Chapter

Effect of Environmental Aging on Tensile Properties of Post-Consumer Recycled (PCR) Polycarbonates

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Abstract

In this chapter, tensile properties of different grades of post-consumer recycled (PCR) polycarbonate (PC) plastics have been compared with conventional or virgin PC before and after different aging conditions. 50 and 75% recycled PCs showed comparable yield strength (~57 MPa), maximum tensile strength (~70 MPa) and maximum strain (~190–200%) before aging, when compared to virgin PC of same melt flow rate (MFR of ~10 g/10 min). From the fractography analysis (optical and scanning electron microscopy) of the both virgin and 50% recycled PC, it is evident that the fracture morphologies are very similar and they are indicative of ductile failure. It is observed that with the presence of temperature and humidity (60°C 90% RH) aging, tensile strength starts to drop over time but most importantly both 50% and 75% PCR grades showed similar aging behavior compared to virgin PC (10–13% strength degradation after 500 hours of aging). Reliability modelling showed comparable B10, Weibull Alpha and Weibull Beta values between Virgin PC and PCR grades after different aging conditions. Fractography analysis of fresh and aged 75% PCR also showed ductile features.

Keywords: Post Consumer Recycled, Tensile Strength, Melt Flow Rate, Elongation at Break, Weibull Analysis

1. Introduction

Plastics are a versatile class of materials which can be found in products ranging from single-use packaging to components used in automotive and durable goods. Unfortunately, plastics are also identified as an environmental pollutant due to poor recycling rates and poor end-of-life waste management [1, 2]. This has led to many organizations, such as the Ellen MacArthur Foundation, to promote a circular economy for plastic [3].

The circular economy for plastic is based on three tenets: reducing the use of plastics, reusing a product multiple times and recycling at end of life. The first two components are directed more toward plastic packaging but recycling at end of life can be applied to all types of products and industries. Post-consumer recycled (PCR) resin is the recycled product of waste created by consumers and is defined by

ISO 14021 [4]. It is commercially available from multiple suppliers, but not all grades are created equal. However, there needs to be a demand for recycled plastics for the circular economy to work properly. Regrettably, there is a misperception that recycled plastics are always inferior to virgin plastics and therefore can only be used in "down-cycled" applications. As engineers and scientists interested in both the production of high-quality products and environmental sustainability, we questioned the validity of this misperception and initiated this study to answer the following questions:

- Can recycled plastics be used in consumer hardware?
- Does the use of recycled plastics have any influence on the reliability of the product?
- Are there any manufacturing constraints associated with the use of recycled plastics?

Although there are many factors associated with completely answering the questions above, the factor which we will be evaluating in this paper is strength. Strength of plastics can be quantified by measuring tensile, bending, shear, compression, flexural, and impact properties, among others. Each molded plastic resin's mechanical properties can vary depending on molecular weight, crystallinity, molding parameters, and additives/fillers. The mechanical properties can be defined by testing specimens in compliance with ASTM [5, 6] or ISO [7] testing standards. The advantages of mechanical property testing following ASTM or ISO testing standards are

A. Standard specimens can be obtained from material supplier

B. Useful for comparison of different grades/suppliers

C. Studying the effect of environmental conditions.

Since a plastic's strength degrades over time as it ages in the environment, it is crucial to take this degradation into account when designing parts. Therefore, the aging behavior of plastics needs to be understood thoroughly. As real-time aging can take a significant time (i.e., years), most aging studies are performed using accelerated aging tests utilizing temperature, temperature and humidity, temperature cycling, UV exposure, and/or chemical exposure [8]. The Arrhenius-based accelerated life model is the most popular model to understand the acceleration of aging due to temperature. The rate of reaction, *R,* based on the Arrhenius model can be explained by

$$R(T) = Ae^{-\frac{E_a}{K.T}} \tag{1}$$

where A is a material constant; E_a is the activation energy (eV), K is the Boltzmann's constant (eV/K), and T (K) is the absolute temperature. Based on this model, the acceleration factor (AF) can be calculated as

$$AF = exp\left[\frac{E_a}{K}\left(\frac{1}{T_u} - \frac{1}{T_t}\right)\right] \tag{2}$$

where,

T_u is unit localized temperature during field usage (K).

T_t is unit localized temperature in the test (K).

E_a is activation energy.

K is Boltzmann's constant (8.617385 x10–5 eV/K).

The acceleration factor for temperature and humidity-based acceleration is derived from Peck's Model:

$$AF = \left(\frac{RH_u}{RH_t}\right)^{-n} exp\left[\frac{Ea}{k}\left(\frac{1}{T_u} - \frac{1}{T_t}\right)\right] \quad (3)$$

where,

RH_u is relative humidity in field (%).

RH_t is relative humidity in the test (%).

n is a constant.

Finally, the acceleration factor for aging due to thermal cycling comes from the modified Coffin-Manson model:

$$AF = \left(\frac{\Delta T_{test}}{\Delta T_{field}}\right)^m \quad (4)$$

where,

ΔT_{test} = temperature difference in TC test (°C);

ΔT_{field} = temperature difference in field usage (°C);

m = Coffin-Manson exponent.

Any acceleration-based model depends on the distribution of the data that best fits. The life of a consumer product follows a bathtub curve under variable stress and can be explained better by the Weibull distribution, for which the probability density function can be explained as

$$f(t) = \frac{\beta}{\alpha}\left(\frac{t-\gamma}{\alpha}\right)^{\beta-1} e^{-\left(\frac{t-\gamma}{\alpha}\right)^{\beta}} \quad (5)$$

where β is the shape parameter or slope of the curve, α is the characteristic or Weibull life, and α is the location parameter. This is true for 3 parameter Weibull distribution. Typically, γ is considered to be zero and hence the equation can be derived as

$$f(t) = \frac{\beta}{\alpha}\left(\frac{t}{\alpha}\right)^{\beta-1} e^{-\left(\frac{t}{\alpha}\right)^{\beta}} \quad (6)$$

In this chapter, the scope of the research is to focus on the performance variation of different grades of PCR compared to conventional or virgin PC after thermal cycling and high temperature & high humidity aging. The reason behind picking thermal cycling and high temperature & high humidity aging is because these two are the most common environmental exposures for consumer hardware. The effects of chemical, UV and solar aging will be reported at a later date.

2. Experimental procedures

2.1 Samples

The materials studied were commercially available formulations obtained from one resin vendor. All formulations were identical except for PCR content as specified in **Table 1**. The samples were provided by the resin vendor in the form of ASTM D638 Type V Tensile Bars.

After clearly marking the samples and dimensional measurement (width and thickness), they were divided into 7 different groups (**Table 2**) with each group having ~5 ASTM tensile bars of virgin PC, 50% and 75%.

2.2 Tensile measurement

The first group of ASTM tensile bars with no preconditioning were tested in a universal tensile testing machine with a tensile pull rate of 2 mm/min. 5 samples of virgin PC, 50% PCR and 75% PCR, all with white resin and melt flow rate (MFR) of 10 g/10 mins. Next 50% PCR tensile bars (black) with MFR of 10 and 15 were tested. **Figure 1** shows a schematic of a tensile bar and a set-up image of the tensile test. From the load–displacement curves, yield or necking point, the EAB (elongation at break) and UTS (ultimate tensile strength) were recorded.

2.3 Aging conditions

For studying the effect of aging, two different batches were prepared. One batch of ASTM tensile bars were kept inside an environmental chamber with temperature cycling from −20–60°C. Transfer time of 7 minutes and soak time of 23 minutes were set so that the length of 1 cycle is equal to an hour. At each interval (100, 200 and 300 cycles), 5 tensile bars were taken out of the chamber and tensile-tested in a universal tensile testing machine. Profile for thermal cycling is shown in **Figure 2(a)**. Similarly, the second batch of samples were placed in an environmental chamber for high temperature and high humidity exposure. The profile was set so that peak temperature and humidity reached 60 ± 2°C and 90 ± 3%RH, with ramp up and ramp down time of 2 hours according to the high temperature and humidity profile shown in **Figure 2(b)**. As in the thermal cycling test, at each interval (168, 336 and 500 cycles), 5 tensile bars were taken out of the high temperature and high humidity chamber, dimensions measured (width and thickness) and tensile tested. After

Samples	MFR (g/10 min)	Color
Virgin PC	10	White
50% PCR	10	White
75% PCR	10	White
75% PCR	10	Black

Table 1.
List of samples.

Group #	Aging condition	Check point
1	No Aging	N/A
2	−20–60°C	100 Cycles
3	−20–60°C	200 Cycles
4	−20–60°C	300 Cycles
5	60°C 90%RH	168 Hours
6	60°C 90%RH	336 Hours
7	60°C 90%RH	500 Hours

Table 2.
Different aging condition.

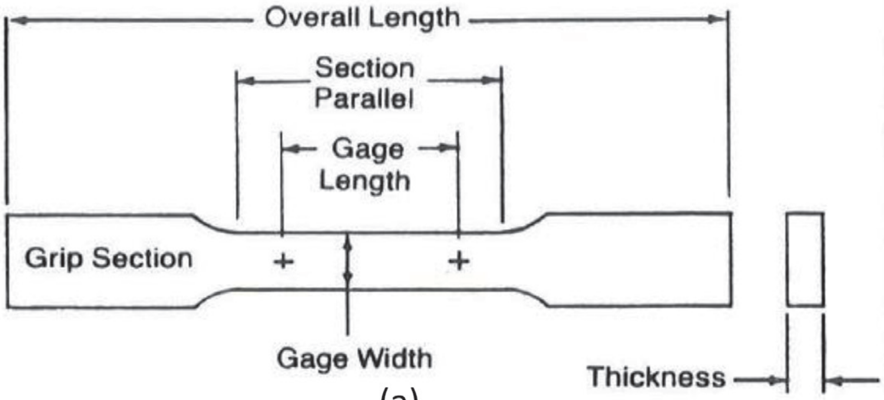

Figure 1.
(a) Schematic of an ASTM tensile bar (type V)[6] and (b) experimental set-up.

tensile testing for all the samples were completed, the fracture surfaces were inspected in optical microscopy and with a scanning electron microscope.

3. Results and discussions

3.1 Dimensional stability after aging

First, the dimensions in widths and thicknesses of each tensile bar were compared before and after aging. **Figure 3(a)** and **(b)** shows the % change in width and thickness after each interval (168, 336 and 500 Hours) of high temperature and high

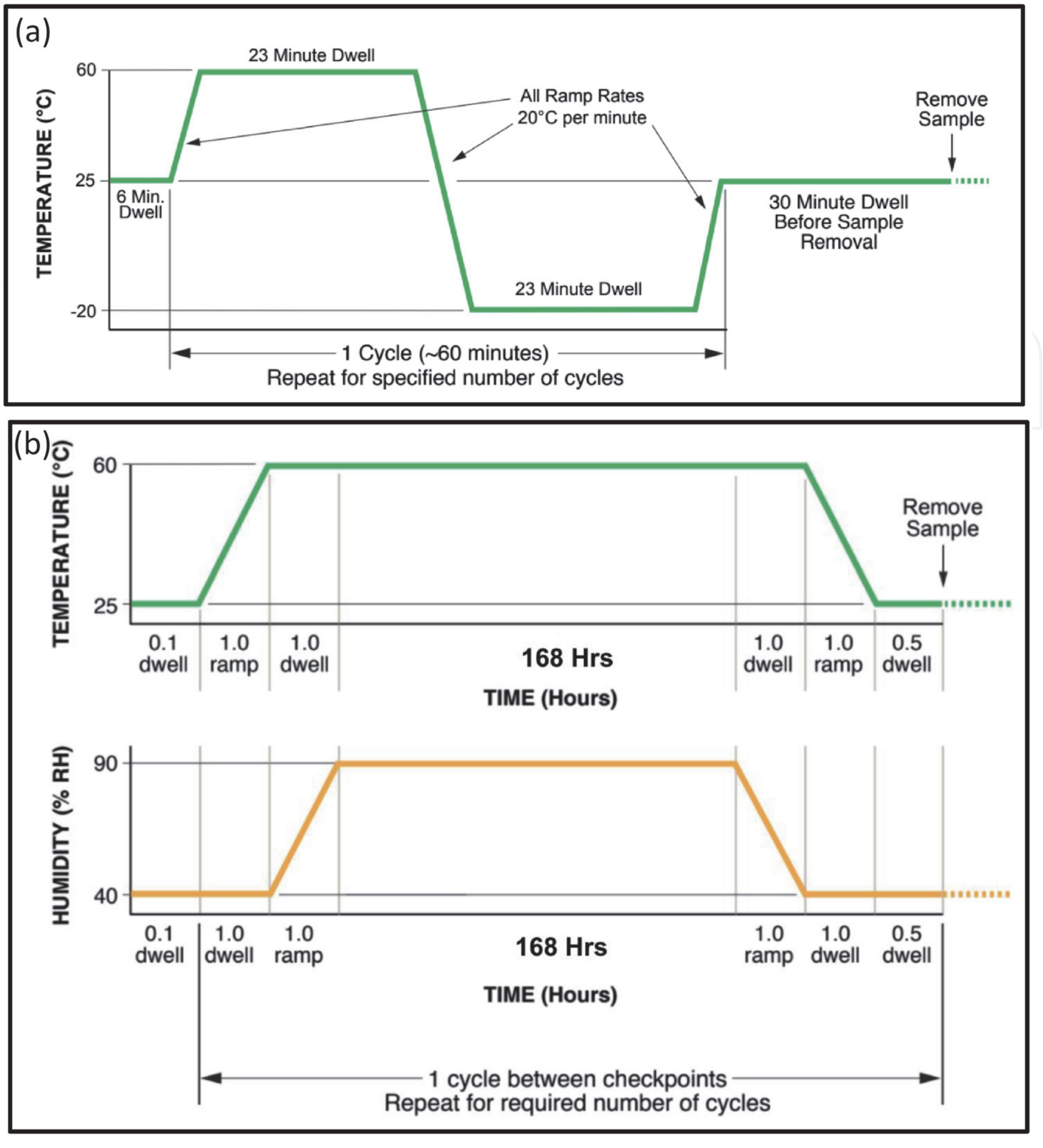

Figure 2.
Profile for (a) thermal cycling test and (b) high temperature high humidity test.

humidity aging. From the figures, it is visible that the dimensions were very stable after aging. Expansion in width and thickness for all the tensile bars were within 0.25%, which were within the measurement error.

3.2 Strength characteristics in unaged condition

Second, we will compare the tensile properties of PCR with virgin or conventional PC at time zero and without any aging. Here breaking strengths of 50 and 75% PCR grades were compared with conventional PC. **Figure 4** shows the load-extension curve of three grades of PC and PCR-PC.

From **Figure 5(a)**, both the PCR grades have comparable tensile strength (at breakage) when compared with a virgin PC of the same MFR. The strength is around 67, 65 and 71 MPa for Virgin PC, 50% PCR and 75% PCR respectively. For comparison, it was made sure the resin color is white for all the grades of PC and PCR. In **Figure 5(b)**, tensile strain at breakage for Virgin PC, 50% PCR and 75%

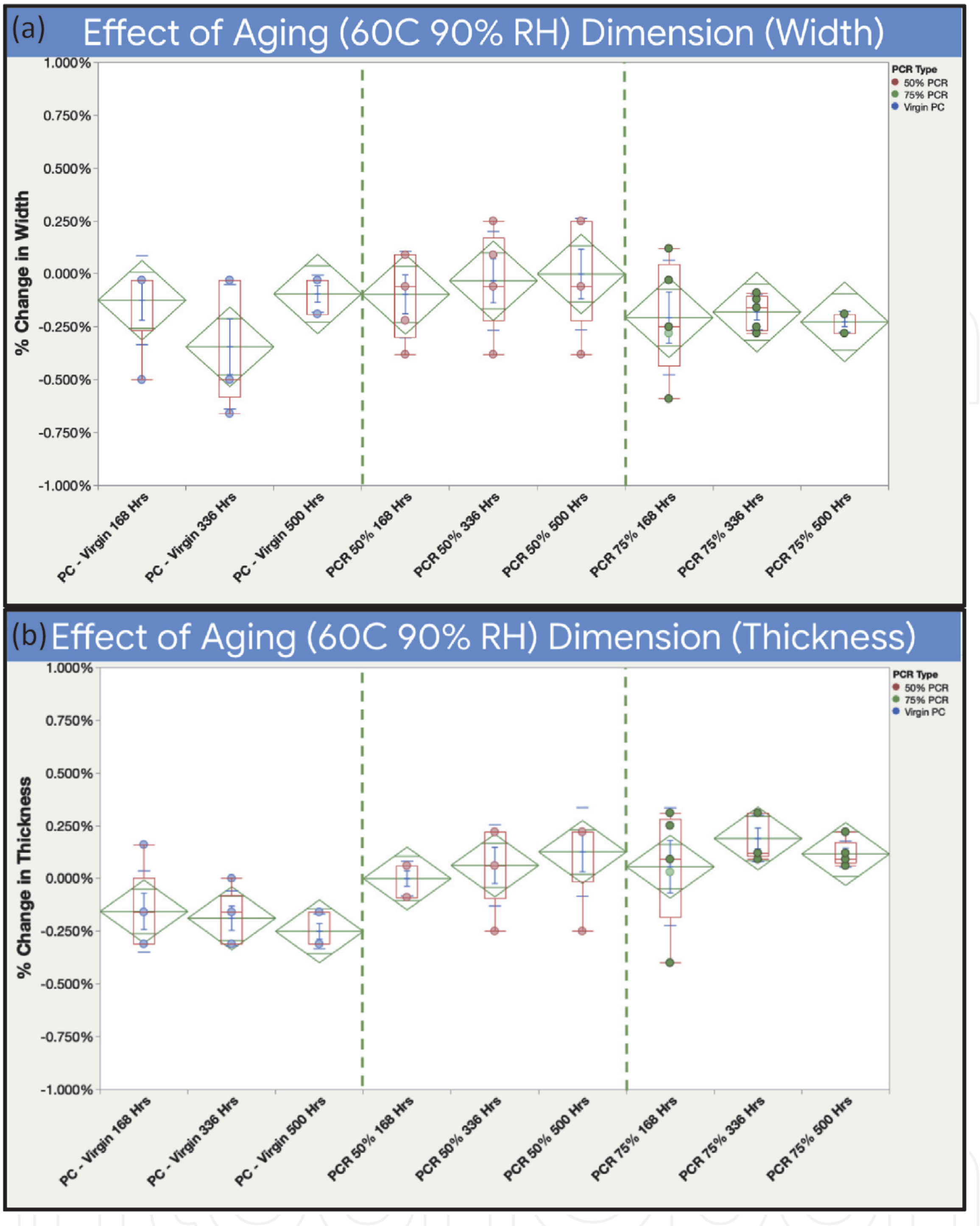

Figure 3.
% change in dimension after aging: (a) width and (b) thickness.

PCR have been compared. The strain follows a very similar pattern as the strength in **Figure 4(a)**. Strain value of 210%, 200% and 213% were recorded respectively for Virgin PC, 50% PCR and 75% PCR. The strain at breakage confirms the ductile behavior for all these three grades of polycarbonates.

3.3 Strength characteristics after aging

Secondly, we studied strength degradation with aging. First, all the three grades were compared at 100, 200 and 300 cycles of the -20° to 60° C thermal cycling. Based on the data recorded in **Figure 6(a)**, temperature cycling does not have a strong effect as the strength did not degrade appreciably for any of the grades.

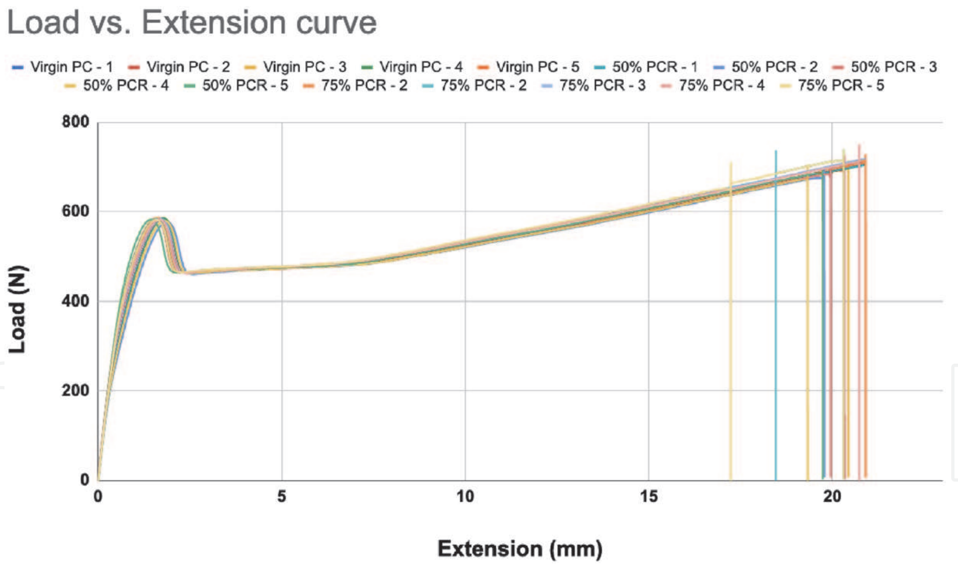

Figure 4.
Load - extension for virgin PC, 50% PCR and 75% PCR before aging.

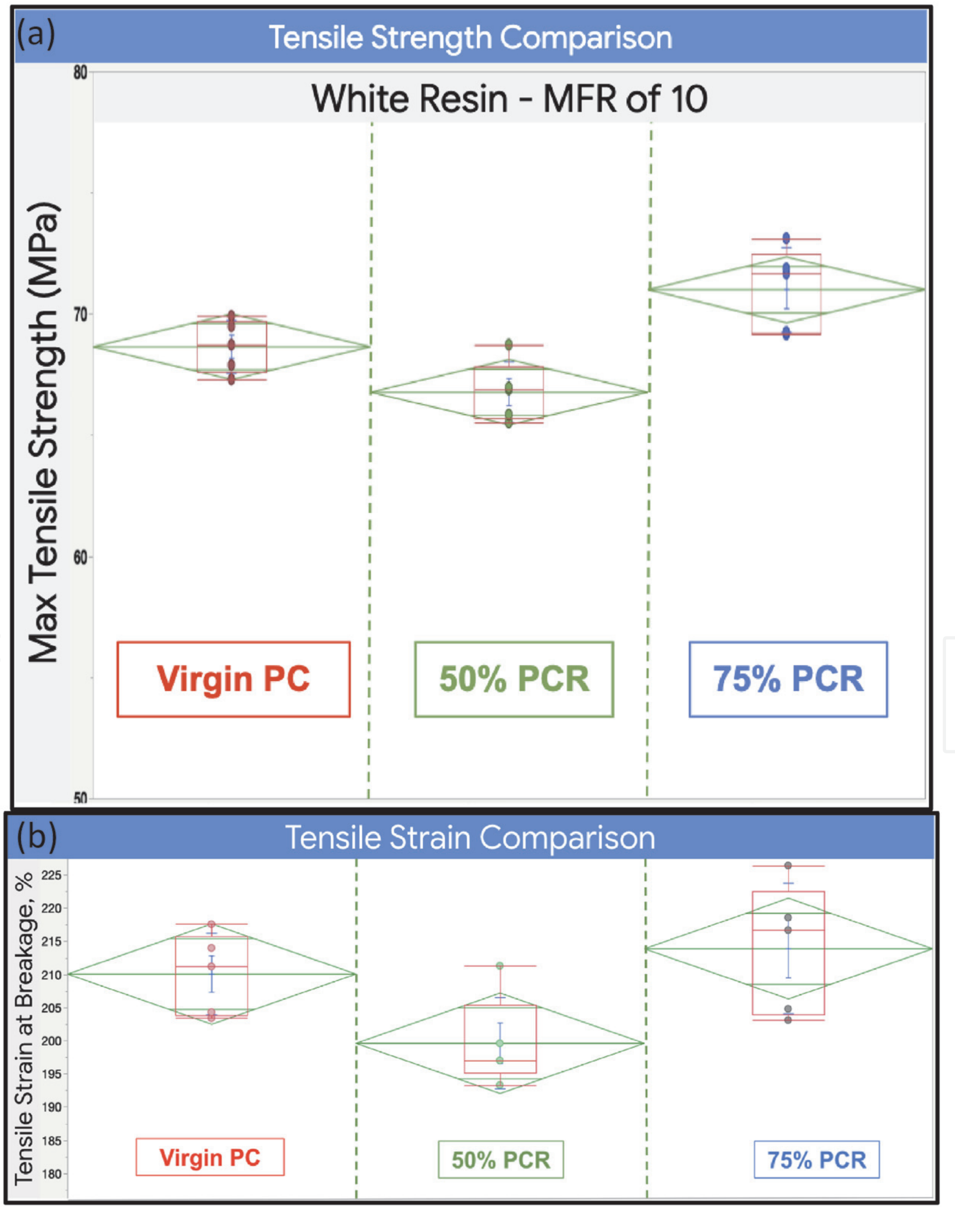

Figure 5.
Comparison between virgin PC and two grades of PCR for (a) tensile strength, (b) tensile strain at breakage.

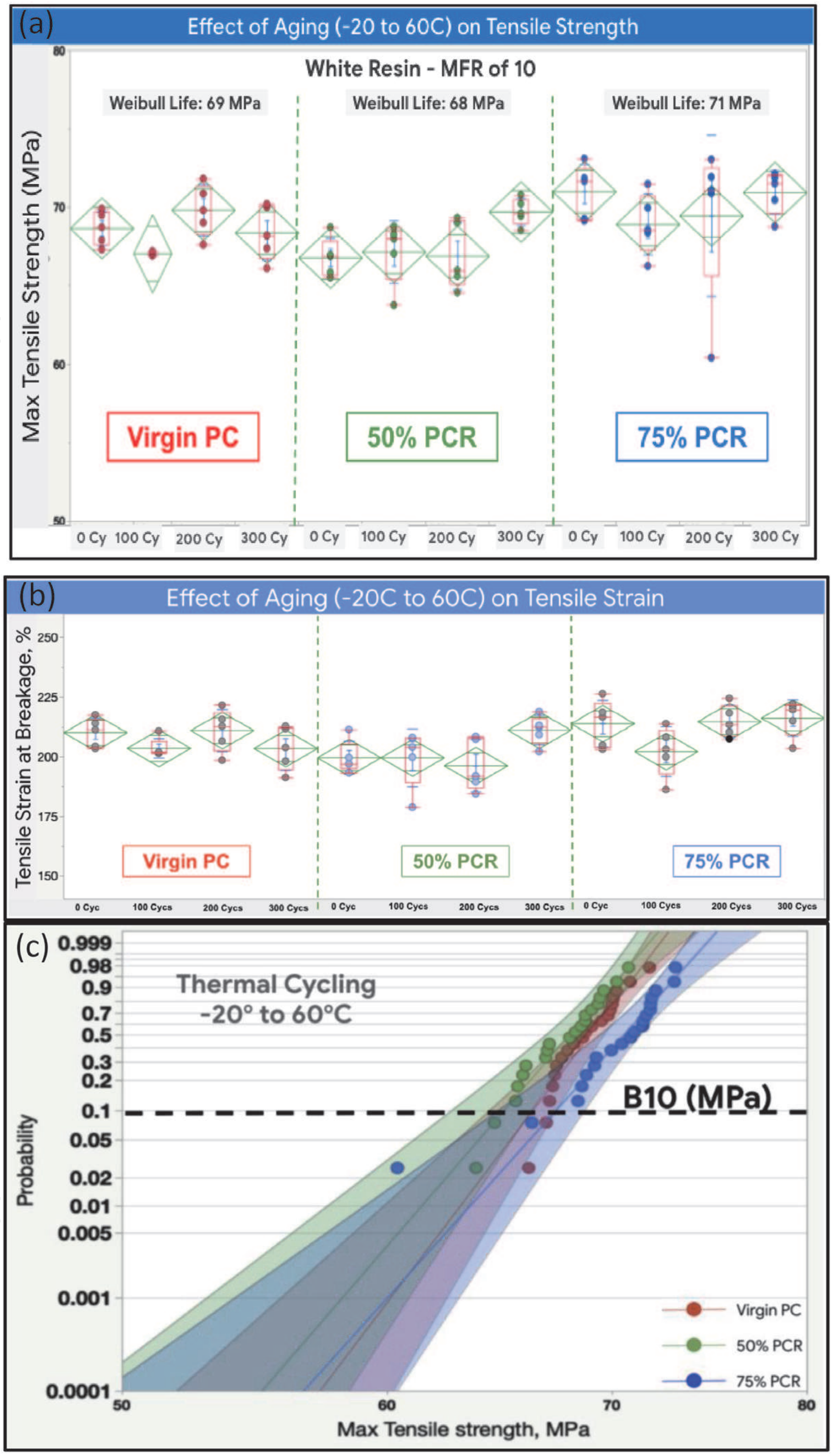

Figure 6.
Effect of thermal cycling on (a) tensile strength, (a) tensile strain and (c) life distribution of virgin PC, 50% PCR and 75% PCR.

Similar results were observed in strain at breakage 6(b). None of the grades show any significant reduction in strain and no pattern was observed for all three grades - which indicates that the tensile bars retained the ductile behavior. The reliability performance was evaluated by B10 (where 10% of the population fails), β (slope of the curve), and *α* (characteristic life). **Figure 6(c)** and **Table 3** shows that the B10

Sample type	Thermal cycling		
	B10	**Weibull α**	**Weibull β**
Virgin PC	66 MPa	69.5	47.7
50% PCR	65 MPa	68.5	42
75% PCR	67 MPa	71.2	40.2

Table 3.
Reliability data after thermal cycling.

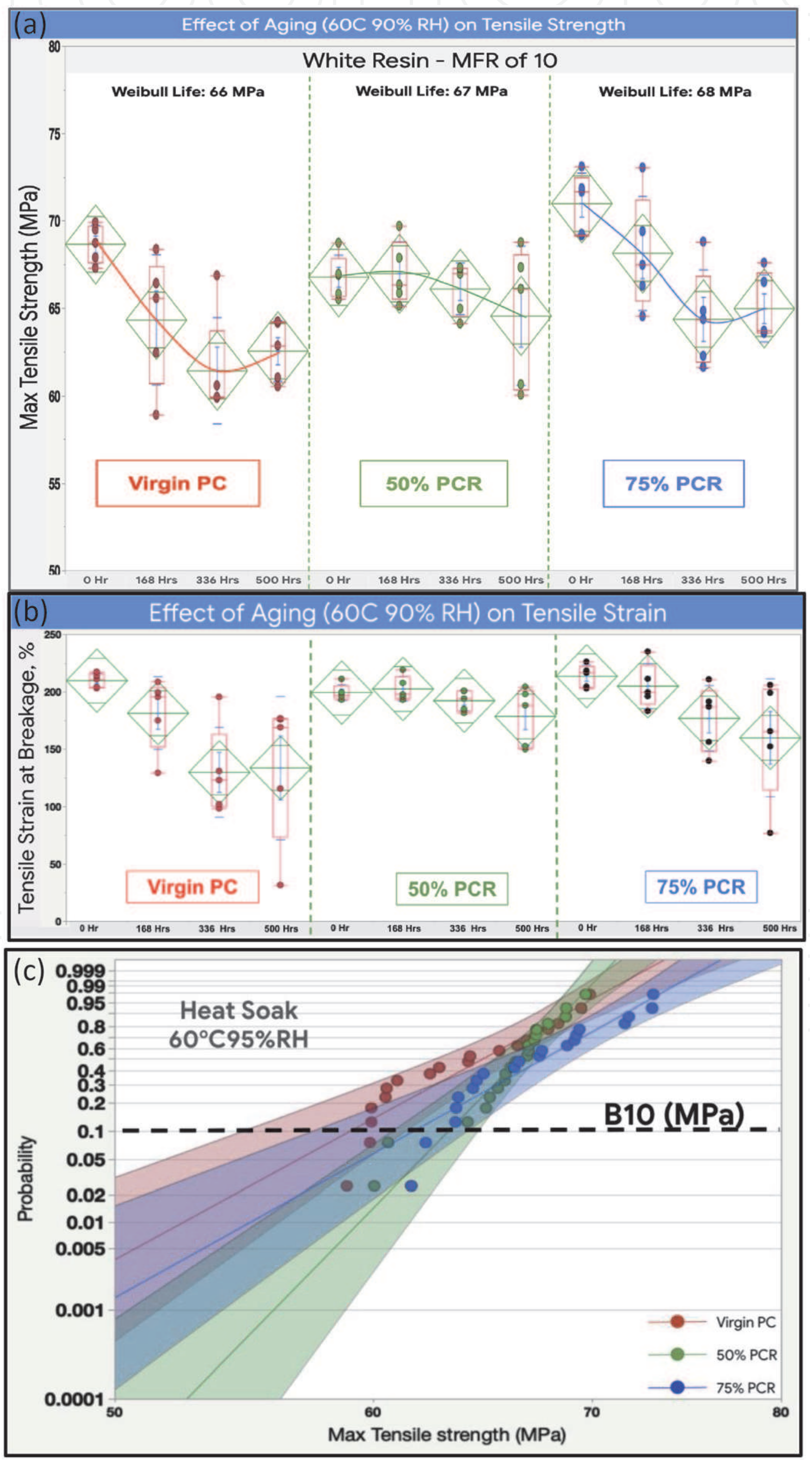

Figure 7.
Effect of heat soak on (a) tensile strength, (a) tensile strain and (c) life distribution of virgin PC, 50% PCR and 75% PCR.

Sample Type	High Temperature and High Humidity		
	B10	Weibull α	Weibull β
Virgin PC	60 MPa	67	20
50% PCR	63 MPa	67.1	28
75% PCR	61 MPa	68.8	20

Table 4.
Reliability data after high temperature and high humidity.

life, Weibull α and Weibull β are very similar for Virgin PC, 50% and 75% PCR respectively [9, 10].

But when the humidity is added to the temperature absolute humidity (gm/m^3) increases from 25.63 gm/m^3 (for 60° C - 20% RH) to 115 gm/m^3 (for 60° C - 90% RH) then the aging effect is more pronounced. The effect in aging is clearly visible in **Figure 7(a)** and **(b)** by the decrease in tensile strength and tensile strain at breakage for all the three grades of PC and PCR. But most importantly, both virgin PC and two grades of PCRs were found to have similar aging behaviors. Literature shows that the molecular weight reduces due to the hydrolysis of carbonate groups [11–15], which leads to the decrease of the tensile strength [16–18]. Prolonged exposure to high heat and humidity eventually induces a ductile to brittle transition [19]. The reduction in tensile strength and ductility are consistent with environmental degradation. Other mechanisms discussed in literature include a decrease in molecular weight due to hydrolysis and formation of small, disk-shaped microcavities or microcracks [11, 14, 15] that cause reduced strength and elongation. In this manuscript, the dominant mechanism has not been verified. In the fractography section, the fracture surface of the unaged and aged samples was analyzed to see whether this hypothesis is in line with the observed features for both conventional PC and PCR grades.

When we take these data into account and model the reliability of destructive degradation (**Figure 7(c)**), we found a comparable B10 (where 10% unit fails) value between virgin PC and two grades of PCR PC after thermal cycling aging. In temperature- and humidity-exposure, the B10 value is understandably lower than the temperature cycle aging but more importantly, virgin PC and PCR show comparable B10 and Weibull alpha values (**Table 4**).

4. Fractography

The purpose of the fractography was to evaluate whether the fracture surfaces added any additional information to the mechanical properties already measured. Four sample pairs were chosen to judge key comparisons:

- Effect of PCR (on unaged, white samples): Conventional PC vs. 50% PCR (white, unaged, MFR = 10 g/10 min)
- Effect of aging (on white samples): Unaged vs. aged (white, MFR = 10 g/10 min)
- Effect of aging (on black, 75% PCR samples): Unaged vs. aged (black, 75%PCR, MFR = 10 g/10 min)

The effect of PCR was gauged by comparing two unaged, white samples with the same MFR. One sample was a conventional PC, while the other was 50% PCR.

From **Figure 8**, both samples have ductile features such as hackle lines, chevron marking (V shaped features) [20] visible across their fracture surfaces. This is consistent with the fact that there were no mechanical property or molecular weight differences between these two samples. The elongation at break and tensile strength between unaged conventional PC and 50% PCR were comparable. Extensions at max load were 20.19 and 19.25 mm and max tensile strength were 67.3 and 65.52 MPa for those specific unaged conventional PC and 50% PCR samples.

The effect of aging on white PCs was determined by comparing two white conventional PC samples with the same MFR. One sample was unaged, while the other was aged for 500 hours at 60°C 90% RH.

From **Figure 9**, the differences in the fractography are more obvious. While the unaged sample has large regions of ductility, the aged sample shows a smoother surface, which indicates a more brittle material. As well, there is an obvious smooth initiation site in the middle of the right half of the surface, which indicates a slower crack growth. This sample still has chevrons and ductile features. The sample on the right (tensile strength: 63.32 MPa) had degraded mechanical properties as

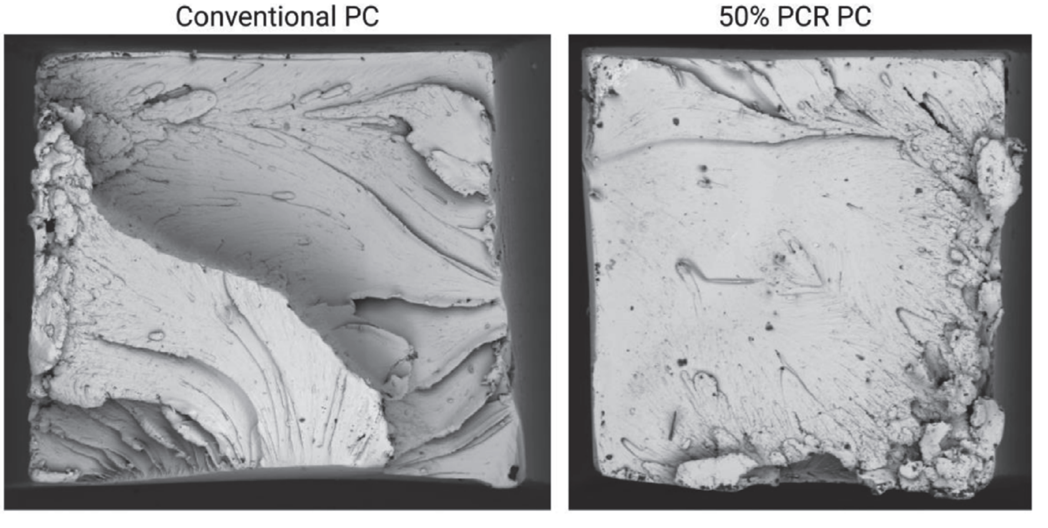

Figure 8.
A comparison of conventional and 50% PCR PC fracture surfaces.

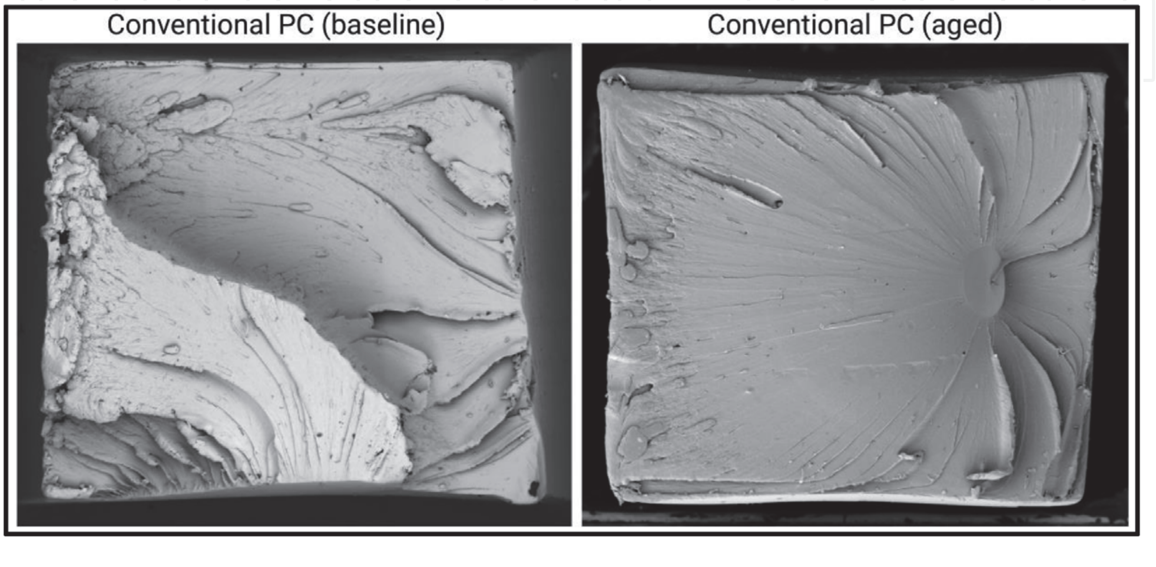

Figure 9.
A comparison of unaged and aged white conventional PC fracture surfaces.

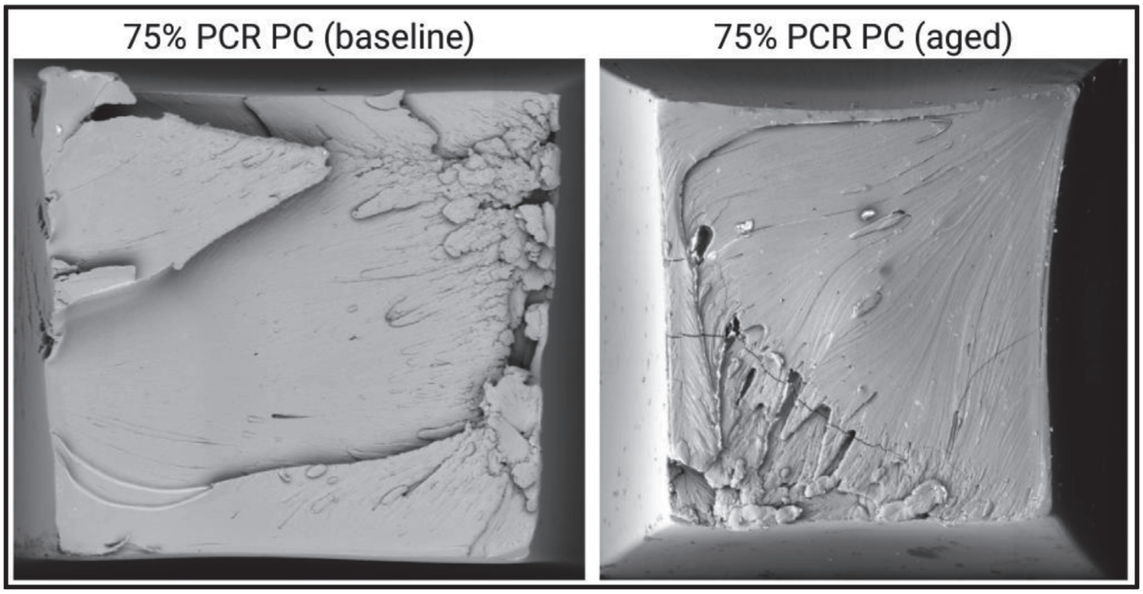

Figure 10.
A comparison of unaged and aged black 75% PCR PC fracture surfaces.

compared to the unaged sample (69.72 MPa), and this is consistent with the differences in the surface morphology.

Finally, the effect of aging on black PCR samples was evaluated. One sample was unaged, and the other was aged for 500 hours at 60°C 90% RH.

Similarly, to the comparison between aged and unaged white samples, the black 75% PCR samples have differences between the aged and unaged samples (**Figure 10**) that agree with the differences in mechanical properties between these two sample groups. The unaged sample has large ductile features, whereas the aged sample has more drawing.

5. Conclusions

In this paper, a comparison between conventional PC and two grades of PCR (50 and 75%) were conducted in terms of the effects of various aging strategies on mechanical strength and fractography. Unaged samples for all three grades with MFR of 10 g/10 min showed comparable strength (67–70 MPa) and the fracture surfaces of conventional and 50% PCR grades indicate ductile failures. As the MFR was increased from 10 to 15 g/10 min, strength is reduced, which is expected in any polymer resin. After thermal cycling at -20° to 60° C, no degradation was observed, whereas after high temperature and high humidity aging (60°C 90%RH) - strength reduction was observed and the degradation was consistent for all the three grades. This can be attributed to the degradation due to environmental aging. In fractography comparison between unaged and aged samples for both conventional PC (white resin) and 75% PCR (black resin), it was also observed that ductile features were less in aged samples. Overall, no significant differences were found between virgin PC and post-consumer recycled PC which indicates that recycled PC can be used in consumer hardware if molding conditions are controlled.

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References

[1] https://www.statista.com/statistics/959995/flow-plastic-materials-worldwide/

[2] The OECD for the G7 Environment, Energy and Oceans Ministers, "Improving Plastics Management: Trends, policy responses, and the role of international cooperation and trade, September 2018. (https://www.oecd.org/environment/waste/policy-highlights-improving-plastics-management.pdf)

[3] https://www.ellenmacarthurfoundation.org/explore/plastics-and-the-circular-economy

[4] International Standard ISO 14021 - 2016, "Environmental labels and declarations — Self-declared environmental claims (Type II environmental labelling)"

[5] ASTM standard - D638-14, Standard Test Method for Tensile Properties of Plastics.

[6] ASTM D638: THE DEFINITIVE GUIDE TO PLASTIC TENSILE TESTING - How to Perform a Tensile Strength Test on Plastics According to ASTM D638. https://www.instron.us/en-us/testing-solutions/by-standard/astm/multiple-testing-solutions/astm-d638

[7] ISO 527-2: Tensile Testing for Plastics: The Definitive Guide to Performing ISO 527-2 Tensile Testing on Plastics

[8] Ho-Huu C, "Influence of physical aging on the thermal and mechanical behaviors of glassy polycarbonate, Thesis of Doctorate of Applied Science, University of Sherbrooke (Quebec), Canada , 2003.

[9] Kahlen S, Wallner GM, and Lang RW, Solar Energy. 2010; 84 (5): 755-762.

[10] Senden DJA, Engels TAP, So¨ntjens SHM, Govaert LE, Journal of Materials Science. 2012; 47:6043–6046.

[11] Robeson LM, Crisafulli ST, Journal of Applied Polymer Science. 1983; 28: 2925.

[12] Gardner RJ, Martin JR, Journal of Applied Polymer Science. 1979; 24:1269.

[13] Ghorbel I, Thominette F, Spiteri P, Verdu J, Journal of Applied Polymer Science. 1995; 55:163.

[14] Joseph EA, Paul DR, Barlow JW, Journal of Applied Polymer Science. 1982; 27:4807.

[15] Golovoy A, Zinbo M, Polymer Engineering and Science. 1989;29:1733

[16] Flory PJ, Journal of American Chemical Society. 1945;67:2048.

[17] Gent AN, Thomas AG, Journal of Polymer Science: A2 Polymer Physics. 1972;10:571.

[18] Bersted BH, Anderson TG, Journal of Applied Polymer Science. 1990; 39: 499.

[19] Vincent PI, Polymer, 1960;1:425

[20] Jansen JA, Technimet S, Fractographic Characterization of Polycarbonate Failure Modes. In: Proceedings of Plastics: Annual Technical Conference (ANTEC 2004); May 16 - 20, 2004, at Chicago's Navy Pier, Chicago, Illinois.