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# COMPARISON OF LONGEVITY OF PE- AND PP-BASED TPO WATERPROOFING MEMBRANES

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## Abstract

This study compared the longevity performance of polypropylene (PP) and polyethylene (PE) based thermoplastic polyolefin (TPO) waterproofing membranes. It was demonstrated that PE-TPO outperformed PP-TPO for both heat aging and standard UV aging in terms of tensile property retention, weight retention and resistance of surface cracking. Better longevity for PE-TPO is attributed to the lack of tertiary carbon which is intrinsic to PP and prone to chain scission.

## Introduction

Membranes used for flat and low-sloped roofing must meet a long, stringent set of norms and requirements for service life, flexibility, weathering/UV resistance and fire performance. Most roof manufacturers offer a lifetime expectancy of more than 20 years in moderate climate conditions. Other key performance attributes include sustainability, cost efficiency and easy, reliable attachment.

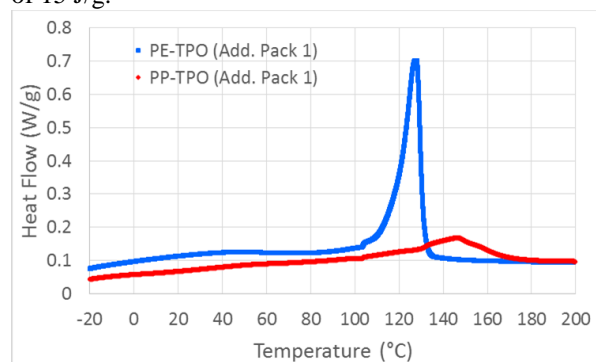
Polypropylene (PP) based material formulations are industry norm for thermoplastic polyolefin (TPO) membranes that provide a heat resistant and economic solution to the roofing industry. As PP material is prone to oxidative chain scission due to the inherent nature of the tertiary carbon, it requires specific stabilization packages for PP based TPO membrane to survive heat aging and UV weathering.

Recent advances in polyolefin catalysis enabled a polyethylene (PE) molecular architecture that combines good thermal resistance and high flexibility at the same time. It has become technically feasible to design PE based materials for roofing and waterproofing membrane applications with excellent heat resistance. PE based materials are expected to offer intrinsically better stability over PP, thanks to the lack of tertiary carbons on the polymer backbone.<sup>1, 2</sup> It is the objective of this study to compare both thermal and UV stability for PP and PE based system in typical TPO waterproofing formulations. Tensile properties, weight loss and surface cracking were monitored as a function of aging conditions.

## Materials and Methods

The PE based formulations used a 70/30 (wt/wt) blend of a polyolefin elastomer and an LLDPE. The polyolefin elastomer had a density of 0.877 g/cm<sup>3</sup> and melt index (190°C at 2.16 kg) of 0.5. The LLDPE had a density of 0.941 g/cm<sup>3</sup> and melt index of 4.0. The PP based

formulations used an industry benchmark PP material with a density of 0.880 g/cm<sup>3</sup> and melt flow rate (230°C at 2.16 kg) of 0.6. Two different additive packages were used that varied in the concentration of hindered amine light stabilizers (HALS), as shown in **Table 1**. The additive package included inorganic fillers (TiO<sub>2</sub> and magnesium hydroxide) and stabilizers such as hindered amine light stabilizers (HALS), organophosphate and phenolic antioxidant. Additive Package 1 contained 0.3% HALS, whereas Additive Package 2 contained 0.5% HALS. Unreinforced, formulated polymer membrane samples were prepared on a direct extrusion line equipped with a 25 mm 40 L/D co-rotating twin screw extruder, a 300 mm flat slit die and a three-roll calender. The nominal thickness of the membrane samples was set to 1.0 mm. The thermograms in **Figure 1** show the melting behavior of the PE-TPO and PP-TPO formulations. The peak melting temperature for PE-TPO is 127°C with an enthalpy of 37 J/g, whereas peak melting temperature for PP-TPO is 146°C with an enthalpy of 15 J/g.



**Figure 1.** DSC curve from 2<sup>nd</sup> heat for PE-TPO (blue) and PP-TPO (red)

**Table 1.** Additive packages by wt%

Ingredient	Add. Pack 1 (wt%)	Add. Pack 2 (wt%)
IRGANOX B225	0.1	0.1
CHIMASORB 2020	0.3	0.5
TiO <sub>2</sub>	2.4	2.4
Mg(OH) <sub>2</sub>	36.4	36.4

Samples were subjected to accelerated thermal aging and to UV weathering according to ASTM D6878. The heat aging was conducted at 116°C in circulating vent hot air

ovens. UV weathering tests were performed in an Atlas Ci 5000 Xenon-Arc light chamber. The weathering condition used 690 mins of light followed by 30 mins of light plus water spray. The irradiance was 0.7 W/m<sup>2</sup>\*nm at 340 nm, uninsulated black panel temperature was 80°C, chamber air temperature was 50°C and the relative humidity was controlled at 50%. The aged specimens were subjected to tensile test and inspection for surface cracking using scanning electron microscope (SEM). The 500x magnification SEM images were reported to compare different samples. The mean of at least five tensile specimens were presented throughout this report. The tensile test followed ASTM D882 to collect tensile strength and elongation at break in machine direction and was carried out by MTS Insight® testing machine with a speed of 20 in/min.

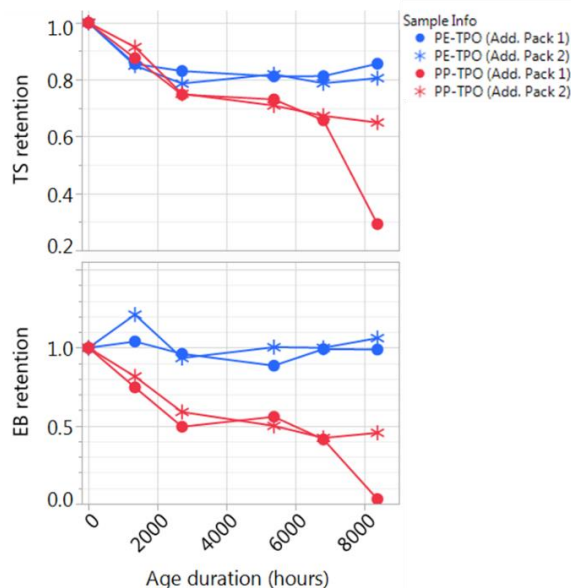
Selected samples were investigated in an EYE Applied Optix SUV-W161 chamber. This equipment utilizes a proprietary metal halide lamp in which optical bandpass filters are in place such that it provides a continuous UV exposure from 295 to 400 nm. The radiation density in the range of (295-400 nm) was set to 1500 W/m<sup>2</sup>, 20 times higher than for ASTM D6878. The SUV chamber uses a customized method (continuous light exposure with black panel controlled at 85°C and 70% relative humidity, cooled sample holders to avoid over-heating in combination with periodic water exposure) to simulate ASTM D6878.

### Results and Discussions

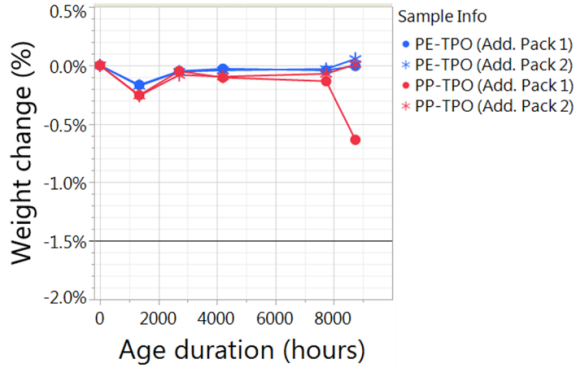
The unreinforced PE-TPO and PP-TPO had comparable initial tensile elongation at break (EB) of around 1000 %. PE-TPO and PP-TPO had an initial tensile strength (TS) of 18 MPa and 21 MPa, respectively. Additive package had no influence on the initial tensile properties. The effect of heat aging at 116°C on TS and EB retention is shown in **Figure 2**. Overall speaking, PE-TPO exhibited better TS and EB retentions than PP-TPO for both additive packages. PE-TPO had a slight loss of TS retention while the more important EB remained at about 100% retention during the test time frame (Add. Pack 1). On the other hand, PP-TPO showed a gradual loss in both TS and EB retention at high stabilizer level, whereas it showed a sudden drop in tensile property retention for the low stabilizer package at an aging time of 8000 hr. This indicate that PE based formulations are more stable in oven aging than PP based formulations, at equivalent stabilizer levels. As a result, lower concentrations of stabilizers are adequate for PE-TPO in order to achieve equivalent or even better heat aging resistance. The additive influence on the tensile properties correlate somewhat with weight change in **Figure 3**. The only sample that exhibited noticeable weight loss was PP-TPO formulated with a lower level of stabilizer (Add. Pack 1). The weight loss results for PP-TPO also indicate that PP-based formulation require a higher level of stabilizers to

retain the same level of long term performance. An explanation for the weight loss could be the volatilization of low molecular weight oxidation products generated by oxidation and degradation of the un-stabilized base polymer.<sup>3</sup>

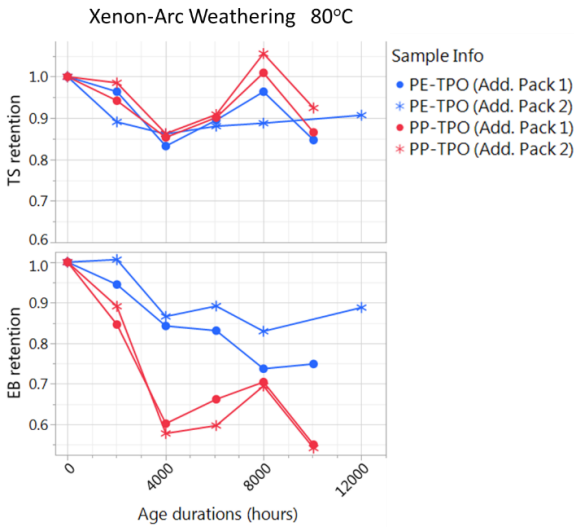
The effect of UV weathering on tensile properties is presented in **Figure 4**. Both PE-TPO and PP-TPO showed comparable performance in TS retention with a minor drop to about 90% after more than 10,000 hours exposure. For the EB retention, which is a more sensitive probe to the embrittlement of the membrane, PE-TPO exhibited distinctly better performance than PP-TPO at both stabilizer package levels. The PP-TPO also showed significantly more weight loss than PE-TPO, **Figure 5**. Though the higher HALS concentration in Add Pack 2 slowed down the weight loss for PP-TPO, it still resulted in a higher and faster weight loss when compared with PE-TPO. It is evident that the extent of weight loss after UV aging is at a higher level in comparison with hot air oven aging. Since the average temperature in UV is at 80°C, significantly lower than 116°C in heat ageing, it is evident that the UV-radiation had a greater impact on the material properties when considering weight loss.



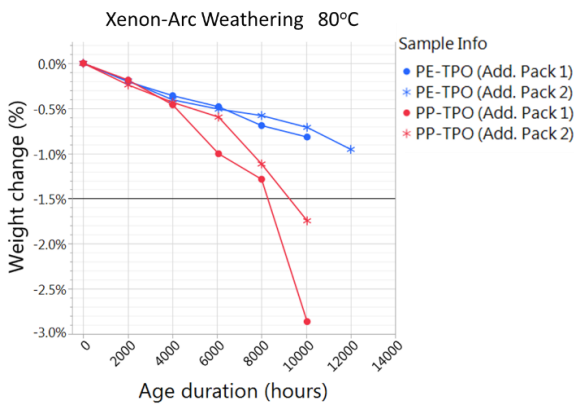
**Figure 2. Tensile strength (TS) and elongation at break (EB) retention post heat aging at 116°C**



**Figure 3. Weight loss after heat aging at 116°C**



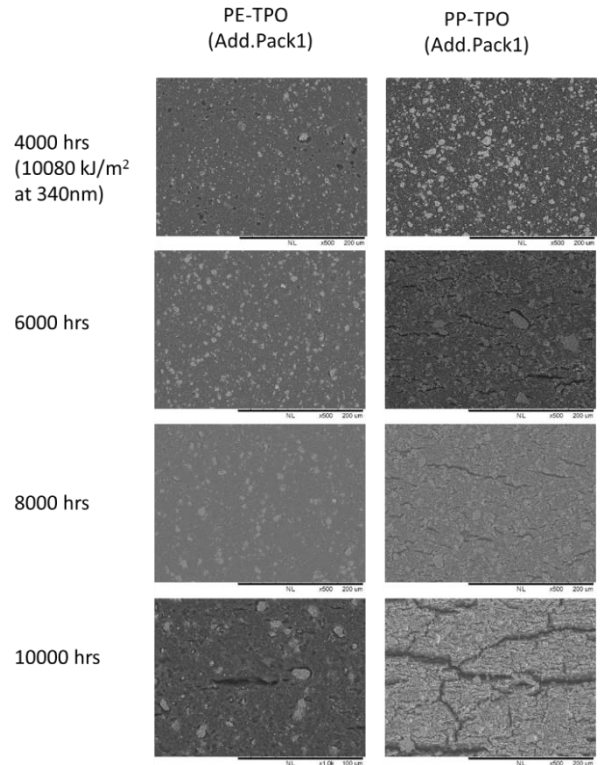
**Figure 4. Tensile strength (TS) and elongation at break (EB) retention post UV aging (ASTM D6878)**



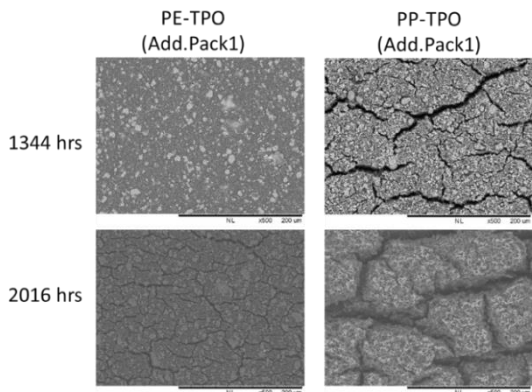
**Figure 5. Weight loss after UV aging (ASTM D6878)**

Parallel to tensile test and weight loss, which characterized polymer bulk physical properties, surface characterization by microscopy was done to track material degradation. Unlike the low magnification (7x) inspection method described in ASTM D6878, SEM was used to identify micro-cracks as a sign of failure and to differentiate sample performance after UV weathering. For the low level

stabilizer package (Add. Pack 1, **Figure 6**), the PE-TPO was crack-free up to 8,000 hours while the PP-TPO developed cracks after 6,000 hours. For the high level stabilizer package (Add. Pack 2, **Figure 8**), both PE-TPO and PP-TPO showed improved crack resistance. PE-TPO remained crack free at 10,000 hours, while cracking was observed for PP-TPO at 8,000 hours. The origin of micro-crack formation, initiation and propagation has been one of the main subjects of polymer degradation research<sup>4, 5</sup> Micro-cracking is generated by internal stresses which are induced by environmental effects such as heat, moisture, irradiation, chemicals and mechanical loads. Upon UV irradiation, polymeric materials often undergo surface embrittlement. A local increase in modulus generates internal stresses that eventually result material failure observed as cracks. For both UV aged PE-TPO and PP-TPO, the initiation of the cracks seemed to originate from the interfaces between polymer matrix and filler particles, where internal stress built up was more pronounced.

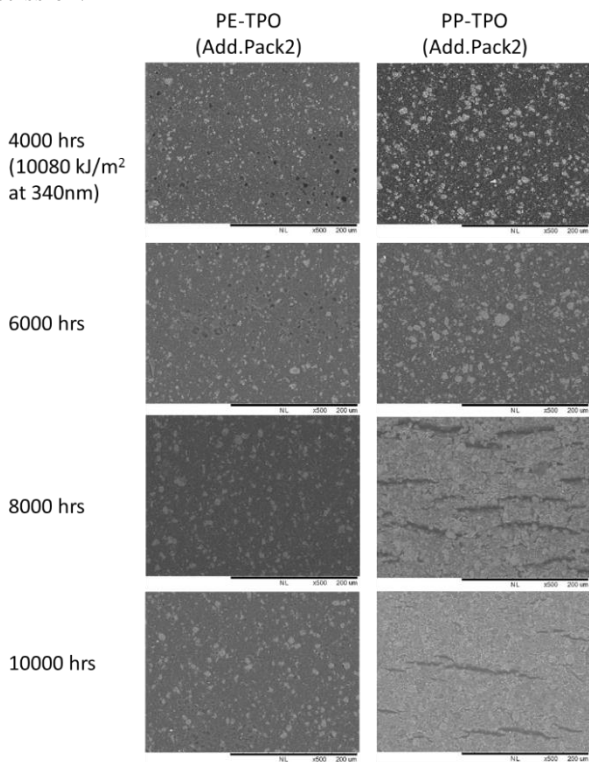


**Figure 6. SEM image for surface cracking for low stabilizer package post Xenon-Arc aging (ASTM D6878)**



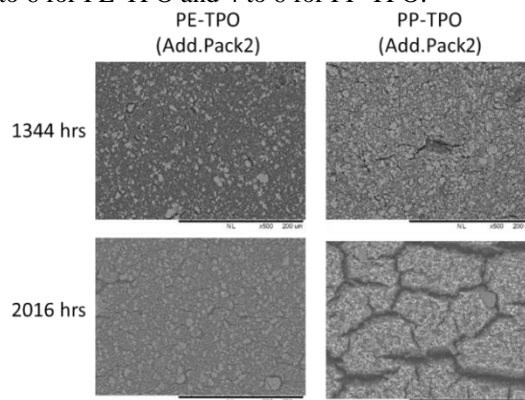
**Figure 7. SEM image for surface cracking for low stabilizer package post SUV**

It is not the purpose of this study to optimize the stabilizer package for TPO membranes. Nevertheless, the stabilizer formulations combining hindered amine light stabilizers, organophosphate and phenolic antioxidant represent a complete package according to industrial practice. The observations that PE-TPO outperformed PP-TPO in terms of tensile property retention, weight retention and resistance of surface cracking for both heat aging and UV exposure, indicates an intrinsically better stability for PE based chemistry versus PP, thanks to the lack of tertiary carbon on the PE-backbone, which is vulnerable to chain scission.<sup>1, 2</sup>



**Figure 8. SEM image for surface cracking for high stabilizer package post Xenon-Arc aging (ASTM D6878)**

A new technique, so called Super UV (SUV), with more intensive UV irradiation, was used to accelerate the weathering for TPO membranes.<sup>6</sup> Surface images by SEM after SUV exposure are presented in **Figure 7** and **Figure 9**. It is apparent that SUV significantly accelerated the surface cracking. At low stabilizer package, cracking was first observed for PE-TPO at 2,016 hrs (12 wks) whereas PP-TPO showed failures at 1,344 hrs (8 wks). This correlates with 10,000 hrs for the initial cracking for PE-TPO and 6000 hrs for PP-TPO when using conventional Xenon-Arc accelerated weathering. The higher level of stabilizer package showed some improvement for both PE-TPO and PP-TPO by reducing the extent of cracking, but the onset of first cracks was the same. The test results by SUV correlate well with UV testing according to ASTM 6878, within a significantly shorter test period. It is suggested that SUV could be a viable alternative weathering method for faster product development. The acceleration factor (AF) of SUV in comparison with Xenon-Arc weathering according to ASTM 6878 was estimated by calculating the ratio of hours required to produce surface cracking. The AF was around 5 to 6 for PE-TPO and 4 to 6 for PP-TPO.



**Figure 9. SEM image for surface cracking for high stabilizer package post SUV**

### Conclusions

This study compared the longevity performance of PP and PE based TPO waterproofing formulations in terms of thermal and UV aging, using an industry standard stabilizer package combining hindered amine light stabilizer, organophosphate and phenolic antioxidant. It was demonstrated that PE-TPO outperformed PP-TPO for both heat aging and standard UV aging in terms of tensile property retention, weight retention and resistance of surface cracking. This indicates the possibility of higher level of heat and weathering resistance for PE-TPO, and thus the option to develop products with an extended service

life. The improved longevity for PE-TPO is attributed to the lack of tertiary carbon which is intrinsic to PP and prone to chain scission. It was shown that a lower concentration of stabilizer may be used for PE-TPO to achieve equivalent longevity in comparison with PP-TPO. A high intensity Super UV (SUV) method showed correlating results when comparing it with conventional Xenon-Arc weathering. This indicates that SUV could be a viable weathering method for fast product development of PE- or PP-TPO infrastructure formulations.

### References

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