국민대학교 자동차융합세미나II 강연:

자동차용 고분자 소재의 웨더링 특성 및 가속시험법

Weathering Characteristics and Accelerated Test Methods for Automotive Polymer Materials

October 11th, 2023

최병호 (고려대학교 기계공학부)

Laws of Hammurabi (1792 ~ 1750 BC)
-Importance of Structural Integrity and Durability

The codes # 228 through #233 of the Hammurabi's Code of Laws (282 codes) represent the rules of construction in Babylonia of that time

- *229 If a builder has built a house for a man and has not made his work sound, and the house he built has fallen, causing the death of its owner, that builder shall be put to death*
- *230 The builder's son shall be punished for harm to the owner's son due to the house failure* (The responsibility extends for the second generation)
- *233 If a builder has built a house for a man, and has not keyed his work, and the wall has fallen, that builder shall make that wall firm at his own expense*

Weathering of Polymers

Introduction

- **Introduction**
  - When polymers are used for outdoor applications, polymers are subjected to many different type of effects: *sunlight, heat, humidity, rain, frost, atmospheric pollutants, wind gusting, sand abrasion, microbes, sea water, etc.*
  - Polymers can have an increased susceptibility to premature outdoor failure due to a variety of reasons: *such as the presence of impurities and chromophores (inherent or acquired during processing), improper formulation (e.g. inadequate stabilizer, antagonistic additive interactions, etc.), fabrication-related factors (design flaws and molding stresses), etc.*
  - Root causes of such premature failures: *the deterioration of the polymer's mechanical properties, leading to embrittlement or catastrophic failure (i.e. cracking) of the product, a reduction of aesthetic properties (e.g. discoloration, loss of transparency)*

Common Weathering-Induced Failure Modes

Common weathering-induced failure modes for a range of different polymers and their respective applications

Polymer	Application	Failure modes[a]
PVC	Window frames and sidings	− Impact strength − Tensile strength + Yellowing + Chalking
PP	Garden furniture and stadium seats	+ Brittleness + Chalking + Cracking
HDPE	Milk crates and irrigation pipes	− Impact strength + Chalking
PMMA, PC	Glazing and street-lamp housings	+ Crazing − Transparency + Yellowing
ABS	Applicance housings	+ Brittleness + Yellowness
Acrylic	Surface coatings	+ Chalking − Gloss + Erosion
Glass-fibre-reinforced polymers	Sheeting and boat hulls	+ Delamination + Fibre protrusion + Accentuation of glass fibre pattern − Transparency

[a] Feature/property: + , increase; − , reduction

Characteristics of Weathering

- **The Effects of Weathering on a Polymer**
  - Primarily, the effects of weathering are confined to the surface layers of the product that is exposed to outdoor factors (e.g. the typical thickness of the weathered layer is ~100 μm
  - Weathering manifests itself at a chemical level by the incorporation of oxygen into the structure of the polymer in the form of carbonyl groups → *Increase of density, reduction in molecular weight due to chain-scission or increase in molecular weight due to crosslinking process*
- **Detection and Quantification of Weathering**
  - Chemical changes can be detected and quantified by some tests : viscometry; FTIR spectroscopy carbonyl index and melt-flow-index changes; *ATR (attenuated total reflectance), SEM and ESCA (Electron spectroscopy for chemical analysis) for detailed characterization*

Main Categories of Weathering

- **Three Main Categories of Weathering**
  - Polymers like LDPE and PP which have chemical changes during manufacturing, processing and storage result in the production of carbonyl and hydroperoxide group → *These group render an otherwise stable polymer photo-oxidizable*
  - Polymers such as PC, PPO and polysulfone where the chromophore responsible for light absorption in near UV range (290 – 350 nm) is the intrinsic structure of the polymer itself → *The repeat units in the backbone are very efficient at absorbing UV light, so this poses obvious problems with the photostabilization of the material*
  - Polymers such as PVC and PMMA whose photochemistry is controlled exclusively by chemical defects

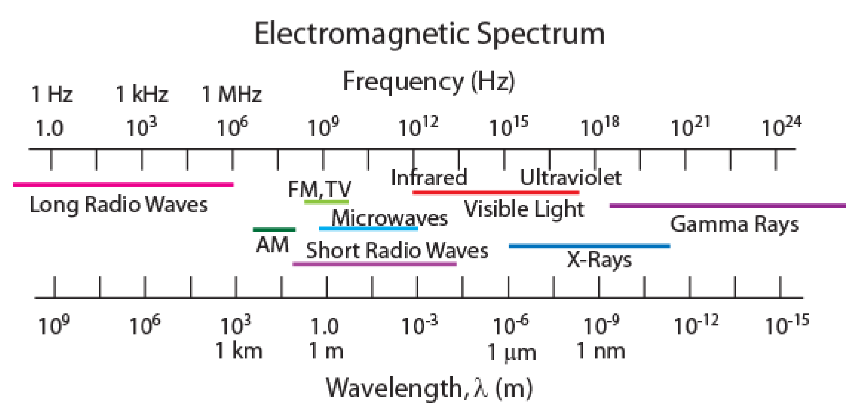


Photo-oxidation of Polymers

- **Photo-oxidation Process**
  - Initial step: *Free radical formation can be formed by light photon absorption*
  - Chain Propagation step: *The free radical reacts with oxygen to produce polymer peroxy radicals (POO•) and generate polymer hydroperoxide (POOH) and new polymer alkyl radical (P•)*
  - Chain Branching: *The formation of polymer oxy radicals (PO•) and hydroxy radicals (HO•) can be formed by photolysis*
  - Termination step: *Cross linking is a result of the reaction of different free radicals with each other*

Initial step:

$$Polymer \longrightarrow P\bullet + P\bullet$$

Chain Propagation:

$$P\bullet + O_2 \longrightarrow POO\bullet$$

$$POO\bullet + PH \longrightarrow POOH + P\bullet$$

Chain branching:

$$POOH \longrightarrow PO\bullet + \bullet OH$$

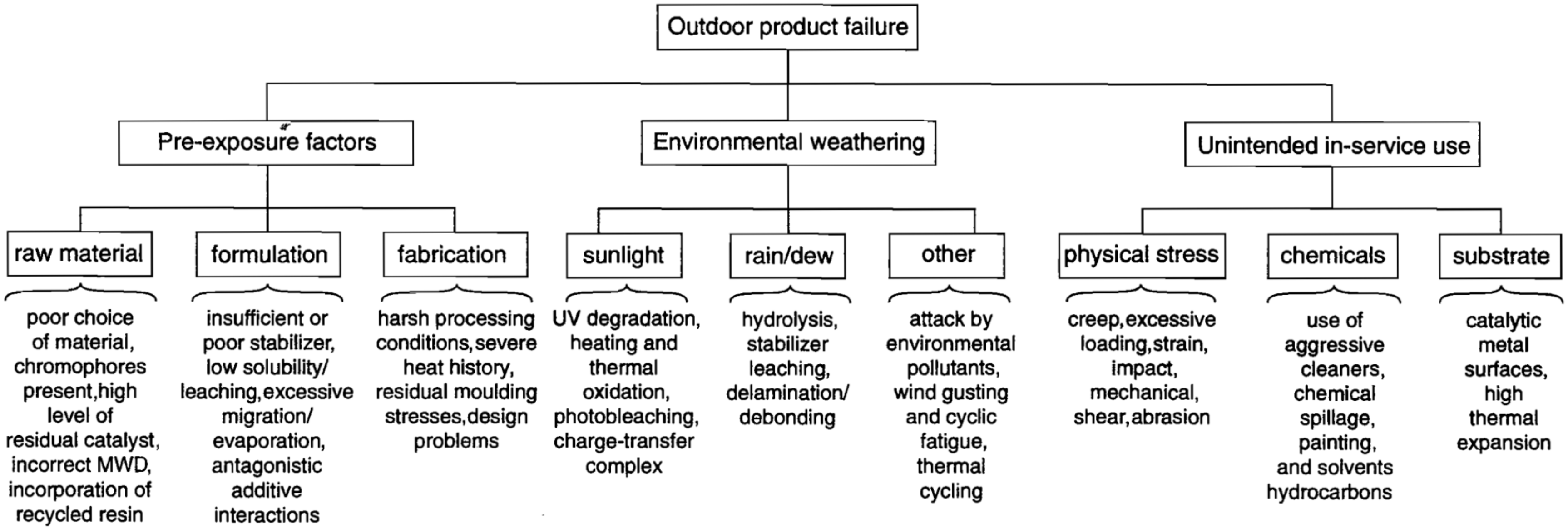
$$PH + \bullet OH \longrightarrow P\bullet + H_2O$$

$$PO\bullet \longrightarrow \text{Chain scisson reactions}$$

Termination:

$$\left.\begin{array}{l} POO\bullet + POO\bullet \\ POO\bullet + P\bullet \\ P\bullet + P\bullet \end{array}\right\} \longrightarrow \text{Cross linking reactions to non-radical products}$$

Common Causes of Failure for Weathered Polymer



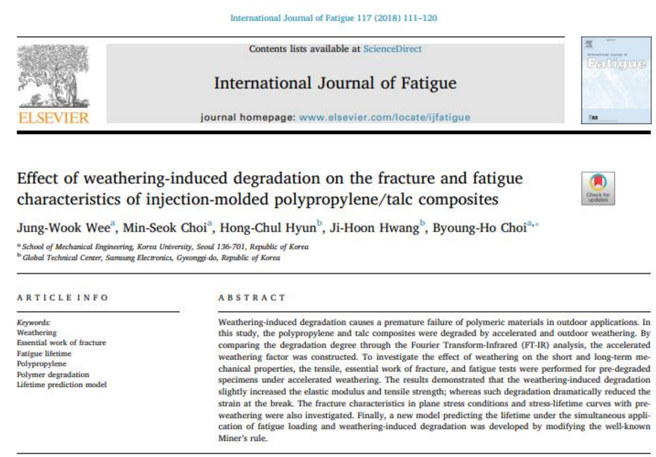
While there are many different potential causes of failure, the effect of each individual causes are by no means unique, especially for products failing towards the end of their design service life → Weathering is a particularly challenging area of analysis since it can involve virtually all types of degradation (e.g. photo-oxidation, thermal oxidation, hydrolysis and microbial attack)

Preliminary Investigations

- **Detail the Problem**
  - Some questions can be arising to weathering investigations
    - *At what stage of the product life cycle of the item did the failure occur?*
    - *Is it an isolated sample of has a batch/several items failed?*
    - *Has the product been used as intended?*
    - *What is the recommended material and stabilization package?*
- **Sample Selection**
  - Reliable reference should be prepared to quantify the weathered polymers
- **Visual/Microscopic Inspection**
  - Checkpoints of the weathered specimen: surface imperfections; *embrittlement; extent and location of cracking; nature of cracking (ductile or brittle); chalking; crazing; discoloration; surface dullness; heterogeneous contamination*
- **Polymer Identification**
  - The composition of the failed polymer component should confirmed by using some analytical techniques such as DSC, FTIR, density measurements, etc.

Case Study:

Observation and Modeling of Fracture and Fatigue Characteristics of Talc-filled Polypropylene under Weathering Conditions



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Effect of weathering-induced degradation on the fracture and fatigue characteristics of injection-molded polypropylene/talc composites

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ABSTRACT

Weathering-induced degradation causes a premature failure of polymeric materials in outdoor applications. In this study, the polypropylene and talc composites were degraded by accelerated and outdoor weathering. By comparing the degradation degree through the Fourier Transform-Infrared (FT-IR) analysis, the accelerated weathering factor was constructed. To investigate the effect of weathering on the short and long-term mechanical properties, the tensile, essential work of fracture, and fatigue tests were performed for pre-degraded specimens under accelerated weathering. The results demonstrated that the weathering-induced degradation slightly increased the elastic modulus and tensile strength; whereas such degradation dramatically reduced the strain at the break. The fracture characteristics in plane stress conditions and stress-lifetime curves with pre-weathering were also investigated. Finally, a new model predicting the lifetime under the simultaneous application of fatigue loading and weathering-induced degradation was developed by modifying the well-known Miner's rule.

Introduction

- **Introduction**
  - Polymers are applied to many structural applications by improving mechanical properties with adding some fillers
  - Once, the structure is used in outdoor conditions, the effect of mechanical and chemical degradations is quite significant for the lifetime of the structure

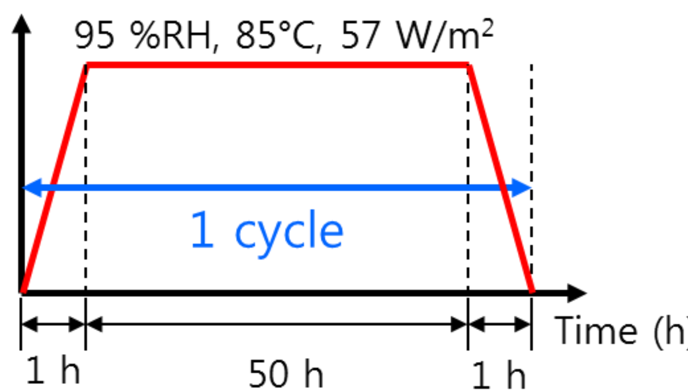
- **Objectives**
  - Quantifying the oxidative degradations using carbonyl index and constructing the relationship between accelerated weathering and field weathering
  - Observation of fatigue properties of polypropylene filled with talc under accelerated weathering conditions
  - Development of the new fatigue lifetime assessment model by considering both of mechanical (fatigue) and oxidative (weathering) degradations

Test Methods and Specimens

• Test Conditions

	Unit	Value
Temperature	[°C]	85
Relative Humidity	[%RH]	95
Xenon-Arc lamp	[W/m^2]	57 (at 0.5R)
Aging time	[hours]	0, 100, 200, 400

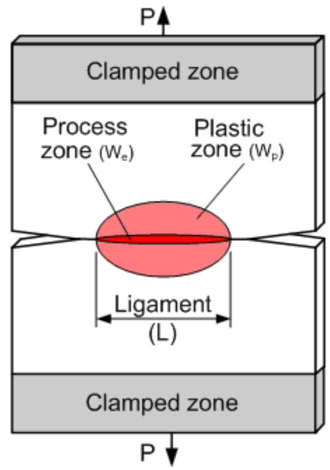
	Unit	Value
Temperature	-	RT
Frequency	[Hz]	5
R-ratio (no acc. weathering)	-	0.1, 0.2, 0.3
$\frac{\text{Maximum loading stress}}{\text{Ultimate tensile strength}}$	-	0.9, 0.85, 0.8, 0.78

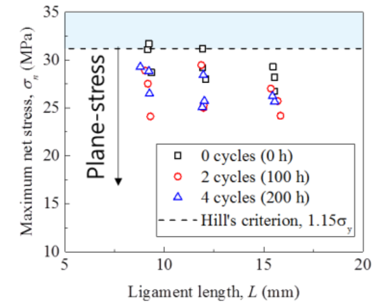


Variation of Mechanical Properties

- **Test Specimens**
  - Sample: *Polypropylene + GF 20wt%*
  - Tensile test specimen: *ASTM D638 Type I*
  - Fracture test specimen: *ESIS TC4 EWF Test Protocol*

    : Plane stress condition should be satisfied

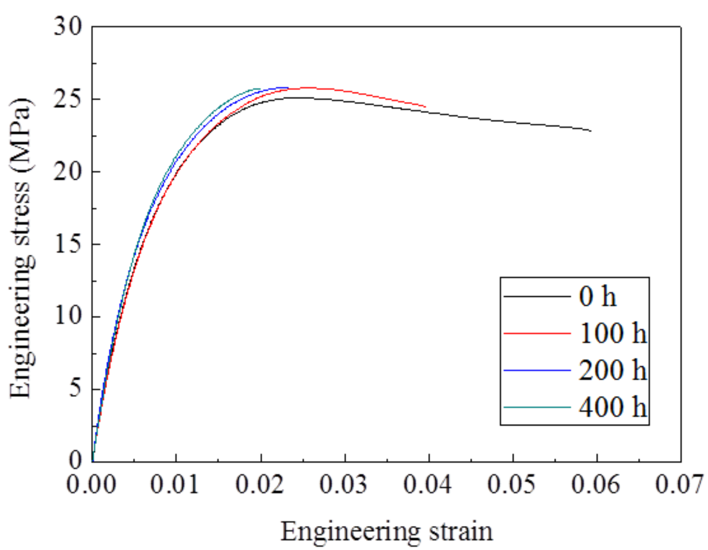


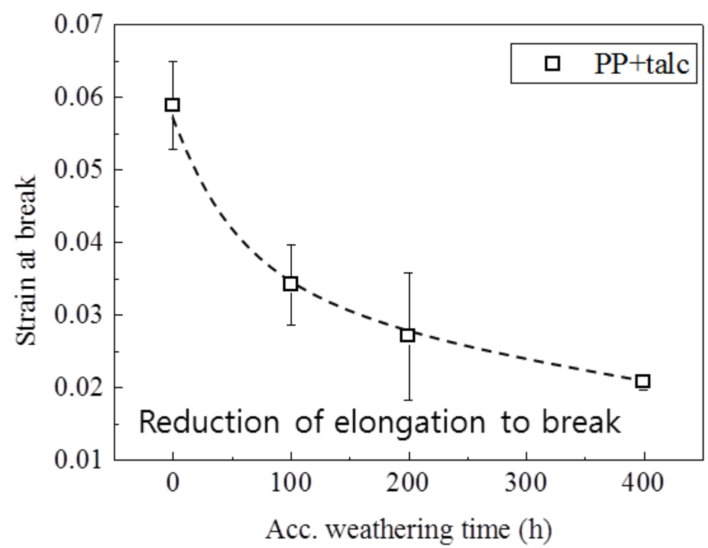


$$\frac{P_{max}}{Lt} \le 1.15\sigma_y$$

→ plane stress

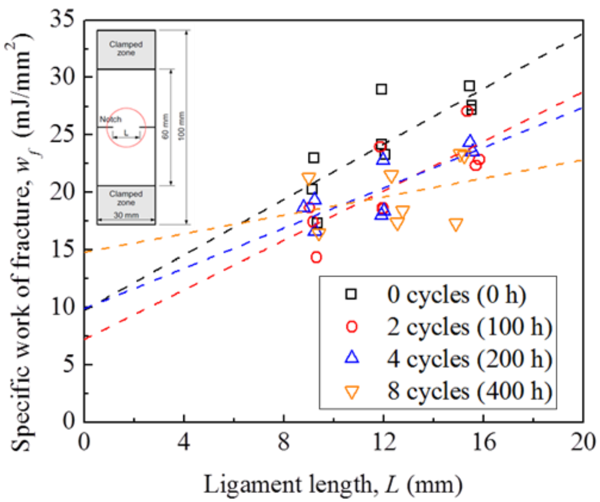
- **Tensile Properties**

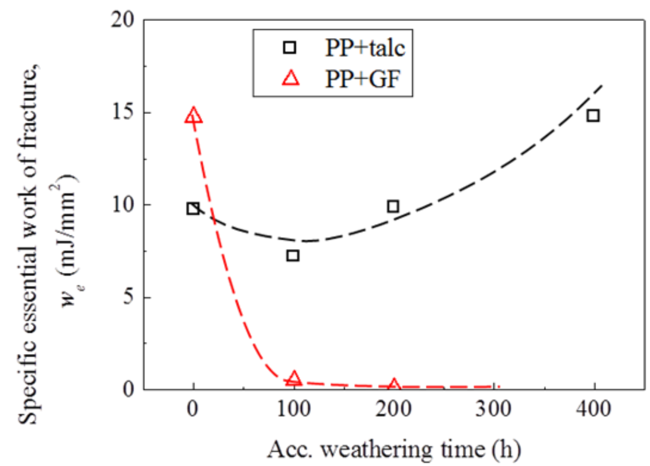


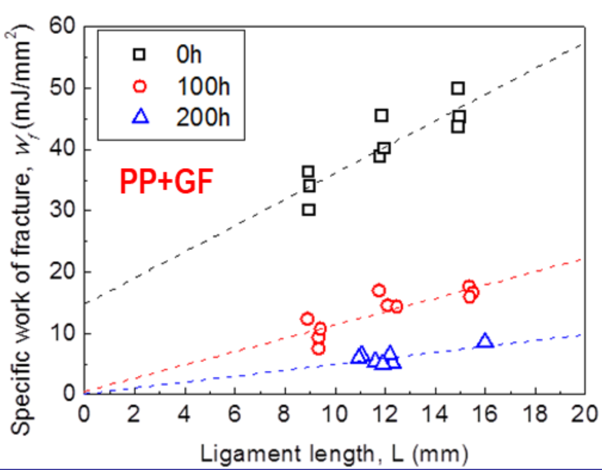


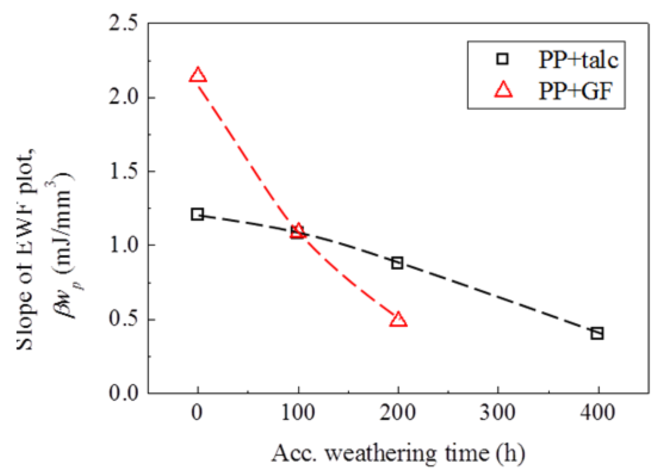
Effect of Weathering on EWF

- **Fracture Toughness and Crack Growth Resistance**



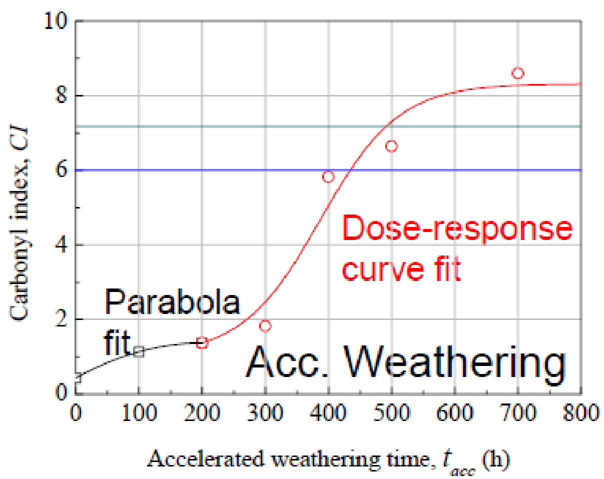


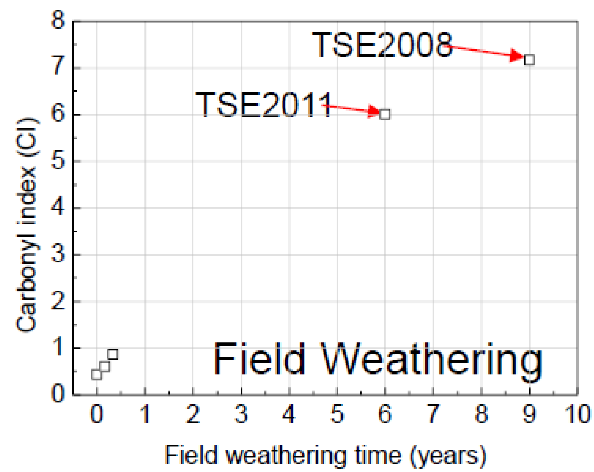


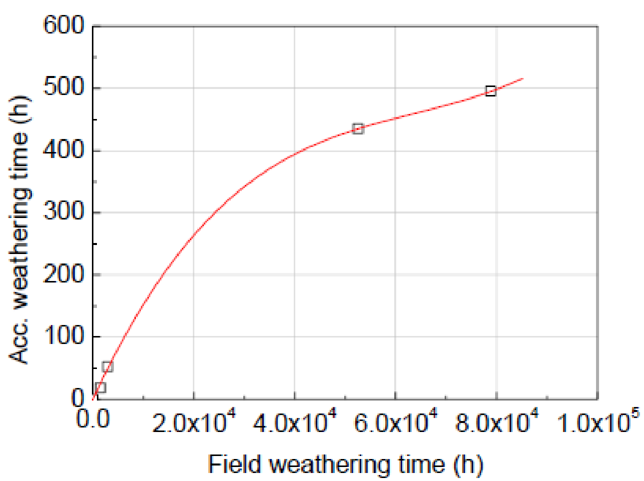


Relationship between Accelerated and Field Tests

- **Carbonyl Index**







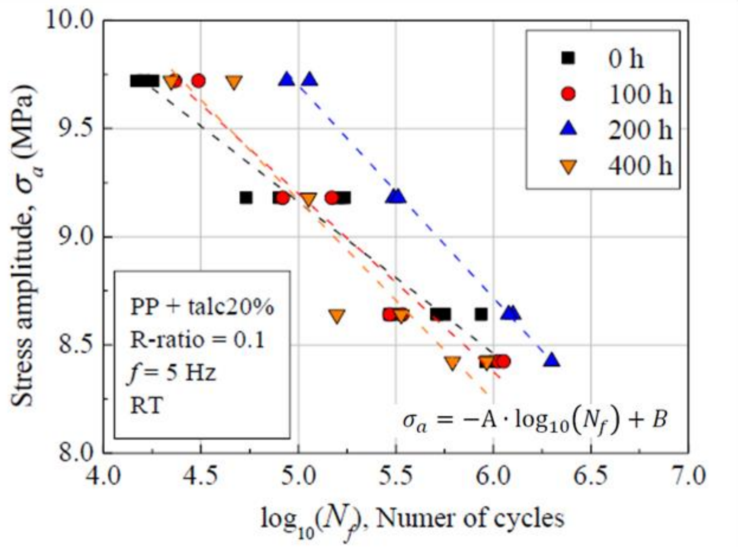
Acc. weathering vs. Field weathering

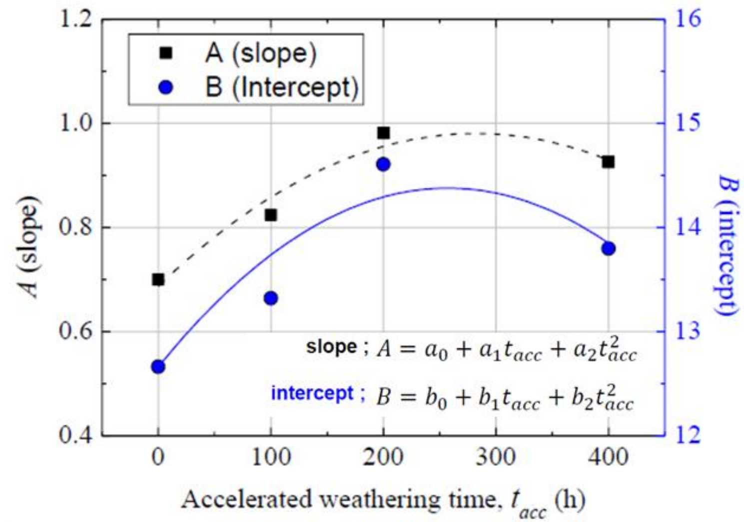
$$t_{acc}(h) = 0.01755\,(t_f) - 2.4351 \times 10^{-7}\,(t_f)^2 + 1.2746 \times 10^{-12}\,(t_f)^3$$

Acc. weathering 525.6 h
≒ Field weathering 10 yrs (87600 h)

ex-situ Fatigue Tests

• Fatigue Tests Results with New/Aged Samples



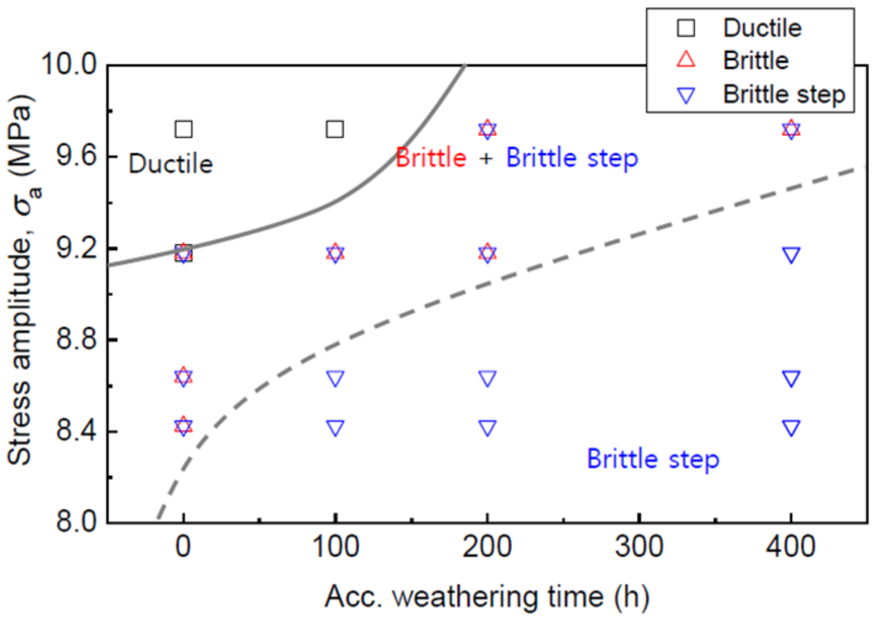


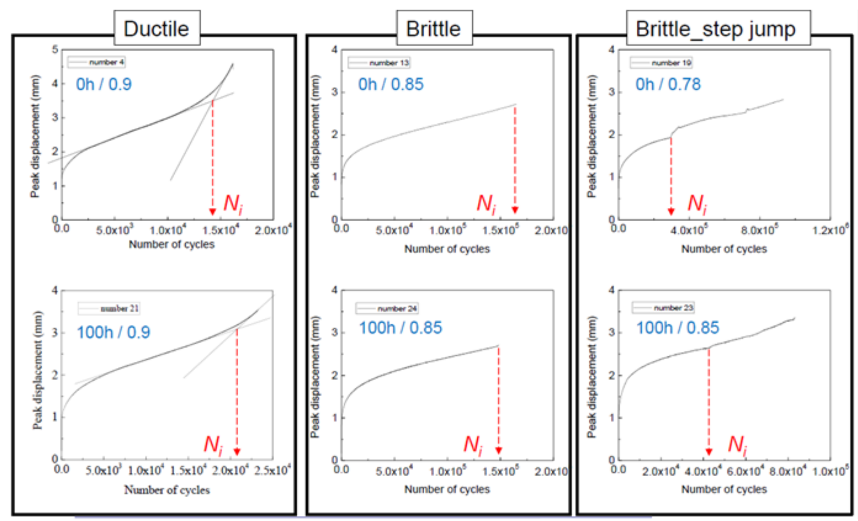
UV exposure Time (h)	CI	A (Slope)	B (Intercept)
0	0.4335	0.7002	12.6619
100	1.134	0.82405	13.3200
200	1.373	0.98153	14.6072
400	5.822	0.92546	13.7967

	Value			Value
a_0	0.68733		b_0	12.662
a_1	0.00208		b_1	0.01335
a_2	-3.681E-6		b_2	-2.5963E-5

Fatigue Fracture Mechanism Maps

- **Introduction**
  - Brittle step is the dominant fracture mechanism for low stress amplitude regardless of weathering time
  - No ductile failures with relatively long accelerated weathering conditions
  - Ambiguous section between brittle and brittle step fracture mechanisms is observed





Effect of Weathering on Fatigue Lifetime

- **Fitting Processes for Modeling**

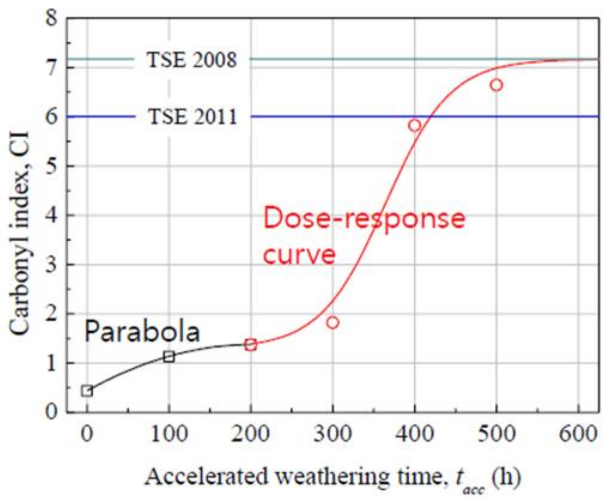
❑ Fitting equation

$$\sigma_a = A \cdot \log_{10}(N_f) + B$$

$$-A = 1.0206 + \frac{(0.7002 - 1.0206)}{1 + \exp\left\{\frac{(CI - 1.1815)}{0.2694}\right\}}$$

$$B = 14.52 + \frac{(12.18 - 14.52)}{1 + \exp\left\{\frac{(CI - 0.9753)}{0.2459}\right\}}$$

❑ Conditions
- For PP+talc20%,
- Tensile specimen (KS-13B)
- R-ratio=0.1
- f=5 Hz
- RT



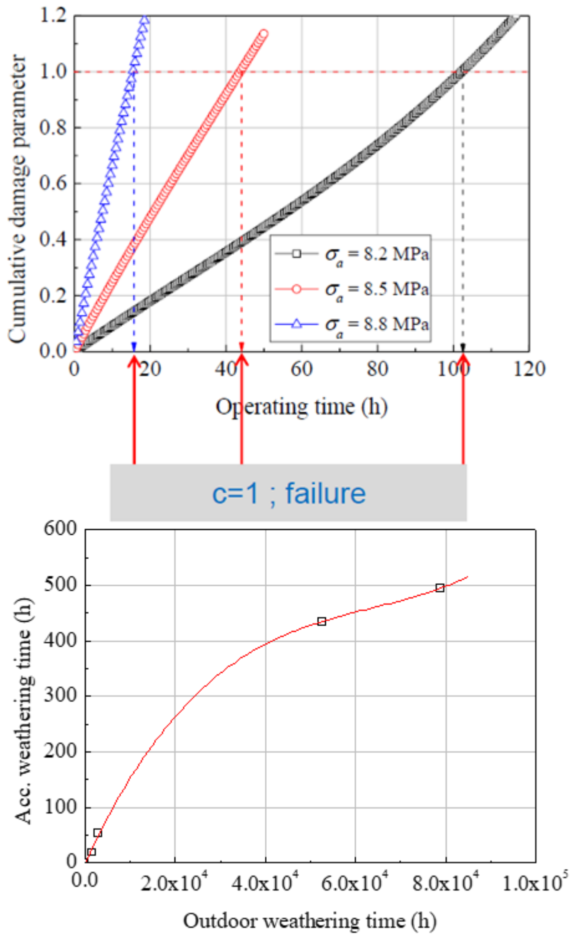
$$CI(t_{acc}) = 0.438 + 0.00931(t_{acc}) - 2.31 \times 10^{-5}(t_{acc})^2 \quad \text{for } 0 \le t_{acc} < 200h$$

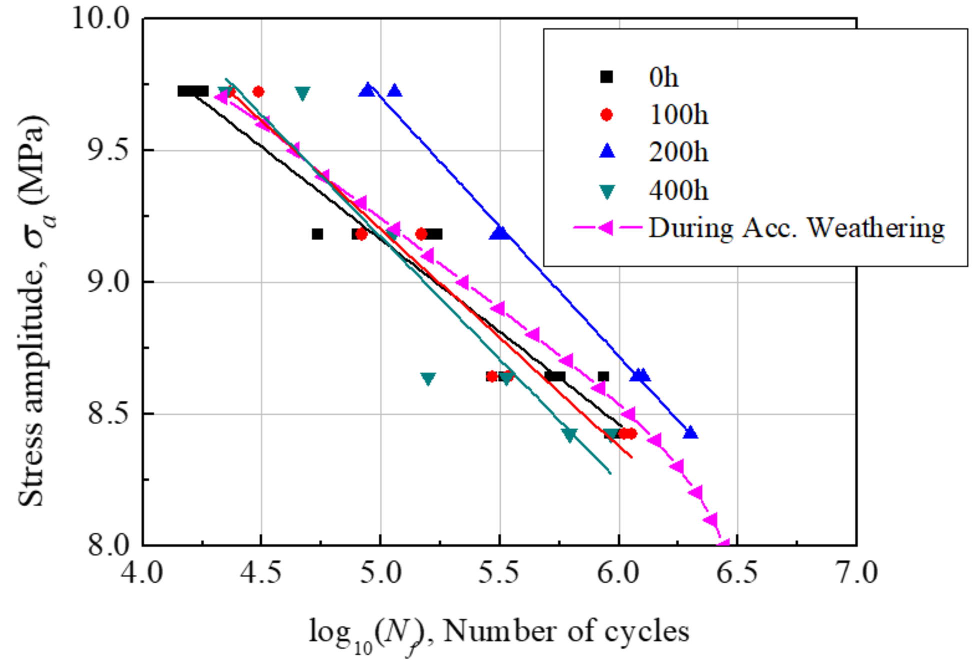
TSE2008

$$CI(t_{acc}) = 1.30 + \frac{\boxed{7.17} - 1.30}{1 + 10^{0.011 \cdot (364.3 - t_{acc})}} \quad \text{for } 200 \le t_{acc} \le 500h$$

Lifetime Prediction with Weathering

- **Fatigue Lifetime Estimations with Continuous Degradations**





Acc. weathering time (h)	Equivalent field weathering time (h)	CI	A (Slope)	B (Intercept)
0	0	0.4335	0.7002	12.6619
100	4801	1.134	0.82405	13.3200
200	8882	1.373	0.98153	14.6072
400	50564	5.822	0.92546	13.7967

Summary

- *Weathering of polymers*
    - *Characteristics of weathering*
    - *Photo-oxidation of polymers*
    - *Examples of weathering degradations of polymers*
    - *Accelerated weathering tests*
    - *Interpretation of accelerated weathering test results* Degradation mechanisms of *rubbers*
- *Case Study*
    - *Observation and Modeling of Fracture and Fatigue Characteristics of Talc-filled Polypropylene under Weathering Conditions*

Thank you very much for your attention!!

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자유 정의 진리