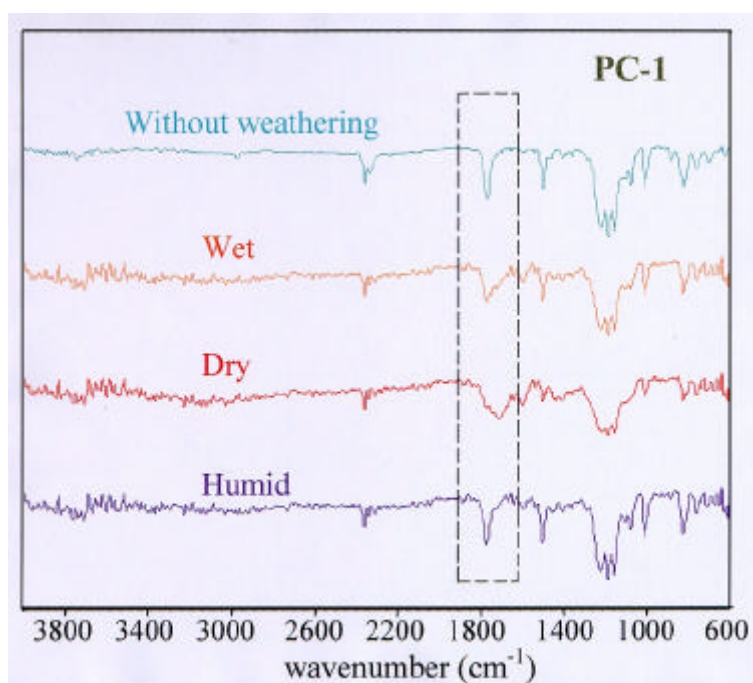


Figure 12. Infrared spectra of PC-1 exposed to different moisture conditions (168 days)

For example, as moisture condensates on the polymer surface, the area for diffusion of oxygen from air to the sample would decrease. This could explain why the samples which were covered by a layer of water during weathering (Wet) showed a slower degradation than those weathered at high humid conditions exposed constantly to a vapour phase containing about 20 % of oxygen.

4 CONCLUSIONS

The Photodegradation of plastics glazing currently used for transparent roofing made from PMMA, PC or combinations of both materials is accelerated by the presence of water during weathering. In the case of stretched PMMA plate material, the presence of liquid water during weathering or other conditions guarantying high water content in the polymer proved to be the “Worst Case” scenario of the weather conditions in practice. Chemical changes by hydrolysis promoted presumably by UV radiation seem to be more likely responsible for the decrease of mechanical fastness than the fatigue by the frequent changes in volume by wetting and drying as claimed in former publications (Lehmann 1997).

In the case of Polycarbonate humid-warm climatic conditions guarantying high contents of water and oxygen simultaneously in the surrounding vapour phase proved to be the “Worst Case” scenario. However the photo oxidation promoted by water in gaseous condition seemed to be the predominant reaction in comparison to hydrolysis, as to the exact mechanism by which water facilitates photo oxidation this will have to be investigated further.

5 ACKNOWLEDGMENTS

The authors would like to thank Januar Gotama for his assistance with the color measurements and Anja Geburtig for performing the WYKO profilometry.

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