

Failure Analysis of Polypropylene Used in a Hot Water Environment – Effect of Different Stabilizer Systems

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ABSTRACT

Polypropylene has been used for many years in hot water applications with varying degrees of success and lifetimes are controlled by the stabilizer package. Failures in one instance were traced to a stabilizer package that inadequately protected the polymer in a hot, chlorinated water environment. This same stabilizer system performed extremely well in oven aging tests. The current study involved examination and analysis of failed samples from the field, along with laboratory aging studies designed to replicate the field failures and compare the performance of the stabilizer system in different environments.

INTRODUCTION

Polypropylene has been used in hot water applications since the early 1960's. The material studied here was formulated for the aggressive hot water environment and was designed to function in the application for its design life of 5 to 10 years. The parts made from this formulation of polypropylene worked well in the application. The formulation included a polypropylene base polymer, a processing stabilizer, a primary hindered amine antioxidant and several percent of a filler that also contributed to the materials stability in hot water.

A second formulation was developed in the late 1980's and early 1990's as a replacement material for the polypropylene formulation that had been used for many years. This formulation included lower amounts of the primary hindered amine antioxidant, included a processing stabilizer, and two secondary antioxidants; a phosphite and a thioester stabilizer. In many cases there is a synergistic effect that occurs when using secondary stabilizers along with the primary hindered amine stabilizers.

Parts made from this newer formulation began to fail prematurely in the application, failing after only 12 to 18 months in service. A failure analysis and testing program was initiated to determine the cause of the premature failures. Allegations were made that the problem was poor processing and improper mixing of the formulation. Analysis and testing showed that the real problem was in the formulation itself and was not a result of processing problems. The test program included examination of samples returned from the field, aging in chlorinated water of specimens cut from retained lots of unused samples and substantial chemical and mechanical characterization testing.

ANALYSIS AND EXAMINATION OF FAILED PARTS

Several parts that were returned from the field were examined and characterized as part of a failure analysis. The failures could be generally divided into three groups: 1) parts that exhibited localized degradation at a point of higher stress or water turbulence, 2) parts that exhibited gross general oxidation of the surfaces of the part including holes from loss of material, and 3) parts that did not appear to have any significant problems.

Figures 1 through 3 show examples of the types of material degradation failures that were observed. Many of the failed parts exhibited some level of surface oxidation, in some cases very severe. Some samples that were in service for a couple of years did not show severe degradation, while others (likely in more severe environments) showed extensive oxidation. Micro-FTIR spectroscopy was utilized to measure the degree and location of oxidation in the samples. Oxidation of polyolefins, including polypropylene, results in the formation of carbonyl groups onto the polyolefin molecules. These groups have characteristic infrared absorption frequencies. Among these groups, the strongest absorption peak is observed at about 1710 to 1720 cm^{-1} . Weaker peaks are seen at about 1735 and 1775 cm^{-1} . The primary stabilizer compounded into the polypropylene compound has a carbonyl group with a characteristic infrared absorption peak at 1740 cm^{-1} . When oxidation occurs, a peak near 1710 cm^{-1} to 1720 cm^{-1} is formed, which progressively increases in intensity as the degree of polymer oxidation increases. The Carbonyl Index is defined as the ratio of this carbonyl absorbance to that of a polymer absorption band at 1465 cm^{-1} . The use of this ratio compensates for any differences in sample thickness and serves as an internal standard. Carbonyl index values greater than 0.02 indicate significant oxidation. Carbonyl index values for severely degraded material (crumbling) are typically greater than 0.10. The data are shown in Table 1.

Table 1. FTIR-Carbonyl Index of Field Return Parts

Sample / Time in Service	Maximum Carbonyl Index at Surface
Original / 5 years	0.00
New Formula / ~4 years	0.00
New Formula / <3 years	0.06
Localized Failure New Formula	0.121

Oxidation induction time (OIT) measurements were also performed in order to judge the remaining level of antioxidants in the parts. The measurements were performed according to ASTM D3895. The OIT was measured at 200°C on the surfaces and the core of the parts. The OIT of the surfaces and core of the field return parts approached zero at 200°C. The typical core OIT value of the earlier formulation approached 1 hour at 200°C for unused parts. The OIT results for the field returned parts are shown in Table II.

Table 2. Core OIT of Field Returned Parts

Sample	Core OIT at 200°C, minutes
Original / 5 years	15.6
New Formula / ~4 years	0.0
New Formula / <3 years	0.0
Localized Failure New Formula	0.0

It was surmised that the main differences between the types of failures observed and the non-failed samples was the duration in service and the varying service conditions (temperature, pH and chlorine content of the water). An early response to the failures was to create an “enhanced” version of the new formula with increased levels of the secondary antioxidants in the formulation. As time passed, it was evident that the additional secondary antioxidants had little effect on the failure rate of the parts and the manufacturer switched back to the original formula. Later an enhanced original formula was used, with increased levels of the primary hindered amine antioxidant.

AGING OF DIFFERENT FORMULATIONS

An aging study was set up that monitored the oxidation and OIT of various lots of unused retain parts molded from the new formulation, retained parts molded from the original material, and samples of newly compounded material using the new formulation and the (enhanced) formulation with additional secondary antioxidants. Aging baths were set up for flowing hot chlorinated water at both 85°C and 95°C. In addition to this, aging was also performed at 85°C and 95°C in air for the compounded formulations.

The chlorine water aging was set up with water controlled at 5 ppm chlorine and a pH of 6.8 that was pumped into a stirred flask containing the specimens to be aged. The flow was directed to the bottom of the stirred flask and overflow was allowed to drain out the side arm of the flask into a tank. The aging setup is shown in Figure 4.

The time to oxidation was shorter for the new formulation and enhanced new formulation than that of the samples using the original formulation. The extent of degradation was also greater for the newer formulations.

Figures 5 and 6 show the increase in carbonyl index for the surface and core of samples aged in 5 ppm chlorine at 95°C. The data for 85°C aging showed similar results. The new formulation and enhanced formulation became extremely oxidized after exposures between 119 hour and 380 hours. The original formula did not show this level oxidation until approximately 1124 hours. The new formulation samples show significant oxidation after 2000 hours, while the core of the original formulas do not exhibit any oxidation of the core. At this point the original formula parts have residual life, while the new formula parts are beyond the end of their useful life.

Figures 7 and 8 show the carbonyl index results at the surface and core for aging (95°C/5 ppm Cl) for lab-processed samples of the new formulation, enhanced new formulation and the base resin (having only the primary antioxidant). These results mirror the results from the sample parts, showing that mixing of the formula was not an issue in the deterioration.

Figure 9 shows the core OIT results for the samples aged in chlorinated water at 95°C. The OIT was measured on the new formulation samples at 180°C in order to get a measurable OIT for the unaged samples. The new formula parts show that the OIT of the surface decreases to near zero between 119 and 380 hours for both the 85°C and 95°C aging tests. The OIT of the lab processed new formula samples mirrored this behavior as shown in Figure 10, with the OIT reaching zero after approximately 164 hours of exposure.

The OIT for the original formula samples was measured at 200°C in order to cut the test times to an hour or less. The OIT at 180°C was several hours for these original formula samples, clearly much longer than that of the new formula. Figure 11 shows the 200°C OIT results at 95°C/5 ppm Cl.

Oven aging was also performed on the lab-compounded samples of the new formulation and enhanced formulation, along with the base resin to compare to the aging in hot chlorinated water. Figure 12 shows the OIT results after oven aging. The oven aging at 95°C showed small, steady decreases in OIT during the more than 5000-hour exposure. No oxidation was detected at the part surface after this aging in air.

DISCUSSION AND CONCLUSIONS

The new AO package was found to work very well for aging in hot air, but was ineffective in protecting the parts that were exposed to hot, chlorinated water. The performance of the original formula was better due to higher levels of the primary antioxidant as well as inclusion of several percent of a filler that may have reacted with the chlorine present in the water and/or slowed down any leaching of the antioxidant. The use of secondary antioxidants that could be leached out of the parts by hot water was the mistake that was made in developing the new formulation. Oven aging of the formulation would have shown very good performance, but as our oven aging studies

confirm, the new formulation and the enhanced new formulation was not suitable for aging in hot, chlorinated water. Oven aging tests should not be used to qualify a material for service in chlorinated hot water environments.

FIGURES



Figure 1. Localized oxidation at point of high stress/turbulence.



Figure 2. Localized oxidation at point of high stress/turbulence.



Figure 3. General oxidation and loss of material.



Figure 4. Chlorine Aging Bath Setup.

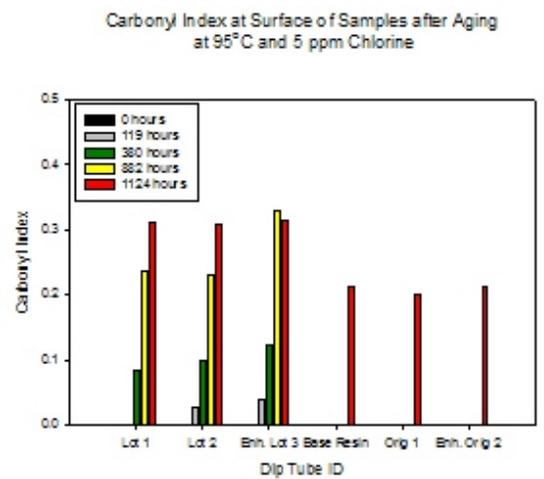


Figure 5. Carbonyl Index at Surface after aging at 95°C.

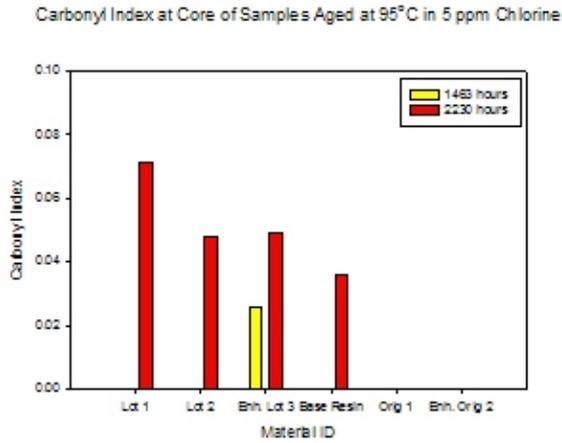


Figure 6. Carbonyl Index at core after aging at 95°C.

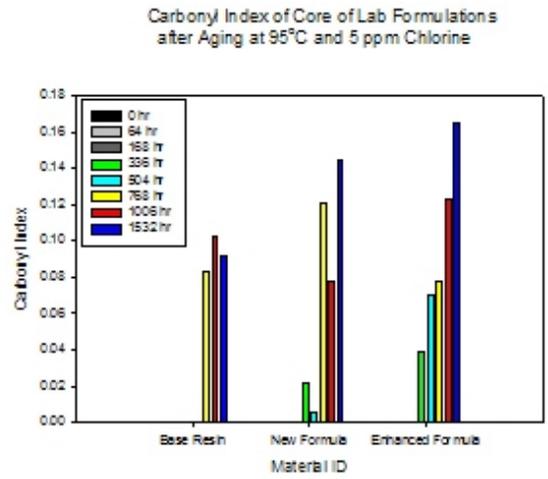


Figure 8. Carbonyl index at core of lab processed samples of the new formula after aging at 95°C/5 ppm Cl..

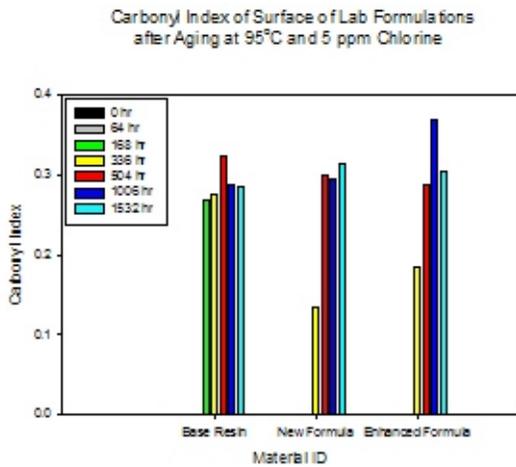


Figure 7. Carbonyl index at surface of lab processed samples of the new formula after aging at 95°C/5 ppm Cl.

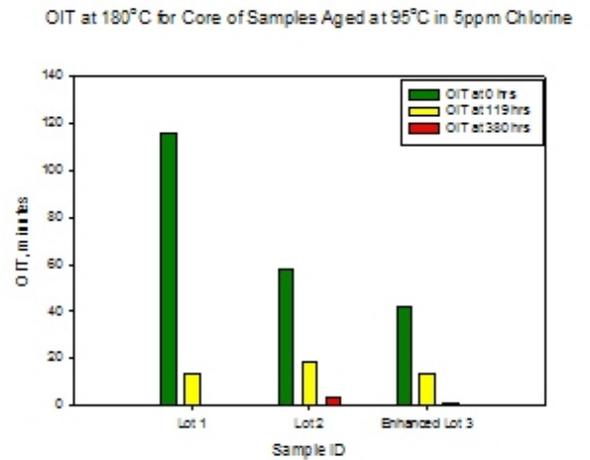


Figure 9. Core OIT at 180°C of new formula after aging at 95°C/5 ppm Cl.

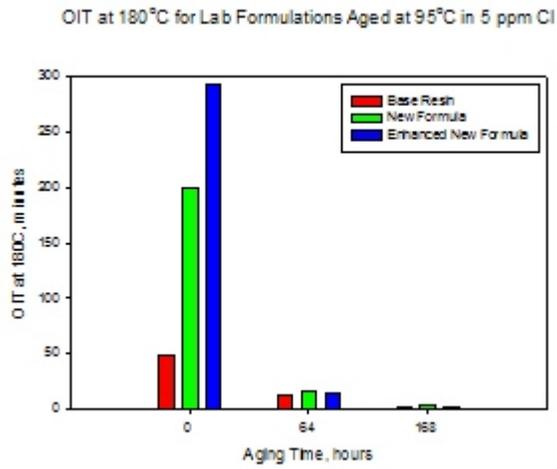


Figure 10. Core OIT at 180°C of lab processed new formula after aging at 95°C/5 ppm Cl

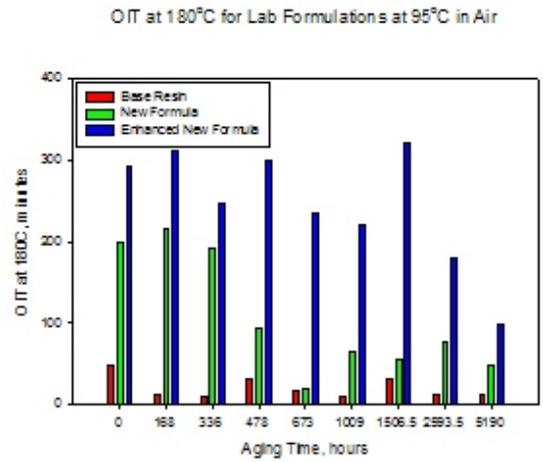


Figure 12. . OIT at 180°C of new and enhanced formulas after oven aging at 95°C.

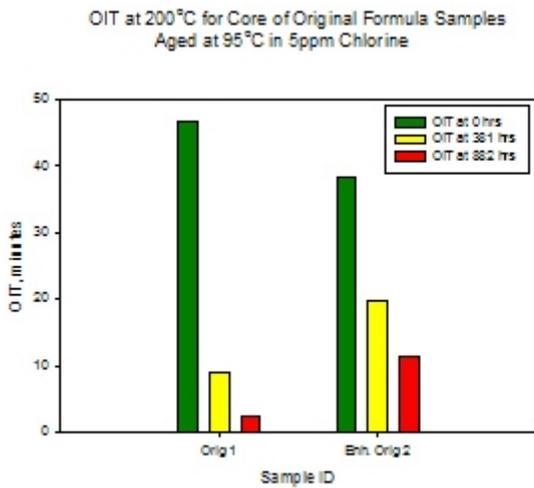


Figure 11. Core OIT at 200°C of original formula aged at 95°C/5 ppm Cl