Eco-friendly QC test on cross-linked polythene by NIR

Save more than 90% test time

Keywords

PEX, QA/QC, cost reduction, cross linked polyethylene, Antaris II, near infrared, gel, pipe, polyester

Introduction

Polyethylene is a commonly used polymer that can be chemically cross-linked to strengthen it for high performance applications. Cross-linked polyethylene (PEX) is often used in hot water radiant heating systems, insulation for electrical cables, and for domestic water piping. PEX pipes have many advantages over other pipe material including: 25 year lifetimes, easy installation with fewer fittings, stability in corrosive environments, and resistance to biofilm buildup. Additionally, the use of PEX in home water distribution has recently increased due to the expense of copper piping. These advantages have resulted in the installation of over 2 billion feet of PEX pipe in the U.S. since 1984.

PEX is manufactured from high density polyethylene that has undergone cross-linking by a variety of techniques. Cross-linking binds the long polyethylene chains to each other which alters its chemical and physical characteristics. Figure 1 demonstrates the difference between non-cross-linked material and cross-linked material. Cross-linking results in an easily manufactured material that has improved strength, serviceability, and thermal stability. The degree of cross-linking is a vital parameter for controlling PEX pipe quality. Low cross-linked material will be weaker, soften at lower temperatures, and be difficult to work with, while higher degrees of cross-linking will result in brittleness, cracking and ultimately, failure of the polymer.



Thermo Scientific Antaris II FT-NIR Method Development Sampling System

Cross-linking may be accomplished using one of three different methods. The Engle process uses a peroxide that is added to the melted base resin before extrusion. The cross-linking occurs during the production of the pipe. The Engle process provides for uniform cross-linking within the pipe but takes more time and is more expensive than other methods. The silane method uses a polyethylene chemical precursor decorated along the backbone with silane moieties. This silane-modified substance is blended into the raw material at appropriate concentrations. After the pipe has been extruded, the material is exposed to hot water or steam which activates the cross-linking reaction. A third method uses an electron beam to break apart carbon-hydrogen bonds, promoting cross-linking. This electron beam method is performed at temperatures well below the polymer melting point after the pipe has been formed. This is simpler and cleaner than the other two methods, but is less controlled and leads to less uniform product. The outer layer may be over cross-linked and prone to cracking while the interior may be under modified.



Figure 1: Non-cross-linked polymer (panel A) does not have chemical bonds between polymer strands. Cross-linked polymer strands (panel B) provide higher strength and thermal stability to the material.



The degree of cross-linking is difficult to quantify and is typically not directly measured. However, a measurement of "gel content" is relatively easy and proportional to cross-linking. This measurement determines the amount of insoluble material in a cross-linked sample. Gel content between 65% and 89% is considered ideal for PEX pipe applications. Various protocols such as ASTM D2765-01 provide detailed standard procedures for determining extent of cross-linking by measuring gel content. These procedures rely on the fact that cross-linked polyethylene is relatively insoluble in numerous organic solvents whereas non-cross-linked polyethylene is readily dissolved.

Briefly, the test PEX material is extracted with hot organic solvent such as toluene, xylene or decahydronapthalene, which removes the soluble portion and leaves behind the insoluble cross-linked fraction. Simple gravimetric analysis is used to determine the percentage of remaining insoluble cross-linked polyethylene. Unfortunately, these extraction methods take a considerable amount of time (up to 24 hours), involve toxic and environmentally hazardous organic solvents at elevated temperatures, and require a skilled technician. In contrast, Fourier transform nearinfrared spectroscopy (FT-NIR) is able to scan solid materials directly and deliver spectroscopic information related to cross-linking nearly instantaneously without using chemicals or requiring a trained operator. The Thermo Scientific™ Antaris[™] II FT-NIR analyzer is ideally suited to collect and analyze data from process and production facilities such as those found in PEX pipe manufacturing plants.

In the current study, an Antaris II Method Development Sampling (MDS) system was used to collect spectroscopic data from a process plant that was manufacturing PEXbased water piping. This system directed near-infrared light through fiber optic cables to the piping as it was being manufactured. The reflected light was collected by a second set of fiber optic cables and returned to the analyzer. The spectra developed from this collected light contain information related to the chemical makeup of the material including the amount of cross-linking or gel content. Figure 2 shows the configuration of the Antaris II MDS collecting on-line data in real time.

Experimental

The Antaris II MDS FT-NIR system was used to collect a series of spectra from PEX pipe immediately after it had been extruded. Collection of each spectrum was accomplished automatically in less than 10 seconds, without the need of a skilled operator. Samples of the pipe were also collected for primary analysis of gel content using extraction in hot organic solvent. The gel content of the samples ranged from 32.5% to 91.0% with an error of approximately 0.8%.

The spectra were analyzed in absorbance using a quantitative chemometric partial least squares (PLS) algorithm with Thermo Scientific[™] TQ Analyst[™] Software. Two similar methods were developed; one for the entire gel content range, and a second that focused more closely on the critically important range between 65% and 89%.



Figure 2: Antaris II MDS interfaced on line with PEX extruder. Probe is held stationary against the formed pipe for continual monitoring (inset on right).

For the method encompassing the entire gel content range, 100 spectra were used in creating and calibrating the chemometric model and 25 spectra were used to validate it. For the method analyzing the narrower range, 94 calibration spectra and 23 validation spectra were used. In both cases, the unsmoothed spectra were analyzed in the region between 4640 and 8600 cm⁻¹ using a linear removed baseline correction. Figure 3 shows a representative spectrum and the region of analysis.

Figure 4 shows the calibration plots for both the wide range and the narrow range methods. The plots allow comparison of the calculated gel content to the actual values generated by the primary analysis. Ideally the calculated values would be identical to the actual values and the data points would fall on the diagonal line with a slope of 1. The quality of the model is illustrated by high correlation coefficients and low errors which are given in Figure 4 for each model. The Root Mean Square Error of Calibration (RMSEC) from the calibration spectra and the Root Mean Square Error of Prediction (RMSEP) from the validation spectra are low and of similar magnitude. It is important that the RMSEP is of the same magnitude as the RMSEC to demonstrate that the method can successfully predict gel content in new unknown samples not used to develop the chemometric model. Using the large range method, the gel content concentration can be predicted to within 2.9% of the actual value; while the narrow range method can successfully predict gel content to within 2.6% of the actual value. Approximately one third of this error is attributed to the imprecision in the primary method of analysis.

Predicted Residual Error Sum of Square (PRESS) plots can additionally be used to evaluate the robustness of the chemometric model. PRESS plots describe the behavior of error based on the number of factors used to develop the method. Factors are used in the chemometric model to account for the variation with the spectra. The first factor accounts for a large part of the spectral variation, and each successive factor accounts for the remaining spectral variation. Typically, the first few factors will describe most of the variation leading to successively smaller error values. At some point, however, calculating additional factors will not produce less error and in fact may increase the error as the model overfits the data. Therefore a robust model will have PRESS plots that dramatically drop to some minimum error then stabilize or increase slightly. Figure 5 shows the PRESS plots for the two methods and demonstrates this expected behavior. Ten factors are used in the chemometric models where minimal error is attained.



Figure 3: Representative NIR spectrum of PEX pipe. The spectra were analyzed in absorbance between 4640 and 8600 cm⁻¹ using a PLS chemometric algorithm.



Figure 4: Calibration plot of the entire gel content range (top) and the critically important narrow range (bottom). Both methods show good correlation between the chemometrically calculated values and the actual measured values. Circles (o) represent spectra used in calibrating the chemometric method and are used to calculate the RMSEC values. Crosses (+) represent spectra used to validate the method and are used to calculate RMSEP. Prediction errors as shown by the RMSEP are less than 3%.

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Figure 5: PRESS plots of the two methods showing characteristic decrease in error as factors used to account for the spectral variation are increased. Increasing the number of factors beyond 10 will result in higher errors in prediction.

Conclusions

The results provided by this study show that on-line analysis of gel content using the Antaris II FT-NIR analyzer successfully predicts the degree of cross-linking in PEX pipes. The analysis provided excellent results with low error across a wide range of gel content percent as well as within the critical range of 65%-89%. Most importantly, FT-NIR analysis avoids the time delays, and the difficulties and demanding conditions associated with extraction by heated organic solvents. NIR allows for automated rapid collection of spectroscopic data within a matter of seconds and instantaneous quantitative analysis cleanly without the use of hazardous chemicals.



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