EFFECT OF AGING IN HOT CHLORINATED WATER ON THE MECHANICAL BEHAVIOR OF POLYPROPYLENE FOR SOLAR-THERMAL APPLICATIONS

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Abstract

Polypropylene (PP) is increasingly considered as a material choice for pressurized components in solar-thermal systems. In these systems, the materials are exposed to superimposed mechanical and environmental loads. The objective of this research is the characterization of the mechanical behavior of three different black-pigmented polypropylene (PP) grades immersed for up to 750 h in chlorinated water (5 ppm chlorine content) at an elevated temperature of 60°C. Hence, values for strain-at-break and essential work of fracture were determined by tensile tests. For the strain-at-break values and for the essential work of fracture values a similar exposure dependence was obtained. Depending on the PP grade, time-to-embrittlement values of 250 h and 750 h were achieved. For one PP grade, both testing methods led to an identical time-to-embrittlement value of 750 h.

Keywords: polypropylene, solar-thermal collector, chlorinated water, aging, mechanical properties

1. Introduction

In novel pumped and non-pumped solar-thermal systems, a growing share of polyolefins, especially polypropylene (PP), is considered for pressurized component applications (Koehl et al., 2012). In conventional solar-thermal systems, polypropylene is mainly utilized for hot water piping applications, whereas in systems with overheat control, polypropylene can also be used as an absorber material (Koehl et al., 2012; Lang and Wallner, 2012; Meir et al., 2008; Wallner et al., 2012). In either configuration, all components are simultaneously loaded with elevated temperatures, mechanical stresses and different environmental media. While the outside of such components may be surrounded by air, the inside is part of the hot water supply system and is exposed to a liquid medium. Usually, water is used as the heat carrier fluid in single-loop solar-thermal collector system. In many regions of the world, water is polluted with bacteria, viruses and parasites. Disinfection of contaminated water is required as a prevention of waterborne diseases (WHO, 2011). Chlorine is the most widely utilized and the most affordable water disinfectant. Chlorine is easy to use and highly efficient against different kinds of waterborne pathogens (Deborde and von Gunten, 2008; WHO, 2011; WCC, 2008). The maximum allowed chlorine content in drinking water is 5 ppm (mg/l) to ensure no further risk for human health (WHO, 2011). Polyolefins exhibit a significant degree of aging when exposed to water disinfectants (Cosgriff et al., 2017; Fischer et al., 2016; Ge et al., 2012; Hassinen et al., 2004; Mitroka et al., 2013; Mittelman et al., 2008; Vibien et al., 2001). Hence, product lifetimes are substantially reduced and, in many cases, premature failure occurs. The structural performance of polymeric materials is dependent on the mechanical and environmental loading conditions (DeCoste et al., 1951; Krishnaswamy, 2005; Lang et al., 1997; Lang et al., 2005; Stern et al., 1998a; Stern et al., 1998b). Therefore, tests of plastics for solar-thermal applications should consider service relevant loading conditions. In previous research, polymer properties were investigated by tests of specimens which were affected by various environmental conditions (Altstaedt and Kausch, 2005; Brown, 1999; Cosgriff et al., 2017; DeCoste et al., 1951; Fischer et al., 2016; Freeman et al., 2005; Ge et al., 2012; Grabmayer, 2014; Lang et al., 1997; Povacz et al., 2016; Schoeffl, 2014; Stern et al., 1998a; Stern et al., 1998b).

This paper describes the characterization of the effect of aging in hot chlorinated water on the mechanical behavior of three different black-pigmented PP grades for solar-thermal applications. Micro-sized specimens of two commercial PP grades and one development PP grade were immersed in a water bath and were removed after

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different intervals. To ensure a constant environment, the temperature, the pH and the chlorine content of the water bath were controlled. The exposure time dependent values for strain-at-break and essential work of fracture were determined by tensile tests.

2. Experimental

Three polypropylene (PP) grades were characterized in terms of their aging behavior. While two materials are commercially available, black-pigmented PP pipe grades from two different manufacturers (PP-B1 and PP-B2), the third material represents a modified PP-B2 grade (PP-B2 mod) containing additional phenolic-based antioxidants (see Table 1). To investigate the aging effect of chlorinated water with a chlorine content of 5 ppm at an elevated temperature of 60°C, micro-sized specimens with a thickness of 0.1 mm (Grabmayer, 2014; Wallner et al., 2013) were immersed in a water bath with controlled temperature, pH and chlorine content (Cosgriff et al., 2017; Freeman et al., 2005; Ge et al., 2012). In order to achieve a range of degradation levels, the exposed micro-sized specimens were removed from the aging device at different intervals (0 h, 125 h, 250 h, 375 h, 500 h, 750 h).

Tab. 1: Material designation and material composition

Material designation	Matrix polymer	Stabilizer system
PP-B1	Polypropylene blockcopolymer	Basic stabilization
PP-B2	Polypropylene blockcopolymer	Basic stabilization
PP-B2 mod	Polypropylene blockcopolymer	Basic stabilization with additional phenolic-based antioxidants

Based on tensile tests, the strain-at-break values of the removed PP specimens were determined. The tensile tests were conducted with specimens with the dimensions 150 mm x 2 mm x 0.1 mm (length x width x thickness) to achieve the relevant stress-strain curves. The time-to-embrittlement was defined as that exposure time when the strain-at-break value of the exposed specimen dropped below the strain-at-yield value of the unexposed specimen.

Furthermore, to characterize the aging effect on the fracture behavior, the essential work of fracture (EWF) method was utilized. Therefore, tensile tests were carried out with specimens with the dimensions 80 mm x 30 mm x 0.1 mm (length x width x thickness). To obtain the EWF values, different ligament lengths (6 mm, 8 mm, 10 mm, 12 mm and 14 mm) are necessary (Bárány et al., 2010) and were realized with a unique cutting device. Based on the load-displacement curves the total work of fracture values were evaluated. EWF values were obtained by plotting the specific total work of fracture as a function of ligament length.

All tensile tests were conducted at 23°C using a screw-driven universal testing machine. The gauge length was 20 mm and the test speed was 50 mm/min.

3. Results and Discussion

Exposure of the three PP grades PP-B1, PP-B2 and PP-B2 mod to hot chlorinated water led to an oxidation induced material degradation indicated by significant changes in the stress-stain curves, which are illustrated in Fig. 1. The exposure time dependent values for strain-at-break and strength are depicted in Fig. 2.

Due to aging, a significant decrease of the strain-at-break and strength was obtained for all PP grades. The lowest initial strain-at-break (for the unexposed specimen) of 364 % was determined for PP-B1. After 250 h of exposure, this material reached the time-to-embrittlement, defined as the exposure time for which the strain-at-break value of the exposed specimen dropped below the strain-at-yield value of the unexposed specimen. PP-B2 and PP-B2 mod exhibit significantly higher initial strain-at-break values of 732% and 1177%, respectively. For both materials, a time-to-embrittlement of 750 h was measured. Up to an exposure time of 500 h for PP-B2 mod the highest strain-at-break values were determined, which indicates a positive effect of the additional stabilization with the phenolic-based antioxidants. In terms of strength for PP-B1, PP-B2 and PP-B2 mod initial values of 31 MPa, 25 MPa and 30 MPa, respectively, were established. After 750 h of exposure, the strength dropped to 3.8 MPa, 6.1 MPa and 7.4 MPa, respectively. Comparing the strength of the three PP grades, the highest exposure time dependent values were obtained for PP-B2 mod.

For all three polypropylene grades, the exposure time dependent values of specific total work of fracture are depicted as a function of ligament lengths in Fig. 3. As alluded to above, exposure to hot chlorinated water led to oxidation induced degradation of the polymers and thus to a more brittle behavior at higher aging times. Hence, with increasing exposure times ligament yielding and crack initiation/growth were superposed. Thus, the EWF preconditions were not fully met. Nevertheless, up to certain exposure times, the EWF concept requirement of self-similar load-displacement curves was fulfilled (Bárány et al., 2010; Mai et al., 2000). For the EWF tests, the time-to-embrittlement was defined as that exposure time when no self-similarity of the load-displacement curves was obtainable. Above this aging time, the EWF preconditions were not met and thus the test conditions and furthermore the results were not valid.

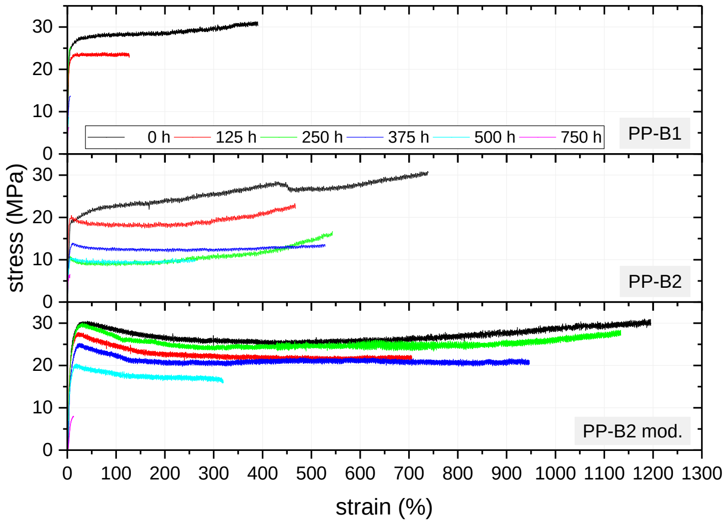

Fig. 1: Exposure time dependent stress-strain curves for the three PP grades.

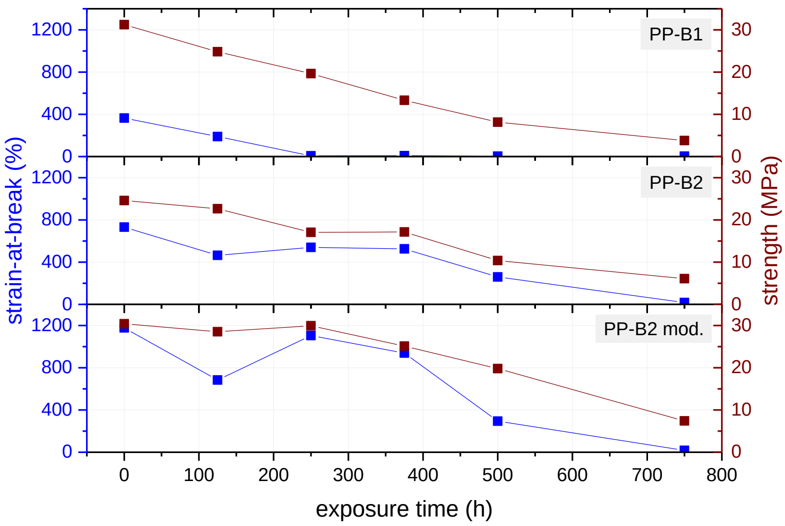

Fig. 2: Strain-at-break and strength as a function of exposure time for the three PP grades.

Based on the curves depicted in Fig. 3, the values for the specific non-essential work of fracture and for the specific essential work of fracture were evaluated. In Fig. 4, these values are plotted against the exposure times. Again, for all PP grades, the essential work of fracture decreased with increasing aging times. For the two commercial

PP pipe grades PP-B1 and PP-B2, the time-to-embrittlement was 375 h, for the additionally stabilized PP grade PP-B1 mod the time-to-embrittlement was 750 h. For PP-B2 and PP-B2 mod exposed up to 250 h, the aging dependent values of specific non-essential work of fracture and specific essential work of fracture are similar. However, due to the additional stabilization with phenolic-based antioxidants, the time-to-embrittlement was greatest for PP-B2 mod (500 h vs. 250 h for PP-B1 and PP-B2)

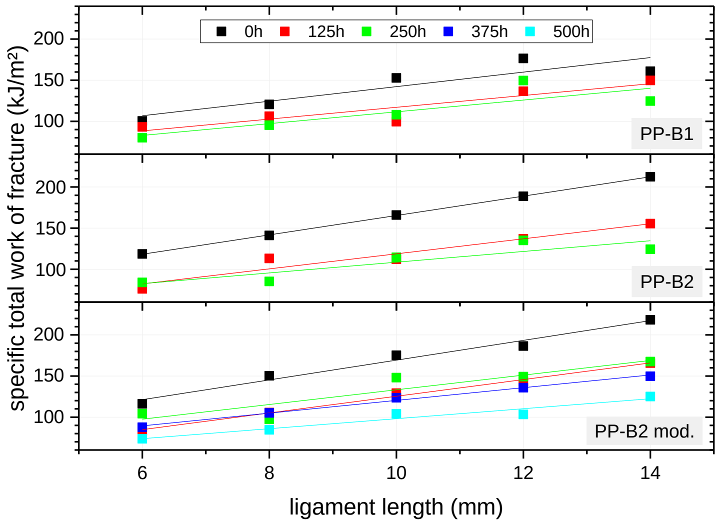

Fig. 3: Exposure time dependent curves of specific total work of fracture vs. ligament length for the three PP grades.

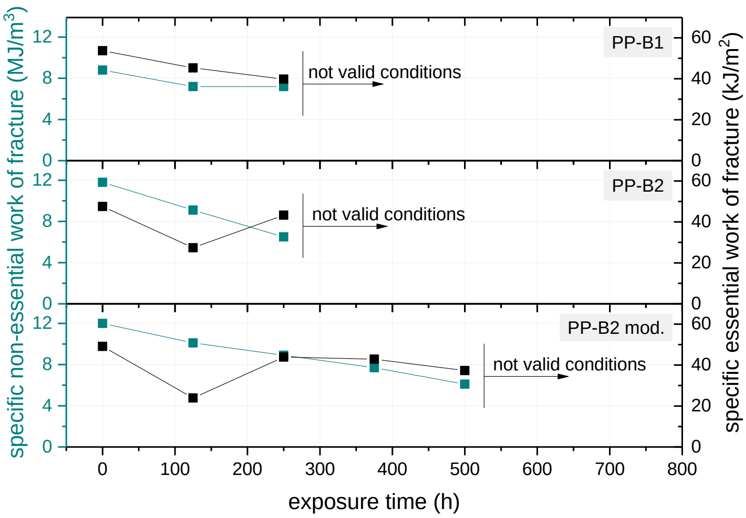

Fig. 4: Specific non-essential work of fracture and specific essential work of fracture as a function of exposure time for the three PP grades.

Exposure time dependent values for strain-at-break and specific essential work of fracture are illustrated in Fig. 5. For all PP grades, the strain-at-break curves exhibit similar aging effects as the EWF curves. Nevertheless, in terms of time-to-embrittlement, only for PP-B2 mod did both methods yield identical values. A comparison of the time-to-embrittlement data (all below 1000 h) with published data for similar materials tested in hot air and in hot heat carrier fluid (Povacz et al., 2016) reveals hot chlorinated water as the most aggressive environment.

Due to the simple specimen preparation and test procedure, the strain-at-break method is recommended for embrittlement tests. To receive further information on the fracture mechanism and the fracture toughness, the EWF method should be utilized.

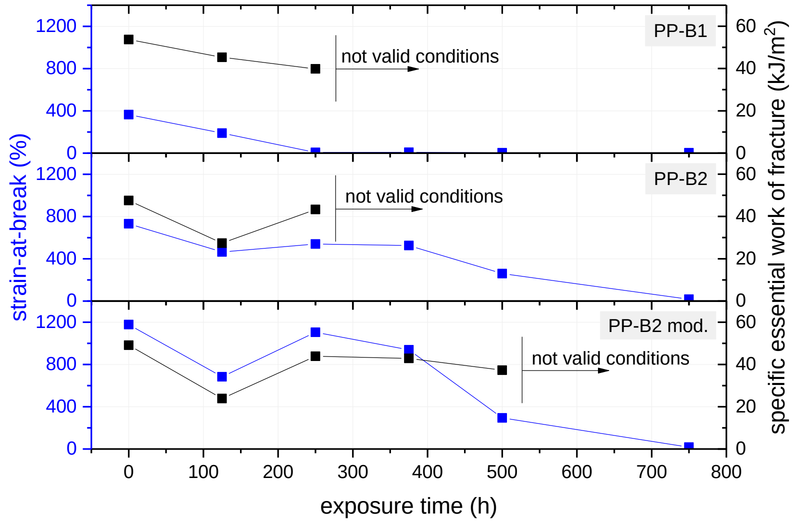

Fig. 5: Strain-at-break and specific essential work of fracture as a function of exposure time for the three PP grades.

4. Summary and Conclusions

Three different polypropylene grades were immersed for up to 750 h in a controlled water bath filled with chlorinated water (5 ppm chlorine content) at an elevated temperature of 60°C. To detect the extent of degradation over time, exposed specimens were removed at time intervals. Based on tensile tests on micro-sized specimens with method specific dimensions, values for strain-at-break and essential work of fracture were determined as a function of exposure time. The strain-at-break data exhibited a similar exposure time dependence as the essential work of fracture data. Depending on the PP grade, time-to-embrittlement ranged from 250 h to 750 h. For the PP grade that included additional phenolic-based antioxidants, the time-to-embrittlement was greatest at 750 h for both test methods.

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