Effect of accelerated weathering on the creep behaviour of additively manufactured Polyethylene Terephthalate Glycol (PETG)

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Abstract

As additively manufactured components move away from short-term usability, such as single-use prototypes, towards commercial products used for longer periods of time, the long-term material properties, such as ageing and creep, are becoming increasingly important design considerations. Moreover, when additively manufactured components are designed for outdoor use, environmental stressors affect these long-term material properties in a process known as 'weathering'. In this research paper, an initial set of experiments assessed the flexural creep behaviour of pellet-printed PETG after exposure to three accelerated environmental stressors: UV radiation, temperature and humidity. The outcomes thereof indicated that UV exposure was the only stressor to increase the creep compliance. A subsequent set of experiments increase the UV exposure duration from 100hr to 200hr and excluded the effects of ageing on creep behaviour during creep tests. The outcome of this second series of experiments showed that the increase in creep compliance can be attributed to the effects of UV alone.

Keywords

Accelerated Weathering, Creep, Ultraviolet Radiation, Temperature, Humidity, Polyethylene Terephthalate Glycol, PETG

1. Introduction

Advancements in additive manufacturing techniques have introduced 3D-printed polymers to engineering applications, rapid prototyping, preliminary testing, and various disciplines throughout the industry, creating a need to understand their properties for product development processes. A thorough understanding of time-dependent mechanical properties is crucial to assess the long-term performance of the additively manufactured components. Such an understanding helps maximise the service life of components, which has clear environmental benefits. Chevali et al. [1] investigated the effect of moisture and ultraviolet radiation of neat nylon 6/6 (NY66), neat polypropylene (PP), and their long fibre reinforced counterparts on a critical long-term property; the creep response. The researchers found that a key creep metric, the creep compliance, increased with UV exposure for the reinforced PP whereas a decrease was found for reinforced NY66.

Accelerated weathering of materials is an established method to quantify the effects of naturally occurring stressors, such as temperature, humidity and UV radiation, to determine the viability and longevity of the material in outdoor applications. Different research groups apply different intensities of these three stressors in accelerated weathering experiments. Regarding UV irradiance [2], 0.7 W/m^2 of UV exposure at 340 nm is an equivalent irradiation to noon in Miami, USA, which is suggested by the majority of standards [3]. Still, other researchers investigated higher irradiance level to accelerate UV degradation, notably: 1.35 [4], 2.1 W/m^2 [1], 3.5 W/m^2 [5] and even 1500 W/m^2 in highly accelerated tests [3]. Regarding temperature, 50^{0}C is commonly used [6, 7] but 70^{0}C has been incorporated into an accelerated weathering cycle [6, 7]. Similarly, humidity values differ amongst research groups from 80% RH [8], 85% RH [5, 6] to 100% RH [7].

The effects of naturally occurring stressors on materials are numerous [9] and, even when focussing on mechanical properties, their impact differs per material. UV radiation breaks the bonds of most polymers [10], which has an effect on their mechanical properties. This effect is mostly, but not always, detrimental [1]. Humidity is known to cause swelling, plasticising and/or hydrolysis [11], but these effects could actually improve impact resilience in polyamides [1]. In other words, different stressors invoke different degradation mechanisms which affect the material properties in different ways. Further complicating the field of weathering is the varying intensity of the environmental stressors, both over time as well as at different locations worldwide.

Limited studies have been conducted on the interaction of these two fields of research: creep of additively manufactured materials; and the effect of weathering on the creep response. Türk et al. [12] assessed the temperature influence on creep of additively manufactured samples whereas Altaf [13] investigated the effects of humidity on the creep response of thermosetting Accura 60 printed using the stereolithography method.

Once a plastic in a molten state has cooled sufficiently, it solidifies as its molecular chains are restraint in their movement. As not all chains are permitted enough time to settle into an ideal state of lowest energy during the solidification process, the energy state of the now solid plastic is not in equilibrium [8]. Still, the now solid material is still striving for equilibrium over time and as such its material properties are constantly changing. This process is referred to as 'ageing' and is a universal property of all polymers [14]. When investigating the long-term behaviour of polymers, the effects of ageing, must be accounted for due to its continuous effect on the creep response of polymers [14]. The effects are two-fold; the age of the material before testing needs to be considered and the ageing process during long-term testing needs to be accounted for. Since creep testing entails subjecting samples to long-term loading, these two effects interact; the sample material of a certain age continues to change due to ageing while the creep test is being conducted. As such, the creep behaviour of a material of a certain age can seemingly never be measured as ageing progresses during testing. A solution to this stalemate has been proposed by Struik [14] by limiting the duration of the creep tests to $1/10^{th}$ of the age of the sample. Adhering to this so-called 'snapshot assumption' ensures that the changes in material properties due to ageing during a creep test are small enough to be ignored. This approach to exclude the effects of ageing is followed in this research paper to ensure that the measured effects of weathering on the creep behaviour of polymers are influenced by the environmental stressors alone.

In this study, a method of evaluating the creep response of 3D-printed Polyethylene Terephthalate Glycol (PETG), affected by different weathering stressors, is proposed. Firstly, the methodology described in ASTM C1850 [15] is followed to determine which stressor; temperature, humidity or UV radiation has a crucial effect on the creep response. Secondly, the effects on the creep response of the resulting stressor are then further investigated via a longer creep test, which excludes the effects of ageing during testing.

2. Materials and Methods

2.1 Materials

Additively manufactured PETG, produced through the Fused Filament Fabrication (FFF) method of printing, is the material used in both experiments. Typically, the FFF method uses a filament, which is fed through a heated nozzle, and then deposited on the previous deposited layer. One environmental benefit of FFF-printed PETG is that researchers [16] have proven that filament can be made by extruding a mixture of recycled PETG shredded waste material, mixed with virgin PETG pellets. Alternatively, FFF can use pellets that are heated, extruded, and directly deposited. This option removes the need for filament production which is believed to increase the uptake of recycled PETG in the future. In this paper, all additively manufactured test pieces were produced using a continuous stream of heated virgin PETG pellets to produce a baseline for future experiments where recycled PETG will be added to the virgin material.

2.2 Sample Preparation

Samples were prepared to comply with several standards. ASTM D2990 [17], a standard for flexural creep testing, imposes that the sample shall be conforming to the requirements of ASTM D790 section 5 [18]. ASTM G151 [19], a weathering standard for UV exposure for accelerated testing, establishes that sample dimensions are specified by the test method for properties after exposure. The criteria imposed by both these standards were met by using a 60mm x 12.5mm x 3 mm rectangular bar-shaped sample. Due to the constraints of the pellet printer, a 10mm thick waveform was created, as shown in Figure 1, using the following print parameters:

- Extrusion Temperature: 220°C
- Bed Temp: Unheated
- Enclosure Temperature: ≈38°C
- Volumetric Flow Rate: ≈500mm^3/s or 0.5cc/s
- Layer Height: 2mm
- Layer Width: 5mm

To extract the sample from this waveform, the vertical sections were roughly cut to size, after which these were surfaced on a milling machine to 3mm thickness. The samples were then cut to their final 60mm x 12.5mm size, as shown in Figure 2, using a waterjet cutter, achieving a tolerance of 1-5% on all dimensions.

2.3 Experiment 1

ASTM C1850-17 is a standard focused on the accelerated weathering testing of sealants, but it proposes a methodology to develop accelerated methods in a broader sense [11]. This entails a test phase, which is henceforth referred to as 'Experiment 1', where the severity of the environmental stressors' effects on the material property is evaluated.

Experiment 1 will determine which environmental stressor has a crucial effect on the material behaviour. It will thus serve as a selection tool for a subsequent test, referred to as 'Experiment 2', which will separate the effects of ageing from the effects of weathering on the creep behaviour. Both experiments comprise of two parts; an accelerated weathering experiment, followed by a creep test experiment on the weathered samples.
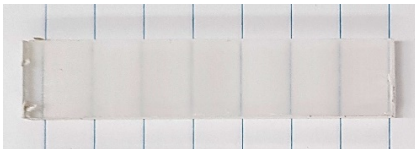

Fig. 1 3D Printed waveform

Fig. 2 PETG sample cut to size

2.3.1   Experiment 1A: Accelerated Weathering

The accelerated weathering testing of the PETG samples was done in accordance with ASTM G154-16 [20]. The Testex TF424 accelerated weathering tester, as shown in Figure 3, was utilised to expose the samples to UV, temperature, and humidity. Samples were mounted at equally spaced intervals in a mounting frame, as shown in Figure 4. Double-sided tape was applied to the sides of the mounting frame to fix the samples in place. One face of the sample was left exposed to weathering while the opposite face of the sample was covered with tape to prevent any exposure. The resulting exposed surface of each sample was 48mm in length. A backing plate and tensioned circlips further secured the samples. The frames were inserted into the Testex with the exposed surface facing the internal four UVA-340 fluorescent tubes. Control samples were stored at standard laboratory conditions of $50\% \pm 2\%$ RH and 23^0C. The sample quantities used for testing are shown in Table 1.

For each of the three stressors in Experiment 1A, samples were exposed for 24 hours using the Testex Machine [21] with the following intensities:

- UVA exposure:
    - Wavelength: 340 nm
    - Intensity: 1 W/m^2
    - Temperature: 50^0C$\pm 2^0$C
- Temperature exposure: 55^0C
- Humidity exposure:
    - Humidity: 90-100% RH
    - Temperature: 50^0C$\pm 2^0$C

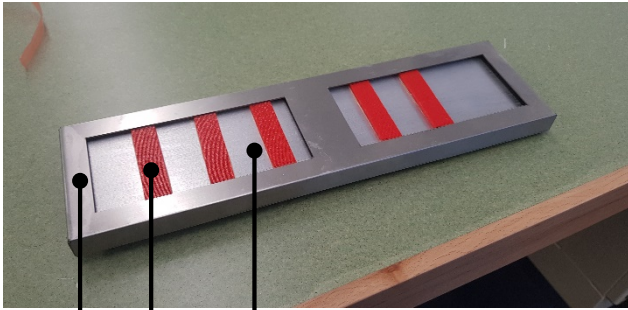*Fig. 3 Testex TF424 accelerated weathering tester (side panel opened)*

Fig. 4 *Samples in a mounting frame. (1) Mounting frame with its exposed surface facing up. (2) Sample. (3) Backing plate which is secured by tensioned circlips (hidden from view)*

Test Parameter	Sample QTY
Control	15
UV	5
Temperature	5
Humidity	5

Table 1:Sample quantities used in Experiment 1.

The amount of UV the sample was exposed to is quantified by the Total UV (TUV) radiance exposure [2] in kJ/m^2 (or $kW \cdot s/m^2$) is:

$$TUV = \text{Irradiance } (W/m^2) \times \text{hours} \times 3.6 \qquad (1)$$

The thermal temperature exposure to the sample is quantified by the Accumulated Thermal Unit (ATU).

$$ATU = \text{Temperature } (°C) \times \text{Time (days)} \qquad (2)$$

2.3.2   Experiment 1B: Flexural Creep Testing

Upon completion of accelerated weathering in Experiment 1A, samples were allowed to cool to room temperature before being transferred to three-point bending creep rigs to determine the creep response. Such a creep rig, that is compliant to ASTM D2990 [17] and includes a temperature-controlled chamber, is shown in Figure 5 and Figure 6. Each sample was placed in the jig in such a way that contact with the loading and support rollers was guaranteed.
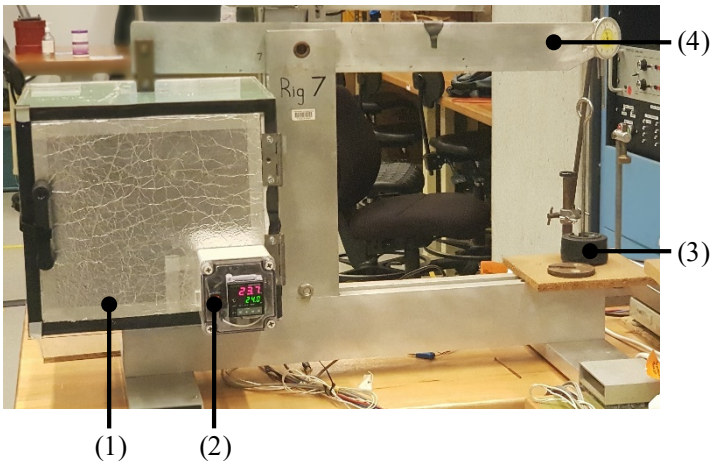

Fig. 5 *External view of the creep rig configuration. (1) Temperature-controlled chamber. (2) Temperature control unit for the temperature-controlled chamber. (3) Disc weights. (4) Lever arm*
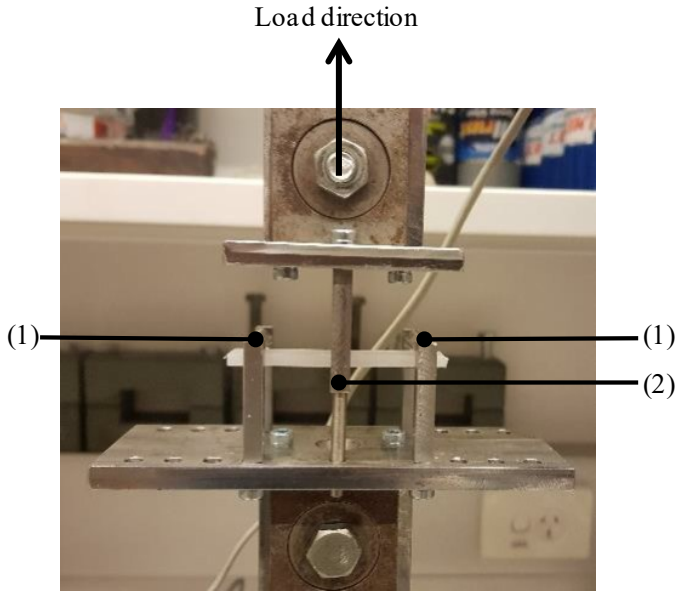
Fig. 6 *Internal view of the creep rig configuration where the environmental chamber is removed for clarity. (1) Support roller. (2) Loading roller which moves along the load direction*

Loads were applied for each test using a combination of disc weights. Three load cases were investigated; 1.4kg, 2.8kg and 4.2kg. The hinge point of the level arm, item 4 in Figure 6, is offset from the midpoint of the arm. This results in a lengthwise 2:1 ratio which needs to be accounted for. Thus, the resulting mass required to achieve the aforementioned load cases is 0.7kg, 1.4kg, and 2.1kg, respectively. To measure the displacement, a linear variable displacement transducer (LVDT) was placed on the lever arm. Data points were recorded via a NI 9205 data acquisition module that interfaced with a computer. The displacement was continuously recorded and reported at the following intervals: 0.6, 1.9, 6, 19, 60, 190, 600, 1900, 6000 minutes. The total duration was 100hr.

All tests were conducted at standard room temperature and humidity.

The data was analysed to determine the maximum fibre stress, σ, and the maximum strain, ε, in the outer-fibre at the mid-span of each sample, in accordance with ASTM D2990[17].

$$\sigma = \frac{3PL}{2bd^2} \qquad (3)$$

$$\varepsilon = \frac{6\delta d}{L^2} \qquad (4)$$

Where:

σ = Maximum stress (MPa)
ε = Maximum strain (mm/mm)
P = Load (N)
δ = Maximum deflection (mm)
L = Span (mm)
b = Sample width (mm)
d = Sample thickness (mm)

The creep compliance, $D(t)$, which is the inverse to the creep modulus, $E(t)$, is calculated as a function of time to quantify the environmental stressor performance on the creep response using:

$$D(t) = \frac{1}{E(t)} = \frac{\varepsilon(t)}{\sigma(t)} \qquad (5)$$

2.4 Experiment 2

The results from Experiment 1 showed that the UV exposure resulted in an increase in creep compliance whereas the other stressors decreased this material property, refer to Section 3.2. UV exposure was thus selected for a 200-hour long creep study where the effects of ageing are accounted for, as described in this section.

The 'snapshot assumption', described earlier, is adhered to in Experiment 2 to eliminate the effects of ageing during the creep tests, thus revealing the UV exposure's effects on creep behaviour alone. In addition, Struik showed that the age of a sample can be reset by exposing it to temperatures above its glass transition temperature for a short duration. Research showed that the creep behaviour of a sample that underwent such conditioning is the same as a newly manufactured sample. In other words, the ageing 'clock' can be reset and with it, adhering to the snapshot assumption, the allowable duration of the creep tests changes.

2.4.1 Experiment 2A: Accelerated UV Weathering

The previously described approach was followed; before the commencement of the accelerated UV weathering, a PETG sample was heated above the glass transition temperature, to $80^0C \pm 2^0C$ within the Testex machine for a duration of 10 minutes, using a temperature-only cycle. The sample was then allowed to cool down to $50^0C \pm 2^0C$ after which the sample was left in the accelerated weathering machine, ready for the UV exposure cycle.

Twelve samples were exposed to UVA radiation at a wavelength of 340nm and an irradiance intensity of $1 W/m^2$. Twelve control samples were mounted in the Testex machine which had both the top and bottom surface masked off with tape. These control samples were thus exposed to the same conditions within the chamber but were shielded from the UV effects.

To investigate the change in creep properties, two exposure durations were applied; 100hr and 200hr. Practically, after a 100hr exposure, 3 exposed and 3 control samples were extracted from the mounting frames and transferred immediately to Experiment 2B. Similarly, 3 exposed and 3 control samples were extracted from the accelerated weathering tester after a 200hr exposure and transferred to Experiment 2B.

2.4.2 Experiment 2B: Flexural Creep Testing

The methodology of creep testing of the UV exposed sample is analogous to the creep testing performed during Experiment 1B with a few exceptions. Firstly, the previously described snapshot assumption was adhered to. The resulting creep test durations for the two exposure times are shown in Table 2.

Sample Age (hr)	Creep Test Duration (hr)
100	10
200	20

Table 2 Sample age and creep duration following from the snapshot assumption

Secondly, the results for Experiment 1B showed that the 4.2kg load case led to premature failure of the samples, refer to Section 3.2. This load case was omitted in this creep test and thus two load cases were assessed: 1.4kg and 2.8kg. Thirdly, the creep tests were performed in the creep rig's temperature-controlled chamber, refer to Figure 6, at $50^0C \pm 2^0C$. This is the same temperature at which the UV exposure took place. Finally, the displacement was recorded at the following intervals from when the load was applied: 0.6, 1.9, 6, 19, 60, 190, 600, 1200 minutes. The total durations of the creep tests are listed in Table 2.

3. Results and Discussion

3.1 Experiment 1A: Results

It has been found that UV exposure is the only stressor that caused observable discoloration of the PETG sample, as shown in Figure 7. This is likely due to photochemical reactions occurring on the exposed surface [1, 22].
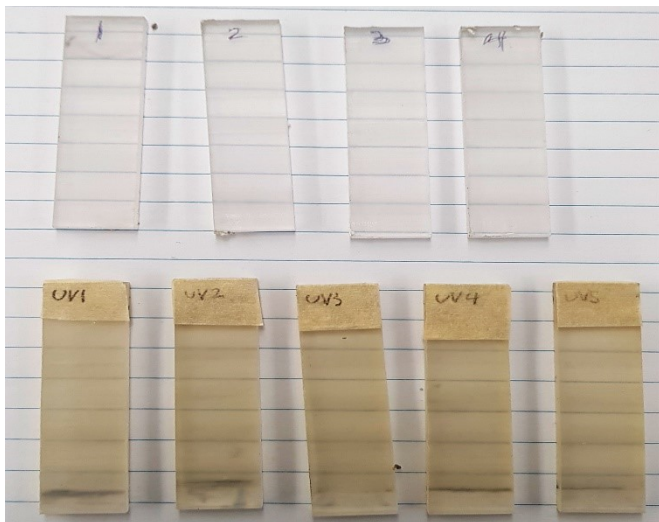

Fig. 7 Comparison of UV exposed specimens (bottom) and the control samples (top)

The samples were exposed to a TUV radiance exposure of 84.83 kJ/m^2. The temperature average of 1 day shall be interpreted as 12hr at elevated temperature in a 24hr period. Since the sample has continuously been exposed for 24hr, this amounts to 2 days of temperature exposure at 55^{0}C which is 110 ATU.

3.2 Experiment 1B: Results

The creep compliance, the inverse of the creep modulus, is the material property used to evaluate the effect of the three stressors on the creep response. This material property eliminates small variations in sample dimensions. The creep compliance per load case for all three stressors are shown in Figure 8, Figure 9 and Figure 10, respectively.
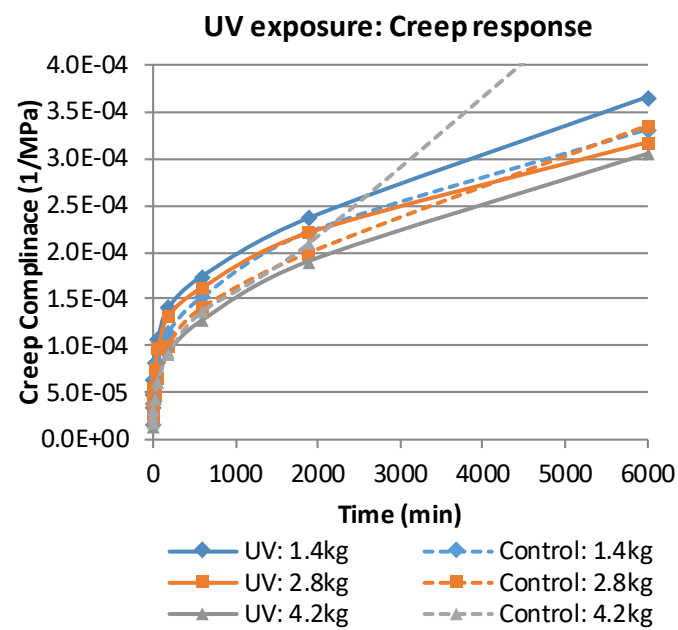

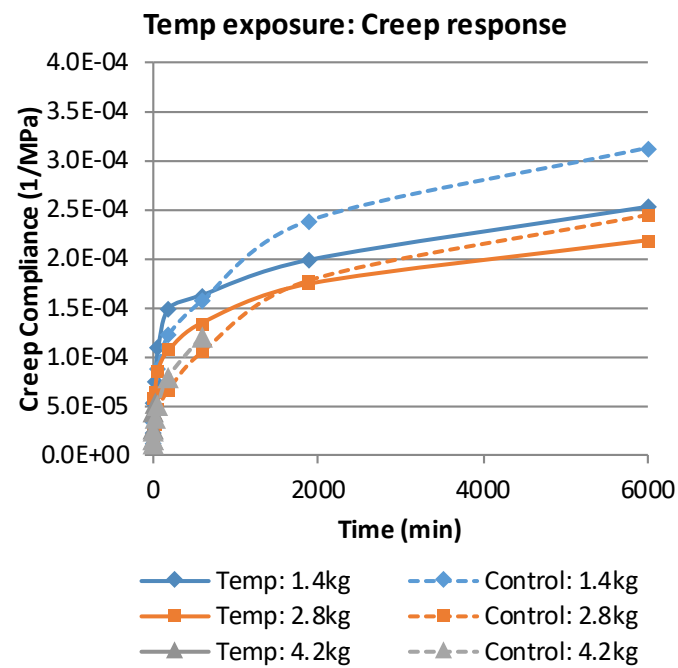*Fig. 8 The creep compliance of the UV stressor experiment*

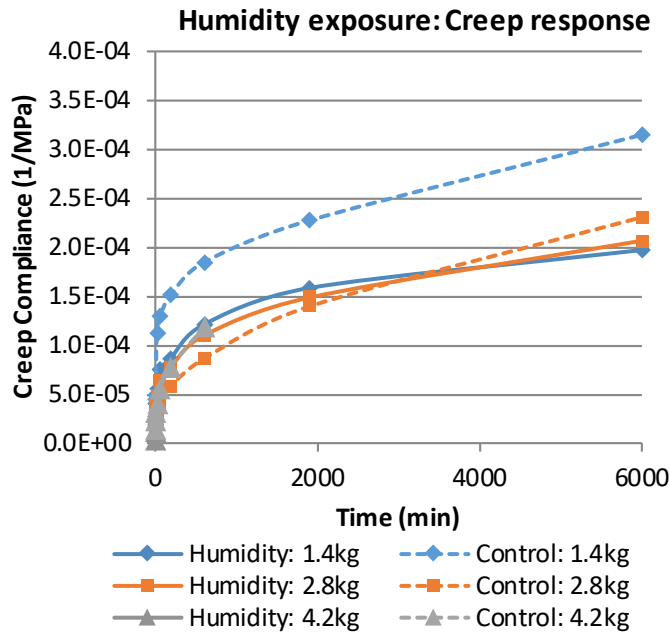*Fig. 9 The creep compliance of the temperature stressor experiment*

Fig. 10 *The creep compliance of the humidity stressor experiment*

A material can be defined as being 'hard' when its Young's modulus $E(t)$, defined as the stress divided by the strain, is high. With the creep compliance being the inverse of the Young's modulus, a hard material thus has a low creep compliance. Likewise, a material can be classified as being 'soft' when it has a low Young' modulus, which translates to a high creep compliance. All graphs show the expected behaviour of the creep compliance over time; a decreasing rate of increase in the creep compliance. In practical terms, this means that while the material becomes harder with time, its hardness increase slows down to a linear trend.

When the exposed samples are compared to the controls, the humidity and temperature exposed samples show a lower creep compliance after 100hr of creep testing, meaning that the exposure has hardened the material. This finding aligns with observed behaviour by other researchers; UV, temperature and humidity result in plasticization and damaging of the chemical structure of material [14].

Regarding the effects of humidity, the absorption of moisture increases the mobility of the polymer's molecular chains [1]. Such an effect results in reduced rigidity, a loss of mechanical properties and thus a higher creep modulus. More specifically for Polyethylene Terephthalate (PET), several research teams concluded that the amorphous regions of the polymer were more susceptible to hydrolysis than the crystalline regions, leaving the latter mostly unaffected [23, 24]. The result of hydrolysis in the amorphous regions is chain scission [1] that leaves shortened molecular chains which then can rearrange in a crystalline form. This process is known as 'chemi-recrystallisation' [25]. Such a process restricts the mobility of the molecular chains which improves the mechanical properties and thus results in a lower creep compliance. Still, other researchers indicated that these hydrolysis effects were only seen in combination with a high temperature, close to T_g, [25, 26] when the ester groups in the material react with water. No hydrolysis occurs for PET at room temperature [25]. Given that the humidity experiments in this study occurred at 50^0C, a combination of effects could be at play; a reduction in chain mobility due to hydrolysis and an increase in chain mobility due to chemi-recrystallisation, with the latter overpowering the former in the experiments outlaid herein.

Regarding the effects of temperature, generally a higher temperature will enhance molecular chain mobility due to an increased free volume [27]. An increase in chain mobility then leads to a more flexible material which expresses itself as an increase in creep compliance. Still, an increase in temperature also introduces random chain scission in the material through the split of ester linkage groups [25]. Again, the shortened molecular chain allows easier creation of crystallised regions, through chemi-crystallisation, which in turn restrict the chain mobility. It is believed that in these series of experiments, these competing effects are visible over time. Fig. 9 shows an initial increase in creep modulus, indicative of a softer material and thus more chain mobility. As time progresses during the creep test, the recrystallisation effect starts to dominate which, in the end, results in the molecular chains being more restricted than the control and a lower creep compliance ensued.

The UV exposed samples show a different behaviour than the humidity and temperature exposed samples, as the 1.4kg test shows a consistently higher creep compliance, and the 2.8kg test only dips below the control equivalent at the last data point. As such, UV exposure was the stressor that has been selected for further investigation in Experiment 2.

Creep failure, due to a complete fracture, occurred during the temperature and humidity creep test at the 4.2 kg load case. Furthermore, the 4.2kg load case caused excessive deformation of the UV control sample. This load case was therefore omitted from Experiment 2.

3.3 Experiment 2A: Results

Similar to Experiment 1A, progressive yellowing of the material was found upon sample extraction after 100hr and 200hr. The TUV radiance exposure the samples are exposed to are listed in Table 3.

UV Test Duration (hr)	TUV radiance exposure (kJ/m²)
100	346.4
200	694.8

Table 3 *TUV radiance exposure at each UV test duration*

3.4 Experiment 2B: Results

Once again, creep compliance was used as a metric to compare the effects of different UV exposure durations on the creep response. Figure 11 shows the creep response for both 100hr and 200hr UV exposure where the test duration has been limited to 1/10th of the sample's age to exclude ageing effect during creep testing.
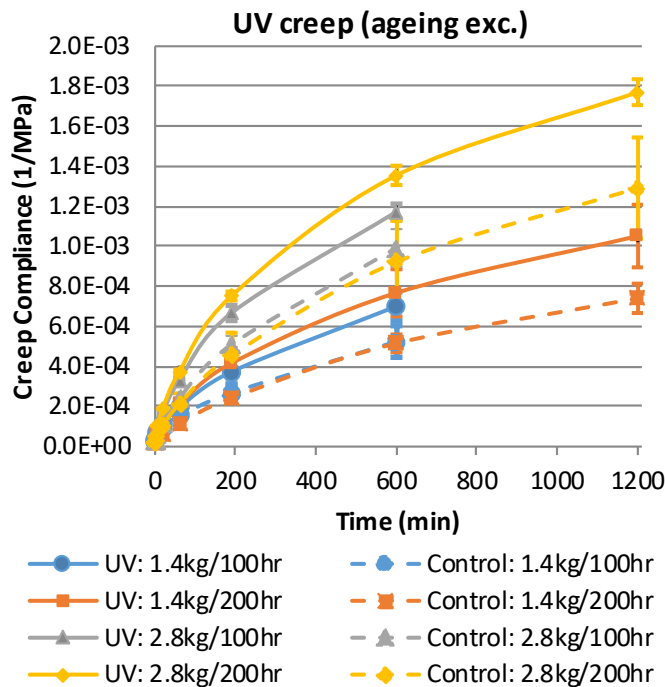

Fig. 11 *The creep compliance of UV exposed samples where ageing is excluded during testing*

Firstly, the difference in creep compliance of the control samples is noticeable. The control's creep responses align at each load case but there is a clear difference between load cases. The creep compliance is thus not independent of the applied stress. This indicates that at least the 2.8kg load at 50^0C produces a creep response outside the linear viscoelastic range where such independence holds. The same effect can be seen for the UV-exposed samples. To exclude the effects of the load on the creep response, the results are separated into results per load case, as shown in Figure 12 and Figure 13.
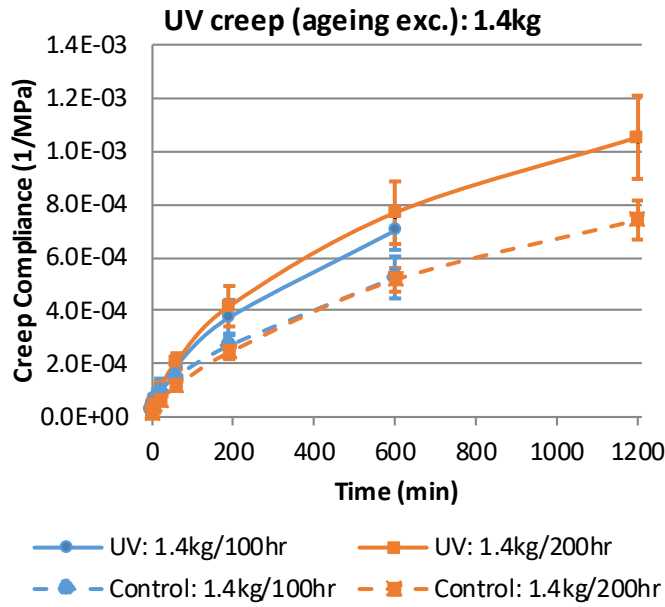
Fig. 12 *The creep compliance of UV exposed samples where ageing is excluded during testing. The applied load is 1.4kg*
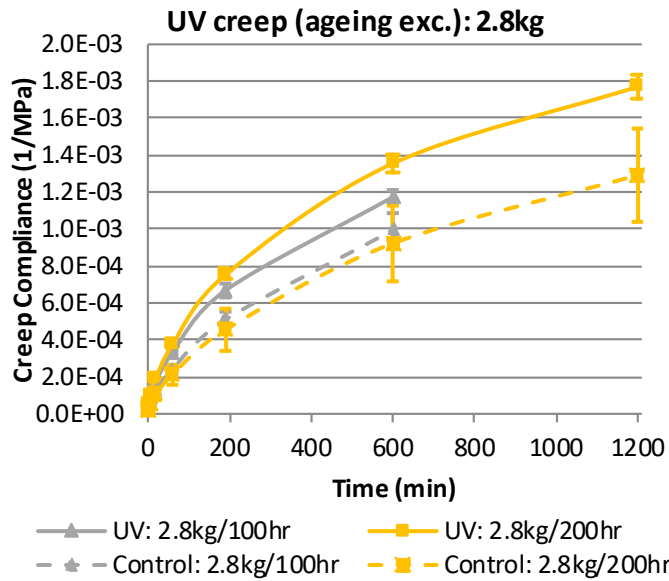

Fig. 13 *The creep compliance of UV exposed samples where ageing is excluded during testing. The applied load is 2.8kg*

The degradation of a semi-crystalline polymer through UV exposure happens by UV energy absorption which, affected by the presence of oxygen, causes chain scission [25, 26]. This effect is limited to a very thin top layer [26]. Since PET can directly absorb UV radiation the possibility exists that both the amorphous and crystalline regions are affected [1, 26]. Due to the decreased chain weight, chain scission thus results an increase in chain mobility. Besides chain scission, UV radiation also promotes crosslinking of molecular chains, which degrades the crystalline regions [1], thereby allowing greater chain mobility. While chain scission occurs more frequently than crosslinking [28], UV exposure introduces two effects that increase the chain mobility and increase the creep compliance. The increase of the overall amorphous region through these two effects were separately found by other research teams for UV exposure of polypropylene (PP). Navarro [28] recorded a higher creep compliance after UV exposure and contributed this to an increase in chain scission. Chevali [1] found that after the UV exposure of the PP, a very small or non-existent increase in crystallinity could prevented chain sliding. These findings support the outcomes from Experiment 1B; the UV exposure has elevated the creep compliance of the PETG samples compared to the unexposed control samples, even without the effects of ageing during testing. Such an increase in creep compliance indicates that the UV exposure has weakened the material in both load cases.

4. Conclusions

The effect of accelerated weathering stressors on the creep response of PETG was studied in this paper. The first set of experiments assessed the effects on the material's creep behaviour of three environmental stressors: UV radiation, temperature and humidity. The creep behaviour was investigated for three load cases. All environmental stressors affected the creep behaviour,

expressed as the creep compliance, compared to the control samples. Noticeably, an increasing creep compliance was only measured for the UV exposure whereas the other stressors showed a decrease in creep compliance.

The effects of UV exposure have been studied in more detail in a second set of experiments where care was taken to avoid the material altering effects of ageing during creep testing. The same effect was witnessed; UV exposure up to 200hr produces a higher creep compliance in pellet-printed PETG samples at 50^0C for two load cases, compared to control samples. Due to the experimental setup of the second experiment, it can be concluded that this effect is not caused by the effects of ageing and stems from the effects of UV radiation alone.

As an extension to the presented results, it would be desirable in future to investigate increased UV exposure times and perform subsequent creep testing. Measurements of the creep compliance after 300hr, 400hr or longer would determine if the increase in creep compliance due to UV exposure keeps growing, plateaus, or shrinks. Naturally, the effects of ageing should be excluded during such testing. Additionally, since the use of a continuous stream of heated pellets in the additive manufacturing process, instead of the more commonly used filament, enables the system to include shredded waste PETG with relative ease. The addition of various percentages of recycled PETG, and the material performance thereof versus that of the virgin material, will be a focus of future research.

5. Declarations

5.1 Funding

5.2 Conflicts of interest/Competing interests

The authors declare that they have no conflict of interest or competing interests

5.3 Availability of data and material

The data that support the findings of this study are available from Mineral Technologies but restrictions apply to the availability of this data, which were used under license for the current study, and so are not publicly available. Data are however available from the authors upon reasonable request and with permission of Mineral Technologies.

5.4 Code availability

Not applicable

5.5 Authors' contributions

Conceptualization: Thomas Romeijn; Methodology: Thomas Romeijn; Investigation: Karanvir Singh; Validation: Thomas Romeijn, Karanvir Singh; Formal analysis: Thomas Romeijn; Data Curation: Thomas Romeijn, Karanvir Singh; Writing - original draft preparation: Thomas Romeijn, Karanvir Singh; Writing - review and editing: Gavin Paul, Michael Behrens; Supervision: Gavin Paul, Michael Behrens; Project Administration: Gavin Paul, Michael Behrens.

6. Acknowledgements

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