

Mechanical and Aesthetic effects of UV and Weathering exposure on SAF™ PA12 and SAF™ PP printed material

Introduction

This whitepaper presents the results of long-term weathering tests on SAF PA12 and SAF™ PP printed material. Printed parts were exposed to a variety of aggressive environmental conditions including UV radiation for up to 62 days and combinations of elevated temperatures and moisture levels. Part performance was quantified by measuring changes in mechanical properties and part colour. Additional UV weathering tests were also carried out on SAF PA12 parts which had been dyed black.

The results show that SAF PP has excellent resistance to UV degradation and is the material of choice for outdoor applications. SAF PA12 in its raw condition is much more sensitive to UV and other harsh environmental conditions. Dying SAF PA12 material black was found to significantly improve its resistance to UV although other weathering tests were not carried out.





Effects of weathering on polymer materials

At Stratasys we provide thorough and reliable technical data sheets for our printed materials. These give information about the properties you can expect from your printed parts straight from the machine. This is useful, however not the full picture. The properties of real, end use parts are not static, but constantly evolving in response to the environment in which they are used. This is universally true of all materials from ceramics and metals through to polymers, although the rates of degradation, and the environments that cause them, vary.

Heat, oxygen, moisture and UV radiation are the four main environmental factors which can lead to degradation of polymers. They all have a very similar effect, breaking down polymer chains in the material and creating brittle compounds. Environmental factors are usually found in combination and interact with each other to accelerate the effects. For example, oxygen exposure alone may have little effect, but when combined with heat, degradation can occur much more quickly.

General Test Methods

Test specimen printing

All testing was done with either tensile or impact testing parts (details in appendix), printed in the ZX (vertical) or XZ (horizontal) orientation in an H350, using standard parameters. For each test (test condition/print orientation pair) 5 specimens were tested. For each material, all test specimens were printed in a single build (Figure 1) with a nesting density of 13.5%. All builds were allowed to cool for 24 hours before being broken out with the parts being cleaned using a Dyemansion Powershot C automated bead blaster.

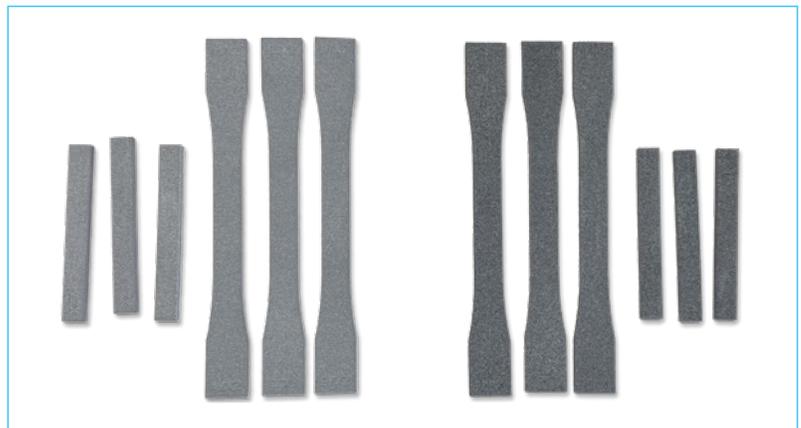


Figure 1: Sample of tensile and impact specimens used during testing. SAF PA12 (left), SAF PP (right)

SAF PA12 Sample Dying

A smaller set of tensile test specimens were taken from the same SAF PA12 build and dyed black using a Dyemansion DM60 and standard dyeing conditions (~150minutes up to 115oC). Dyed parts were subjected to UV testing only. Due to the smaller number of available specimens, the sample size for each test was smaller with 5, 4, 3 specimens for the 500h, 1000h and 1500h exposures respectively.



Preconditioning Test Specimens

The properties of a polymer part can be sensitive to its moisture content. To mitigate this effect and isolate the long-term degradation effects, specimens were pre-conditioned before final testing to remove any extra moisture (unless otherwise specified for water immersion and dried tests). This preconditioning stage consisted of storing the specimens for 7 days at 23 °C, 50% RH after their environmental exposure period.

A control set of test specimens were subject only to the preconditioning stage, with no environmental exposure. These are referred to as “unweathered” in the results.

UV Testing

Both SAF PA12 and SAF PP specimens printed in the ZX orientation were exposed to UV radiation for 500, 1000 and 1500h (roughly 20, 40 and 60 days respectively) in accordance with ISO 4892-3. UV exposure was achieved using UVA-340 fluorescent lamps with a peak output of 343nm, suitable for simulation of global solar radiation, Figure 2. The testing conditions were constantly cycled between 8h of dry and 4h of condensation.

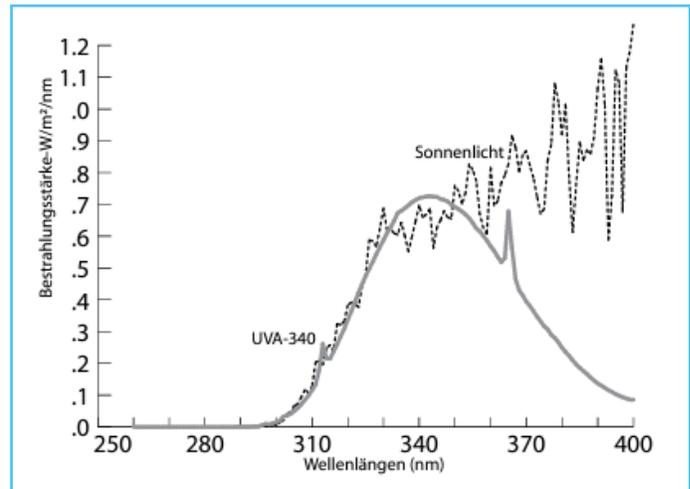


Figure 2: UVA-340 lamp emission spectrum compared with sunlight



Figure 3: Three test specimens loaded into the UV exposure test rig



Mechanical Properties

There is a marked difference between SAF PA12 and SAF PP when exposed to UV radiation. In SAF PA12 mechanical properties including UTS, EaB and impact strength all show a significant reduction after the first 500h exposure. After the first 500h of exposure to UV, SAF PA12 does not show any further reduction in properties.

The resistance of SAF PA12 to UV radiation was dramatically improved by dyeing the material black. Although only tested for tensile properties, the dyeing process removed almost all the degradation effects measured in the raw material. After 1500h of exposure the UTS was unchanged. The samples did display ~15% embrittlement with EaB and tensile modulus decreasing and increasing respectively.

Parts printed with SAF PP show a much greater resistance to UV exposure in their raw condition. None of the mechanical properties had a large response, even after 1500h of testing, with only EaB reducing slightly from 9.8% to 8.3%.

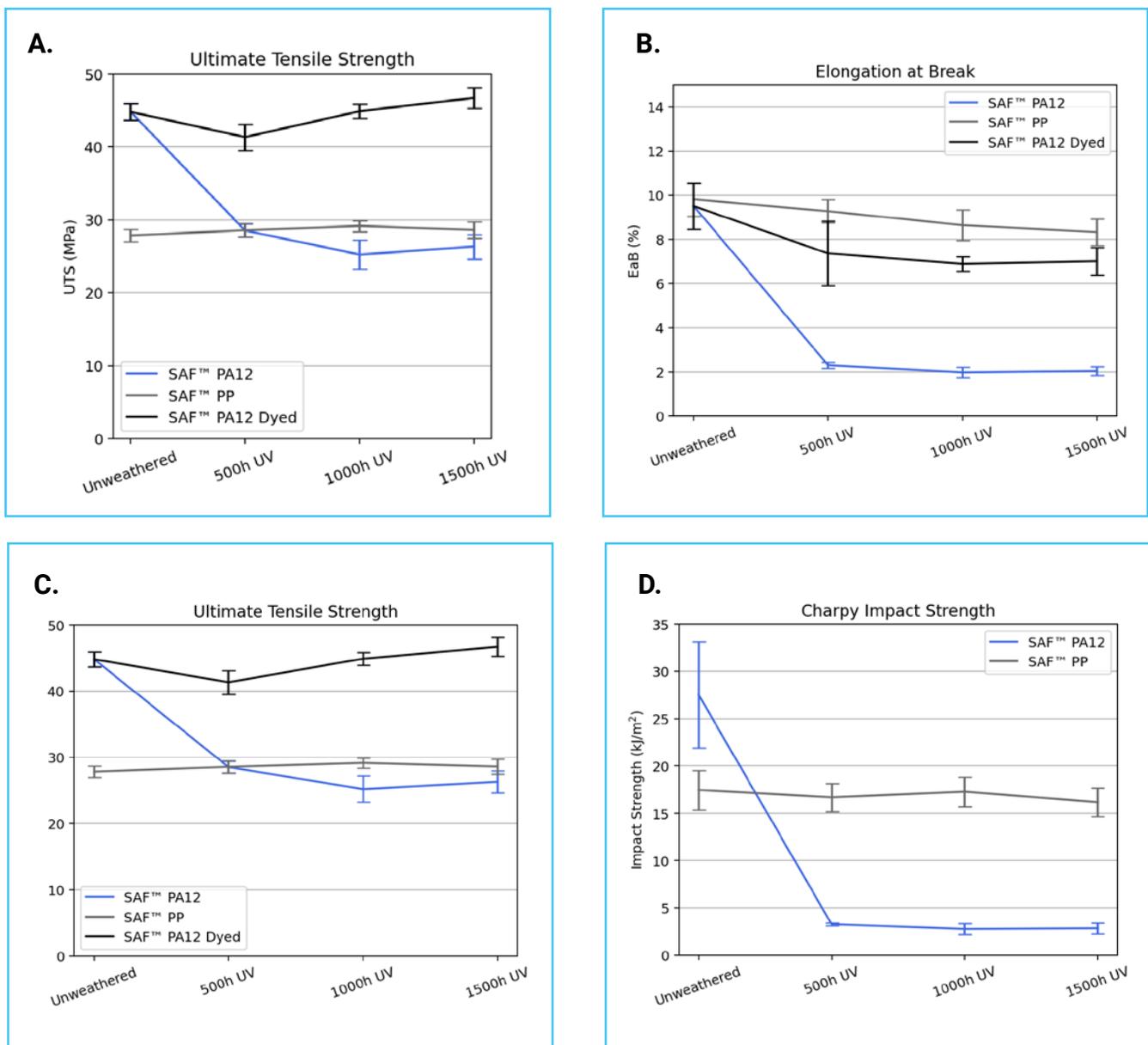


Figure 4: Plots showing the change in mechanical properties of SAF™ PA12 (raw and dyed) and PP after exposure to UV for 500, 1000 and 1500h. All test specimens were printed in the ZX orientation (vertical). The “unweathered” results represent printed material with no UV exposure as a control.



Color Difference

The colour of the specimens was quantified using CIELAB colour space. Specimens were measured before and after UV exposure. An explanation of CIELAB and Just Noticeable Difference (JND) can be found in the appendix. The results in Figure 5 show that the only test to cross the JND threshold was 1500h exposure of SAF PP. Although this sample crosses the JND threshold it is only by a very small amount. In practical terms the colour of both SAF PA12 and PP can be said to be very stable when exposed to UV. Neither material demonstrates any yellowing as is commonly seen in other polymers.

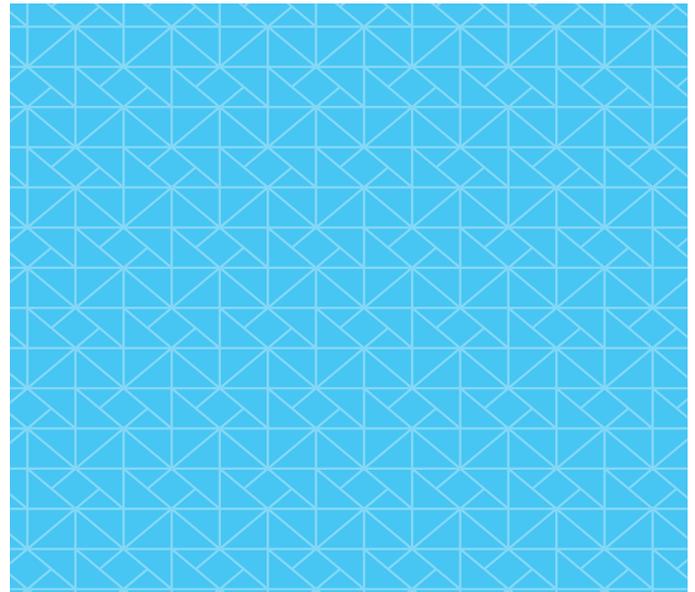
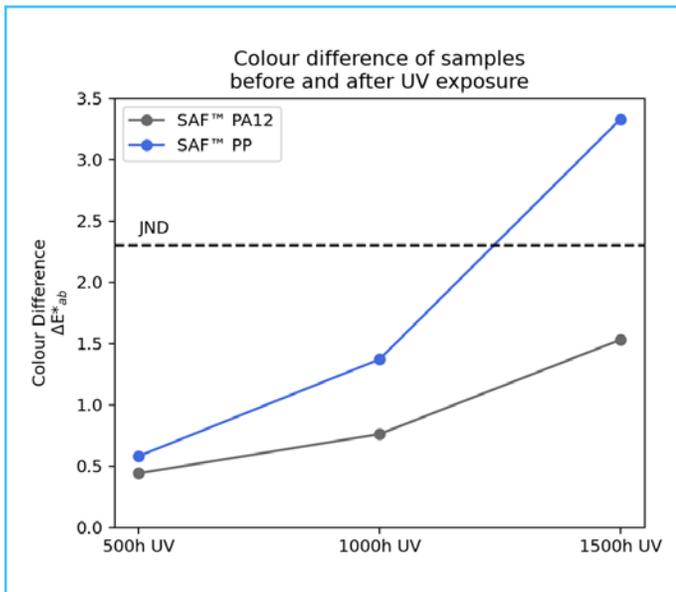


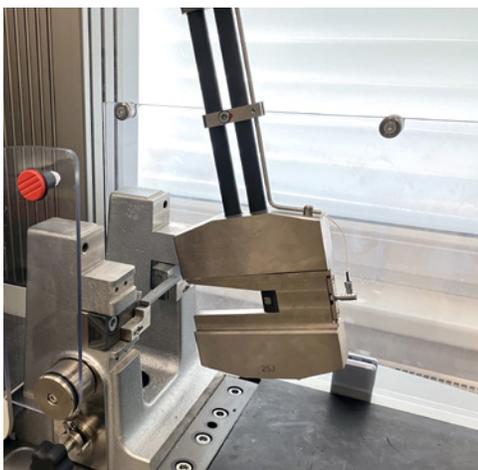
Figure 5: Plot showing the colour difference between specimens before and after UV exposure. Colour difference expressed as ΔE_{ab}^* calculated using the CIE76 definition with the JND threshold set to 2.3.



Weathering

A separate set of tests were carried with SAF PA12 test specimens being exposed to other weathering conditions. The mechanical properties caused by this weathering were tested. The weathering conditions tested are given below in Table 1. The tests cover a range of combinations of heat and moisture levels.

Test	
Water Immersion	Test specimens were stored immersed in a 60 °C water bath for 72 hours prior to testing. These specimens were not preconditioned before final testing.
Dried	Test specimens were stored in an oven at 80 °C for 72 hours with air being constantly circulated. These specimens were not preconditioned before final testing.
Extreme heat	Test specimens were stored in an oven at 100 °C for 1000 hours with air being constantly circulated. These specimens were preconditioned before final testing.
Extreme heat and humidity	Test specimens were stored in a climate-controlled chamber at 80 °C and 80% RH for 1000 hours. These specimens were preconditioned before final testing.





The results below in Figure 6 show a varied response to the different environmental exposures. In each case results are presented as a percentage change from the “unweathered” control sample. A percentage change makes the magnitude of changes more apparent.

For this test, specimens printed were in both ZX (vertical) and XZ (horizontal) orientation. The results show both orientations responding in a very similar way to each test. This suggests that print orientation has no effect on environmental degradation of mechanical properties.

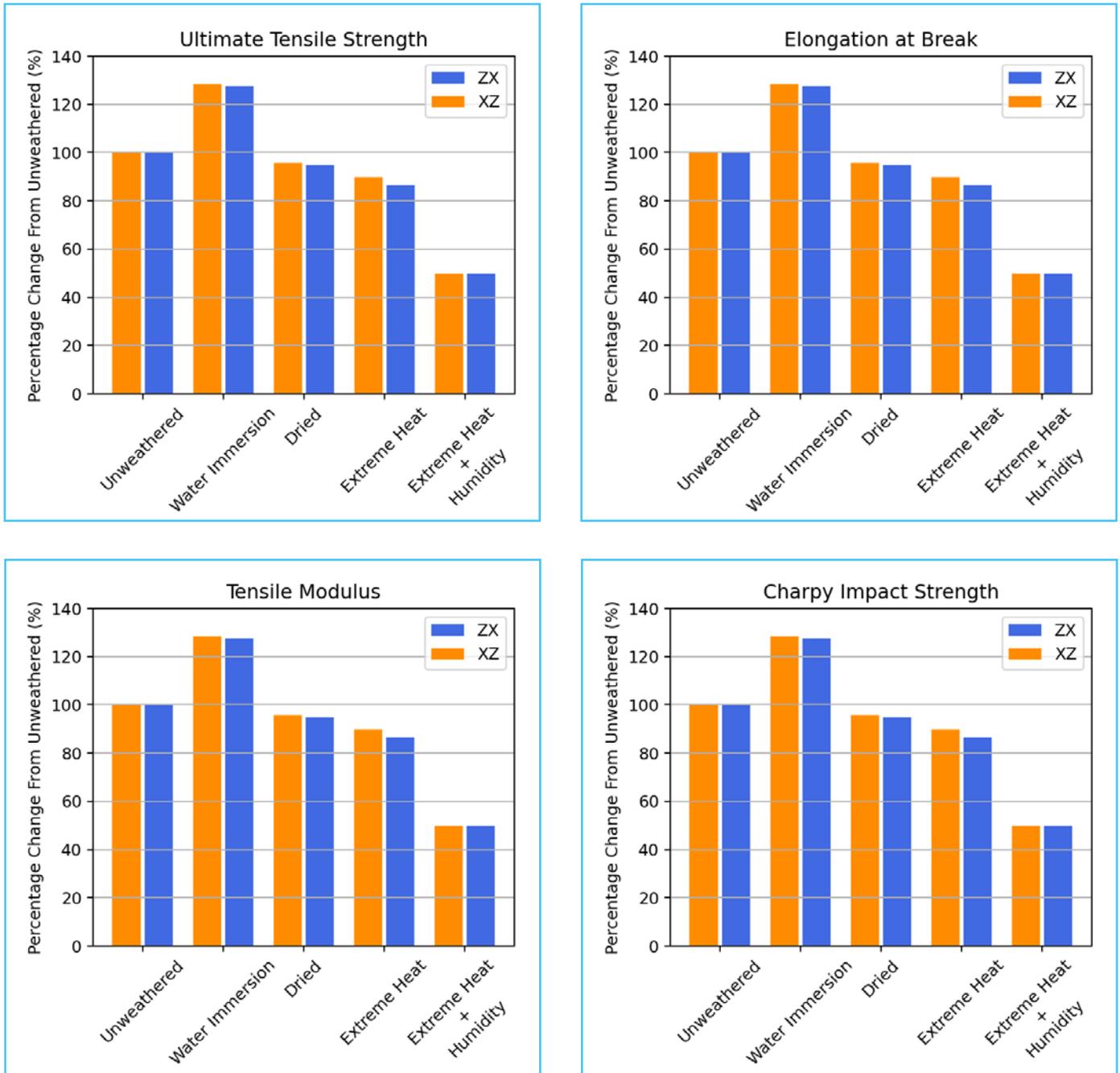


Figure 6: Plots showing percentage change in mechanical properties of SAF PA12 and PP printed material after exposure to different environmental conditions (Table 1). Results from sample printed in ZX and XZ orientations are plotted. The “unweathered” results represent printed material with no environmental exposure.



Water Immersion

The main response to immersion in water was a ~30% drop in stiffness (tensile modulus) and ~30% increases in elongation at break (EaB) and impact strength. This indicates a more ductile material better able to absorb energy.

Dried & Extreme Heat

These test both showed a very similar result. While there were modest changes in the other properties, the ~20% decrease in EaB was the largest change. This indicates the material becoming more brittle.

These results are interesting considering the difference in test conditions between the two. Specimens in the extreme heat test were exposed to 20°C higher temperature for 34 days longer. The results suggest that the degradation occurs relatively quickly, within the first 7 days, but does not continue. The degradation also seems to be relatively insensitive to temperature with 80°C and 100°C producing almost identical results.

Extreme Heat and Humidity

The combination of extreme heat and humidity has an embrittling effect on SAF PA12 material making it unsuitable for use in these conditions. Both EaB and impact strength dropped to ~50% of the control value demonstrating a much less ductile material.

Combined with previous tests, this is an interesting result. Immersion in water was found to improve ductility of SAF PA12 while exposure to dry heat decreased it. This test suggests that there is a negative interaction when both heat and moisture are present together, leading to more severe degradation. There may also be a difference between the way that liquid water and water vapour in the air interact with the material to further accelerate the process.

Summary

The results show that SAF PP has excellent resistance to UV radiation, with mechanical properties and part colour being stable after even 1500 hours of accelerated exposure. Due to variations in climate for different locations it is difficult to translate this precisely to weathering which would be experienced in the real world. A common rule of thumb is that 1500 hours of accelerated ISO 4892-3 testing is approximately the same as 1.5 to 3 years of real world conditions. This makes it the material of choice for end use applications where parts will be used outdoors or otherwise subject to high levels of UV.

SAF PA12 was found to be more susceptible to degradation from environmental exposure in its raw condition. UV exposure, heat and high humidity were all shown to reduce mechanical properties of the specimens. Despite mechanical degradation, PA12 demonstrated excellent colour stability, even after the longest exposure to UV, resisting any of the yellowing commonly seen in other polymers.

Dying SAF PA12 black was found to significantly improve the resistance of its tensile properties to UV exposure although exposure to other weathering was not tested.



Appendix A

Measuring Mechanical Properties

Tensile testing

Tensile testing was done in accordance with ASTM D638-14 using Type 1 dogbones. The testing was conducted using a Hegewald & Peschke Inspekt Duo universal testing machine with a 5kN load cell. A strain rate of 1 mm/min was used for the initial 0.5 mm of each test to determine tensile modulus followed by the completion of the test at 50 mm/min. Strain was determined using grip distance separation to measure sample elongation.

Although still compliant with ASTM D638-14, this testing set up differs slightly from the one used to produce data for Stratasys material data sheets. Results will be internally consistent within this paper, but “unweathered” results may differ slightly from data sheet values.

Charpy Impact Testing

Charpy impact strength was measuring in accordance with ISO179 using unnotched samples. Testing was completed using a ZwickRoell HIT50P and a 25J pendulum.

Measuring colour difference

To get an objective measure of colour change before and after weathering, the colour of parts was expressed using CIELAB colour space and a ΔE^* value was calculated and compared to the JND value.

CIELAB Colour Space

CIELAB colour space is a 3D coordinate system which can be used to represent any colour visible to the human eye. There are 3 coordinates L^* , a^* and b^* which describe a colours position on the lightness, red-green and blue-yellow axes respectively.

Quantifying Colour Difference

By measuring the colour of a part before and after a test, the difference can be expressed as a ΔE_{ab}^* value. In this testing, ΔE_{ab}^* was calculated using the CIE76 definition which is appropriate for the low saturation colour of SAF parts.

To determine whether the ΔE^* represents a significant colour change it is compared to a just noticeable difference (JND) value. The JND value is an estimation of the amount of change that is required for the difference to be detectable at least half of the time. It is the smallest possible change that is likely to be perceived by a human. For the CIE76 definition of ΔE^* the JND value is estimated to be 2.3.



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WHITE PAPER
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