M3LW-16OR0404012
PNNL-25172

Pacific Northwest
NATIONAL LABORATORY

Light Water Reactor Sustainability Program

Characterizing oxidation of cross-linked polyethylene and ethylene propylene rubber insulation materials by differential scanning calorimeter

January 2016

U.S. Department of Energy

Office of Nuclear Energy

M3LW-16OR0404012
PNNL-25172

Characterizing oxidation of cross-linked polyethylene and ethylene propylene rubber insulation materials by differential scanning calorimeter

Leonard S. Fifield, Jian Liu, Qian Huang, Andy J. Zwoster

January 2016

Prepared for the
U.S. Department of Energy
Office of Nuclear Energy

Light Water Reactor Sustainability Program

Characterizing oxidation of cross-linked polyethylene and ethylene propylene rubber insulation materials by differential scanning calorimeter

M3LW-16OR0404012
PNNL-25172

January 2016

Approved by:

1/29/2016

B. Peter McGrail, Laboratory Fellow
Advanced Functional Materials Team Lead

Date

SUMMARY

Identified knowledge gaps in nuclear power plant electrical cable aging and degradation include the combined effects of thermal and gamma irradiation stresses on cable insulation materials. Understanding insulation degradation resulting from heat and radiation is particularly important with regards to the expectation of long term cable aging behavior based on the behavior of cables with shorter term accelerated aging. Key to addressing these knowledge gaps are techniques for measuring cable material state that are 1) sensitive to material changes with exposure and 2) are broadly applicable to cable material systems of interest including cross-linked polyethylene and ethylene-propylene rubber.

Differential scanning calorimetry has been identified as a promising approach for tracking polymer material changes due to environmental aging. Useful variants of differential scanning calorimetry (DSC) include 1) heating with a temperature ramp in the presence of oxygen to determine the oxidation induction temperature (OITP), also known as the oxidation onset temperature (OOT), and 2) holding temperature constant in the presence of oxygen to determine the oxidation induction time (OIT). These techniques can reveal the crystalline content of polycrystalline materials, the volatile component content of plasticized polymer systems, and the amount of antioxidants present in a polymer composite system. These quantities change with exposure to time and to environmental stress and can be used as key indicators of cable polymer aging.

The effects of temperature, gamma dose rate, and total gamma dose on the material properties of cross-linked polyethylene low voltage cable insulation are currently being investigated at Pacific Northwest National Laboratory through a series of controlled-exposure experiments. The effects of thermal exposure of ethylene-propylene rubber low voltage cable insulation is also under investigation. Initial results from the differential scanning calorimetry characterization of these materials is included in this report. These results demonstrate that differential scanning calorimetry is a useful tool for tracking changes in cable insulation materials with exposure. Differential scanning calorimetry will be included in the suite of techniques used to address cable aging knowledge gaps including those related to activation energies, synergistic effects, dose rate effects, and inverse temperature effects.

ACKNOWLEDGEMENTS

The differential scanning calorimetry data for cross-linked polyethylene presented in this report were obtained by Shuaishuai Liu as part of her doctoral research program in the Materials Science and Engineering department of Iowa State University under the direction of Professor Nicola Bowler.

CONTENTS

FIGURES

ACRONYMS

CSPE	chlorosulphonated polyethylene
DSC	differential scanning calorimetry
EPR	ethylene-propylene rubber
LDPE	low-density polyethylene
OIT	oxidation induction time
OITP	oxidation induction temperature
OOT	oxidation onset temperature
PNNL	Pacific Northwest National Laboratory
XLPE	cross-linked polyethylene

INTRODUCTION

Differential scanning calorimetry (DSC) is a commonly used thermal analysis technique for polymer characterization (Menczel and Prime, 2009). DSC measures the heat flow into and out of material samples under controlled temperature as a result of endothermic and exothermic processes. A common DSC experiment involves ramping the temperature of a sample chamber containing an inert or reactive atmosphere and monitoring how the temperature of the sample changes relative to a reference sample. This method can identify the temperatures at which transition events occur such as melting, evaporation or decomposition of sample components. In addition to thermal event peak locations, the area under the heat flow versus time or temperature curve is a measure of the amount of material exhibiting the event.

DSC has been used to measure changes in melting points of nuclear cable insulation materials that occur with exposure to gamma radiation and heat (Gillen and Bernstein, 2010).

When a hydrocarbon sample is heated under an oxidizing atmosphere such as oxygen gas or air with a temperature ramp, the temperature at which an exothermic oxidation event begins to occur can be determined. This temperature is referred to as the oxidation induction temperature (OITP), also known as the oxidation onset temperature (OOT), and is often performed as a variant of DSC, using a DSC instrument.

The time required to induce an exothermic event when the sample is held at a constant temperature under an oxidizing atmosphere can be used as a measure of sample content such as antioxidant concentration. This time is referred to as the oxidation induction time (OIT), and is another useful variant of DSC.

OITP and OIT have shown promise as techniques for monitoring the condition of aged nuclear power plant cables insulation materials (Gillen et al., 2005). It was concluded in the recently completed IAEA Coordinated Research Project on the Qualification, Condition Monitoring, and Management of Aging of Low Voltage Cables in Nuclear Power Plants that OIT can be used to determine the onset of degradation in most [nuclear cable] polymers (Hashemian and Kang, 2015)

Standards exist for the use of DSC-based OIT in measuring the oxidative stability of polyolefins (ASTM 2014) and hydrocarbons (ASTM 2015). There is an international standard for use of OIT in condition monitoring of nuclear power plant cables as part of cable aging management (IEC/IEEE 2011).

DSC OF EPR

DSC analysis was performed on black-colored ethylene-propylene rubber (EPR) insulation samples from Okonite-FMR® Okoseal® Type 600V Power & Control Tray Cable (Okonite Catalog Number 202-10-3203) heated in a mechanical convection oven at 140°C using a Setaram TG-DSC 111instrument. Samples were heated in argon to 300°C at 5°C/min. A photograph of the instrument is shown in Figure 1. Figures 2 through 10 show plots of heat flow versus run time and temperature for EPR samples ranging from 0h of thermal exposure to 1226 h of exposure.

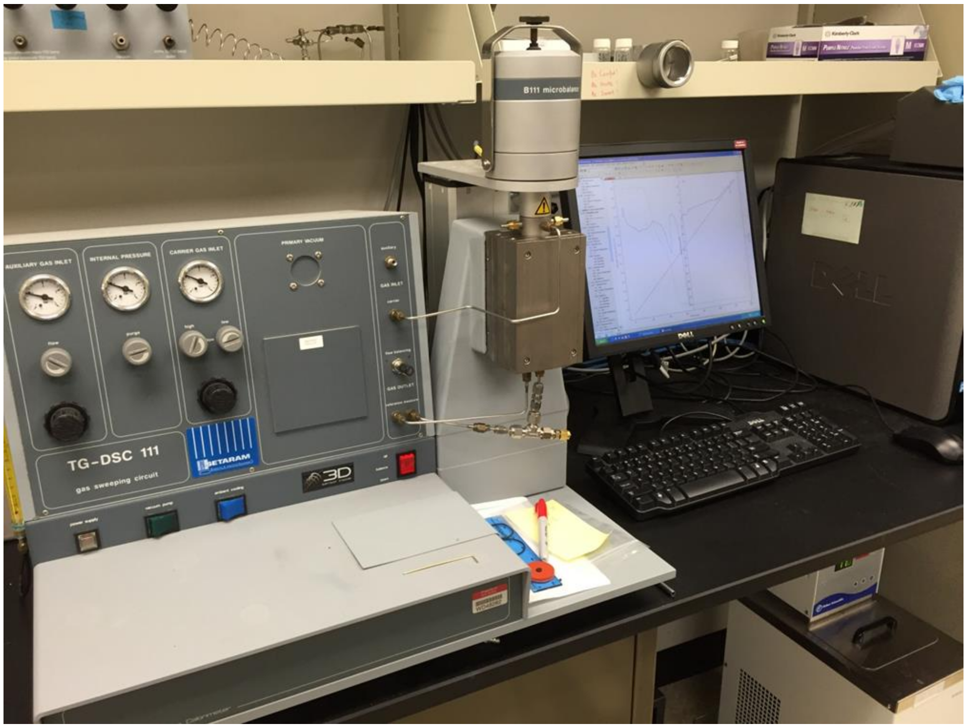

Figure 1. Setaram TG-DSC 111 Instrument.

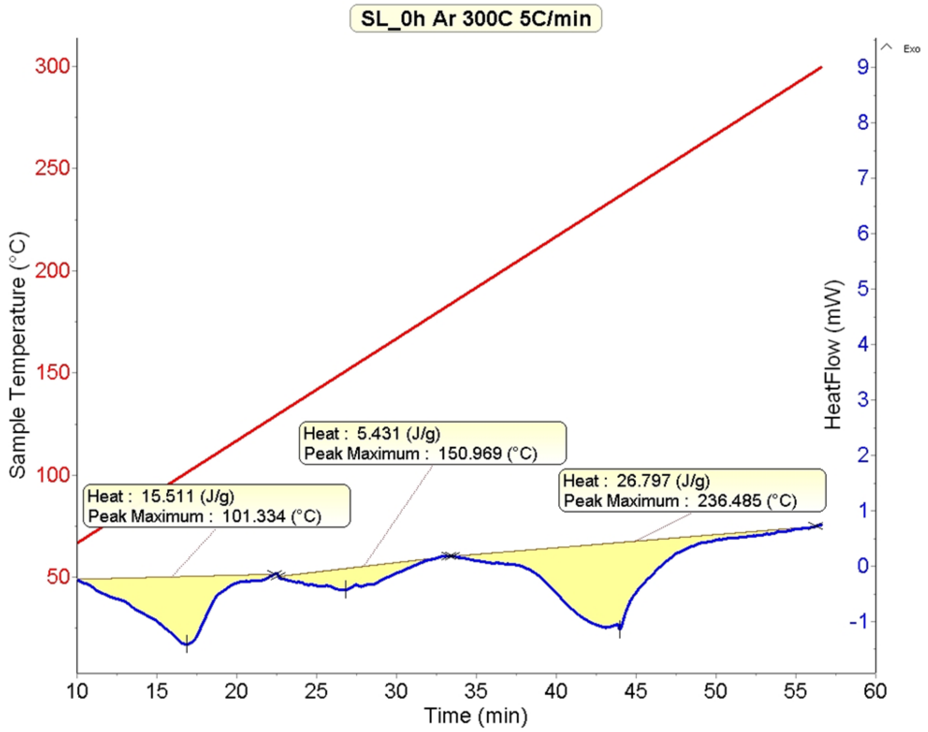

Figure 2. DSC curve of fresh EPR (0h exposure to 140°C).

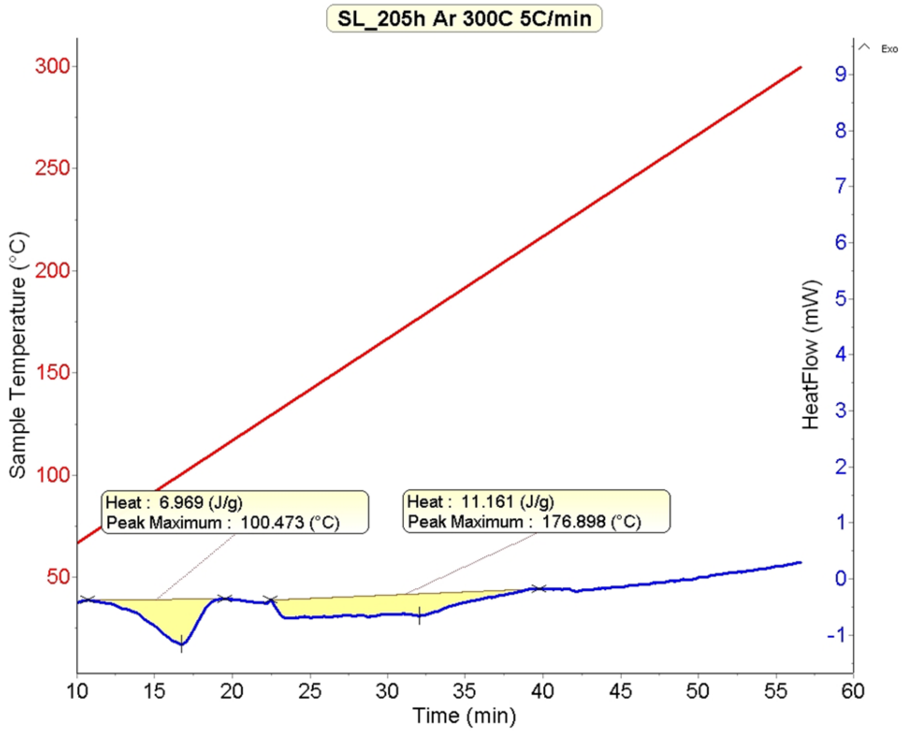

Figure 3. DSC curve of EPR exposure to 140°C in air for 205h.

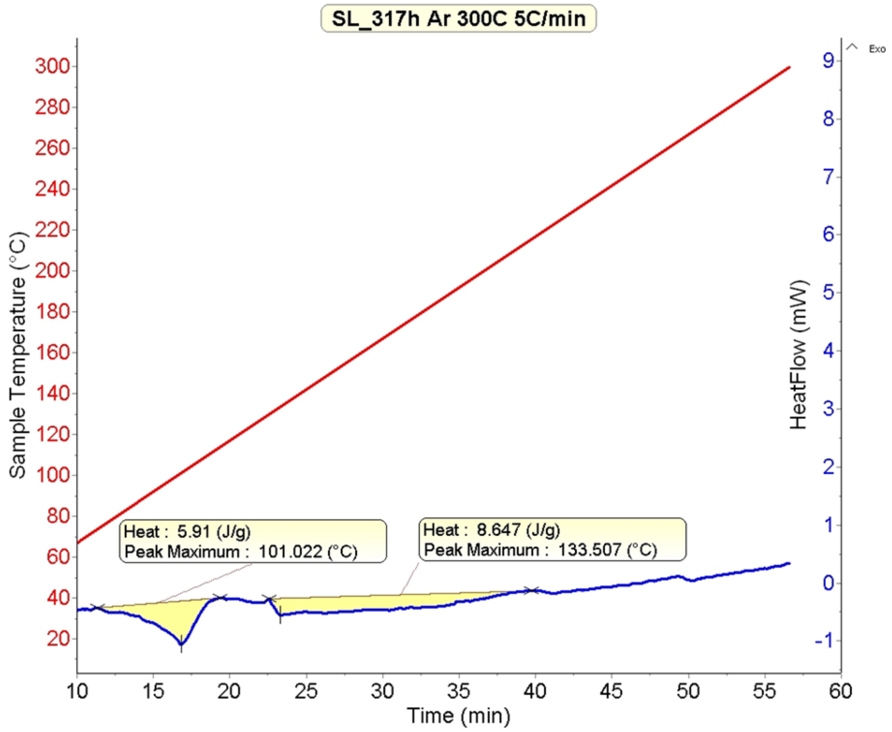

Figure 4. DSC curve of EPR exposure to 140°C in air for 300h.

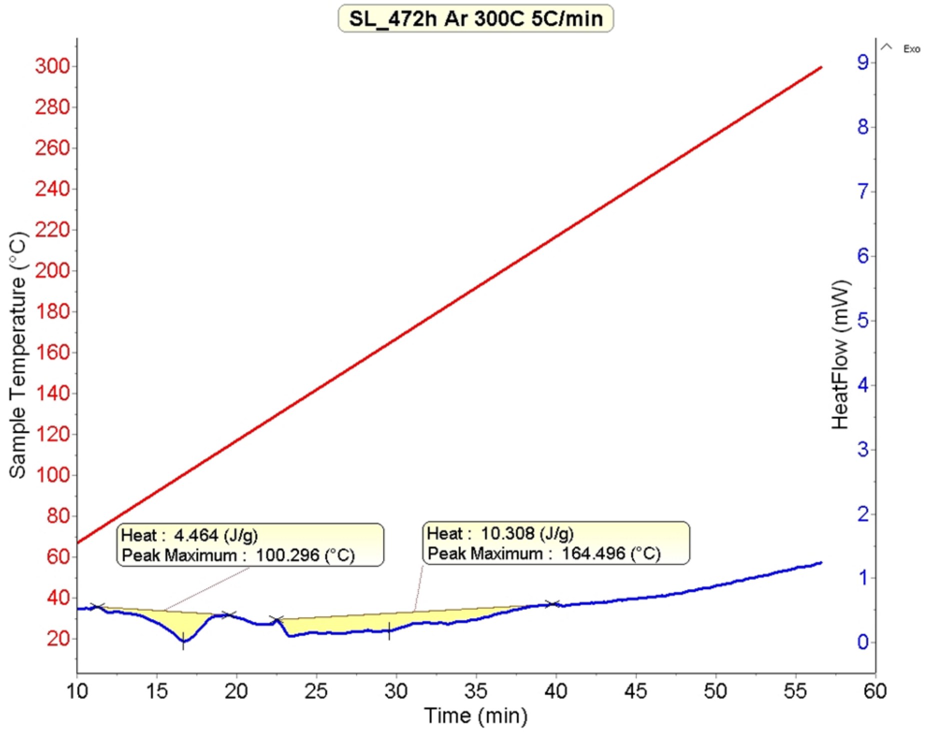

Figure 5. DSC curve of EPR exposure to 140°C in air for 472h.

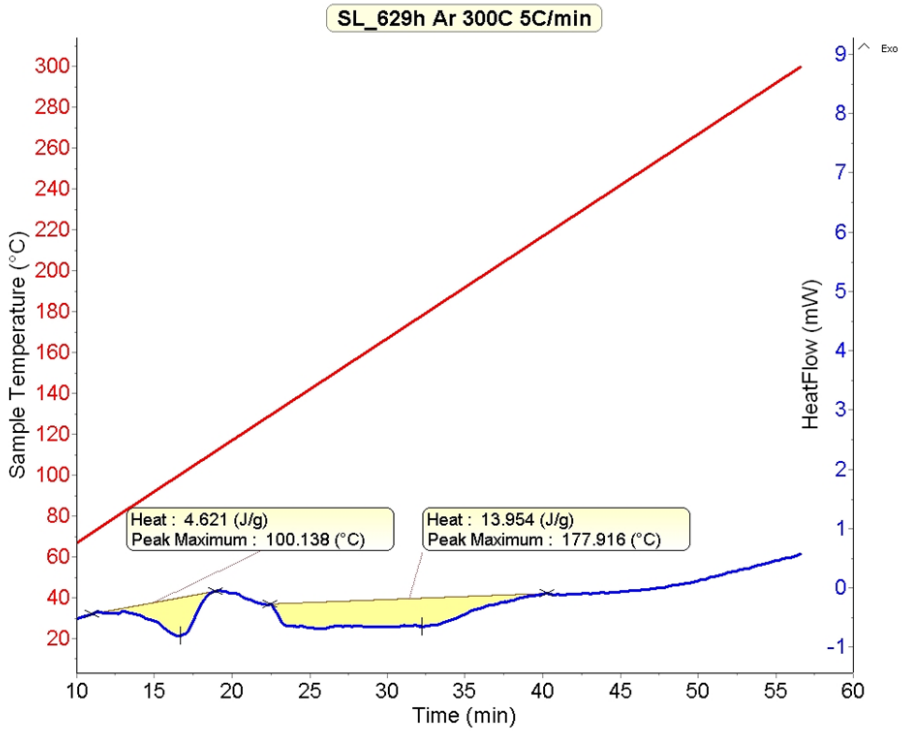

Figure 6. DSC curve of EPR exposure to 140°C in air for 629h.

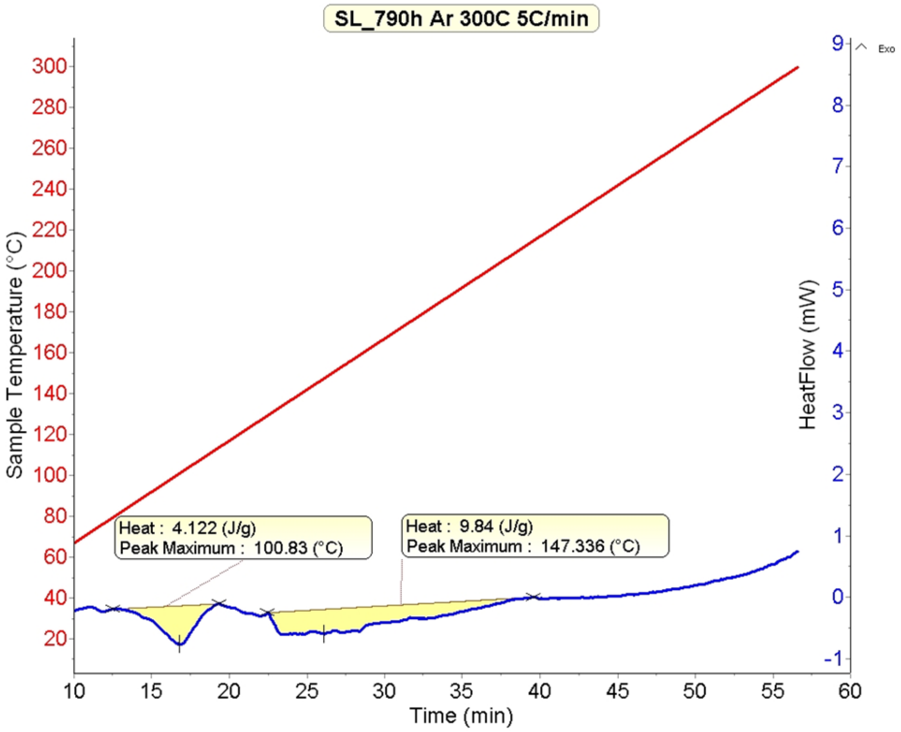

Figure 7. DSC curve of EPR exposure to 140°C in air for 790h.

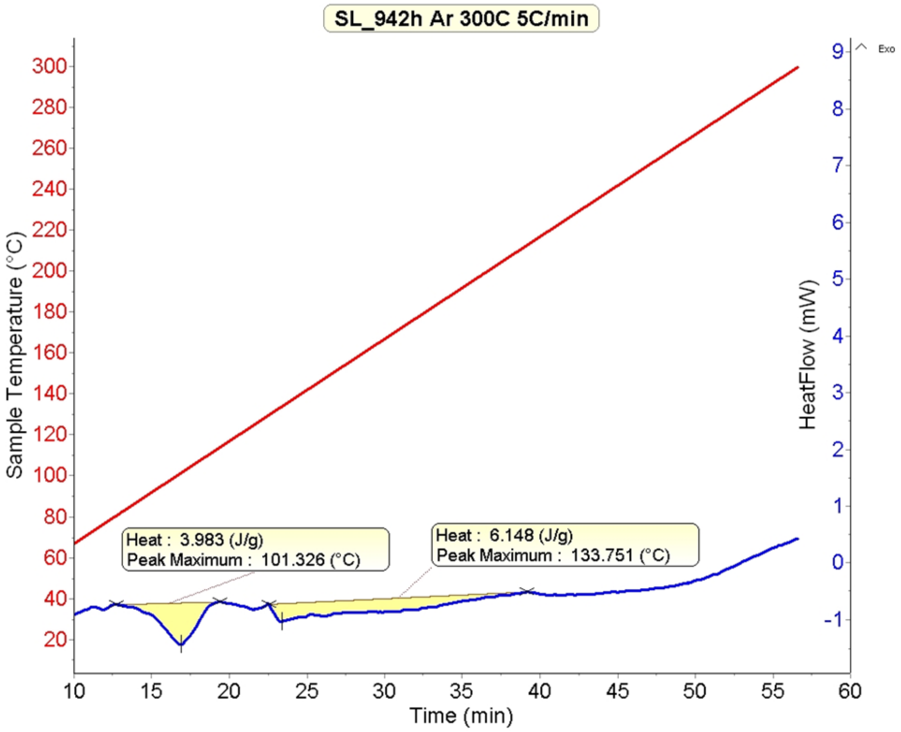

Figure 8. DSC curve of EPR exposure to 140°C in air for 942h.

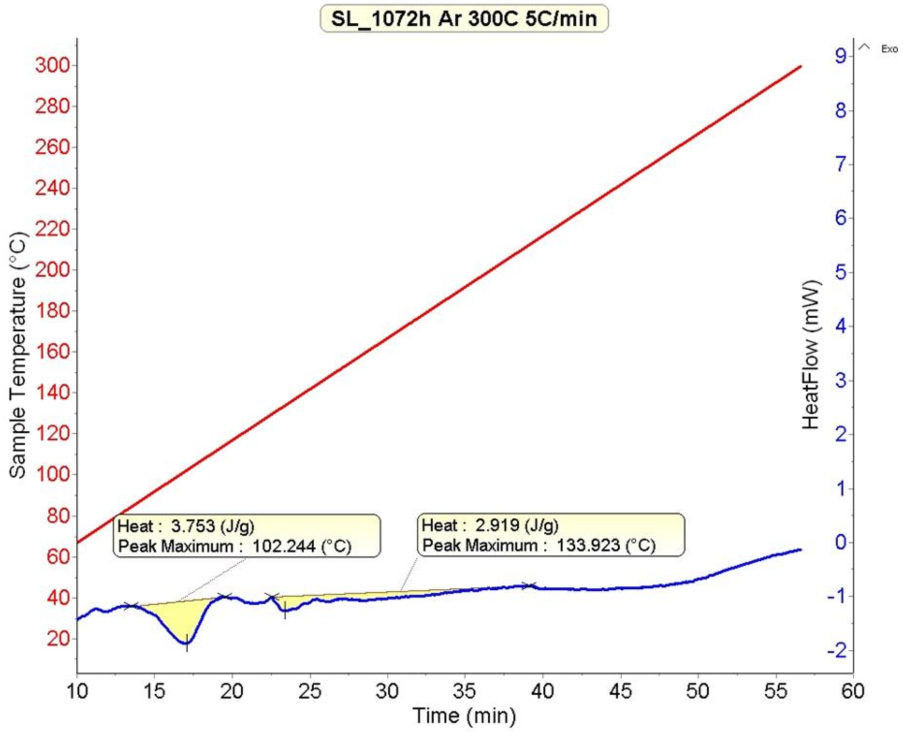

Figure 9. DSC curve of EPR exposure to 140°C in air for 1072h.

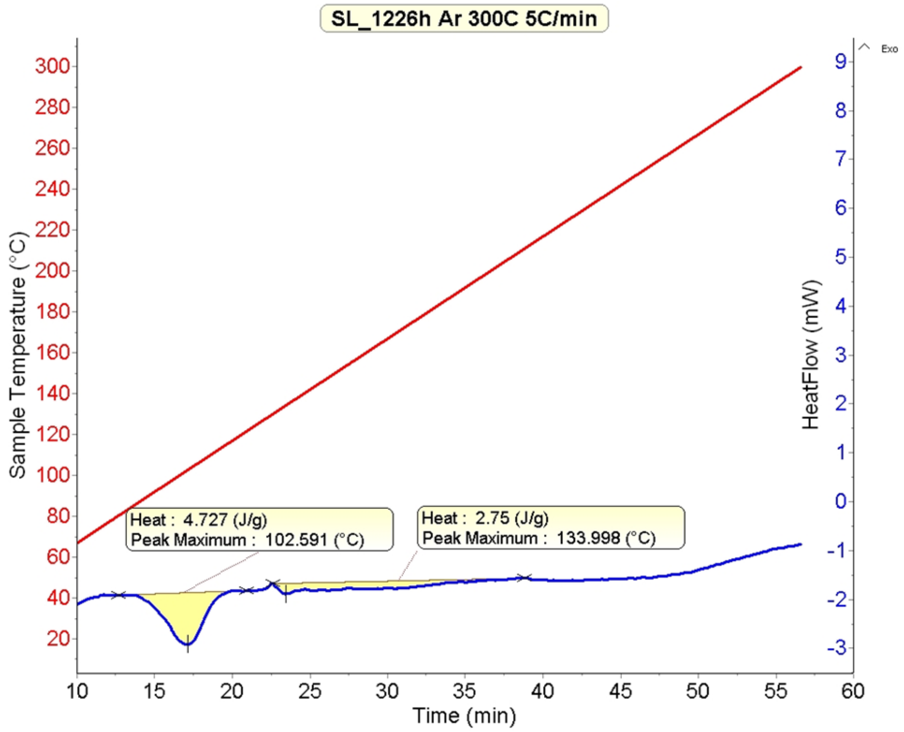

Figure 10. DSC curve of EPR exposure to 140°C in air for 1226h.

The DSC curve of the unaged EPR sample, shown in Figure 2, indicates 3 endothermic peaks, while the oven-aged sample data plot, shown in Figures 3 through 10, indicates only 2 peaks. The two lower temperature events, visible in the data curves of all of the samples, are thought to correspond to the melting of two different polymer components in the EPR formulation. The well-defined peak at around 100°C may correspond to the melting of an additive such as low-density polyethylene (LDPE) or wax in the polymer formulation (see Vanderbilt, 2010 for example EPR formulations). The broad, ill-defined peak in all samples from around 130C to 200°C likely corresponds to melting of the branched and cross-linked ethylene-propylene resin. The approximately 230°C peak in the unaged EPR material DSC data curve likely corresponds to the volatization of organic peroxide byproducts residual from the EPR manufacture. This interpretation of the third peak is supported by a concurrent mass loss observed at this temperature observed when the sample mass is recorded during heating (not shown). A plot of the area under the curve representing the change in enthalpy of the lower temperature transition versus aging time of the EPR sample at 140°C in air is shown in Figure 11. The value is seen to inversely trend with sample exposure time.

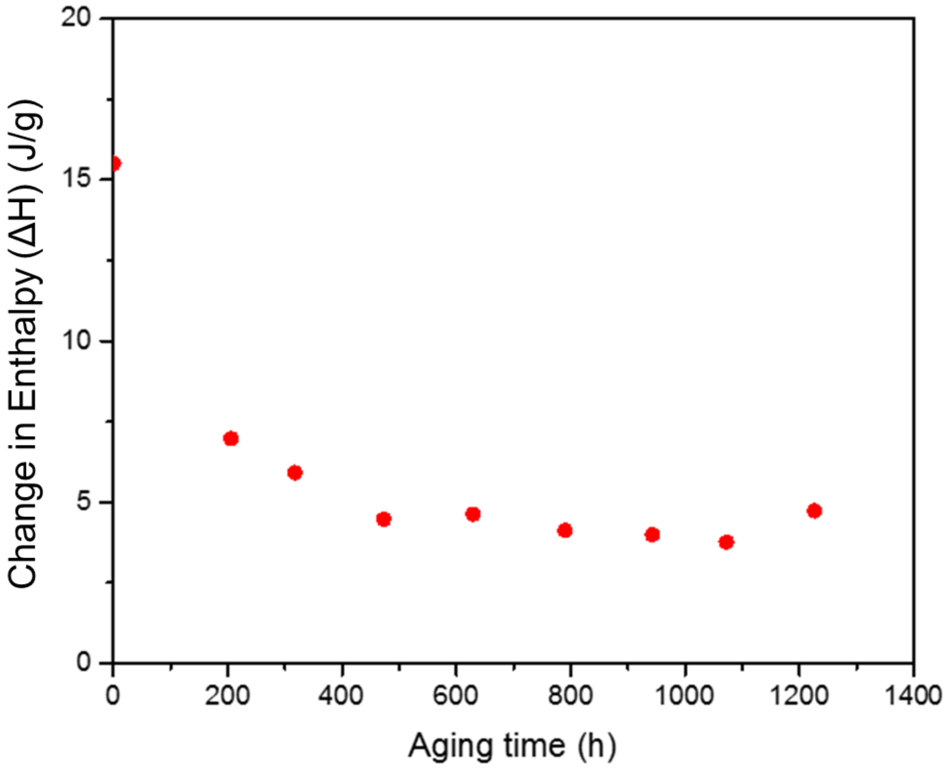

Figure 11. Plot of the change in enthalpy of the ~100°C transition versus EPR exposure time.

The higher temperature, broad transition in the DSC curves of the EPR samples was also observed to trend with EPR exposure time, though the trending was observed to be more complicated with initial decrease followed by increase, then decrease again as seen in Figure 12. This more complex behavior of the heat flow in EPR change with thermal aging may be a result of the complex nature of the cross-linked copolymer EPR matrix as it undergoes oxidative degradation.

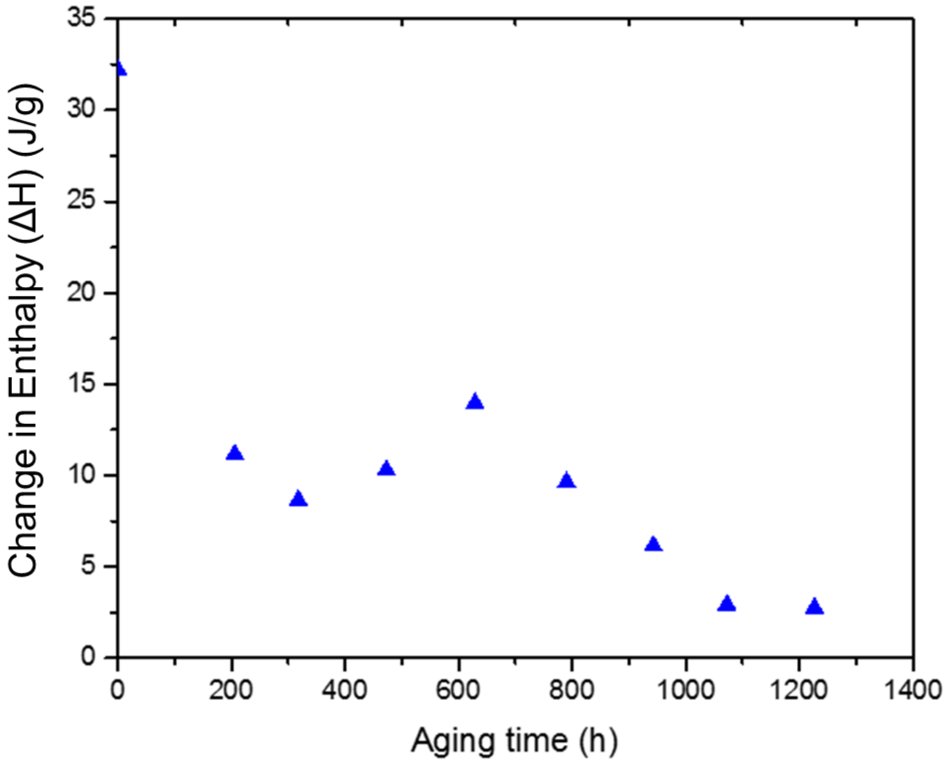

Figure 12. Plot of the change in enthalpy of the ~130-200°C transition versus EPR exposure time.

DSC OF XLPE

White cross-linked polyethylene (XLPE) cable insulation specimens from RSCC® Firewall® III Instrumentation Cable Multi-Conductor Shielded (XLPE/CSPE) (Product Code I46-0021) were heated at 115°C in a mechanical convection oven while simultaneously exposed to gamma irradiation in the High Exposure Facility at Pacific Northwest National Laboratory (PNNL). Dose rates of ~100 Gy/h to ~500 Gy/h and exposure times of 5 to 25 days in 5-day increments were explored. XLPE specimens were also exposed to heating over the same time periods with no gamma dose.

DSC analysis of the XLPE samples exposed to thermal and radiation stress was conducted using a TA Instruments Q2000. In the DSC experiments, samples were heated in helium to 220°C at 5°C/min. The DSC curves for XLPE heated at 115°C with no gamma radiation exposure are shown in Figure 13. As with the EPR samples discussed above, the unaged XLPE sample exhibits an endothermic peak that the aged samples do not. This peak at 110°C may correspond to residual processing aid additive or peroxide byproduct used in the production or cross-linking of the polymer.

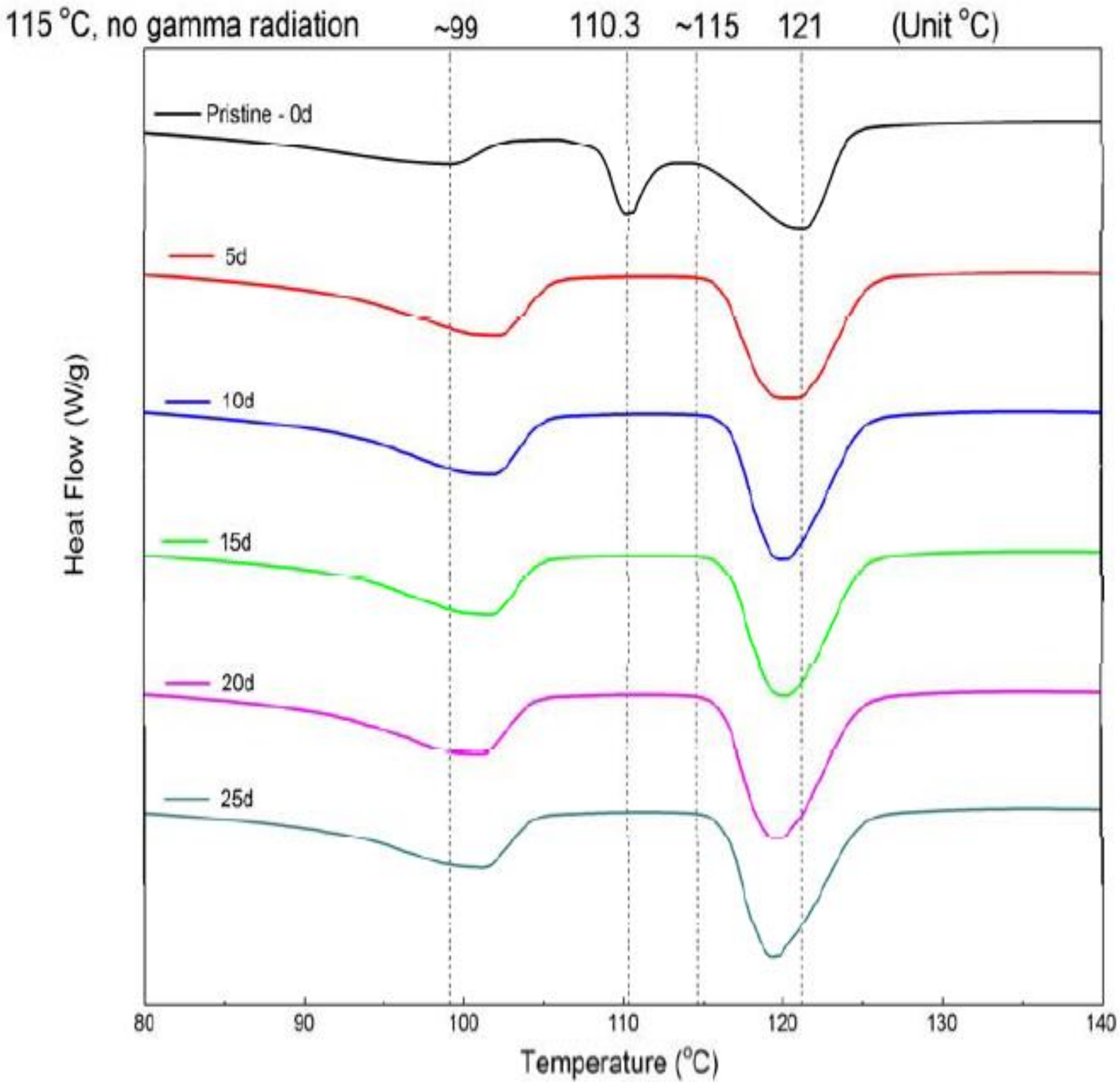

Figure 13. DSC heat flow versus temperature curves for XLPE heated at 115°C for a series of durations.

A series of XLPE specimens were held at 115°C and exposed to gamma radiation at constant dose rates for various durations, producing a range of total doses. The DSC curves for the 230 Gy/h, 350 Gy/h, 450 Gy/h and 540 Gy/h series are shown in Figures 14 through 17, respectively. In general, the higher temperature transition in the DSC curves tends to shift to higher temperature with higher total dose for each of the dose rates explored.

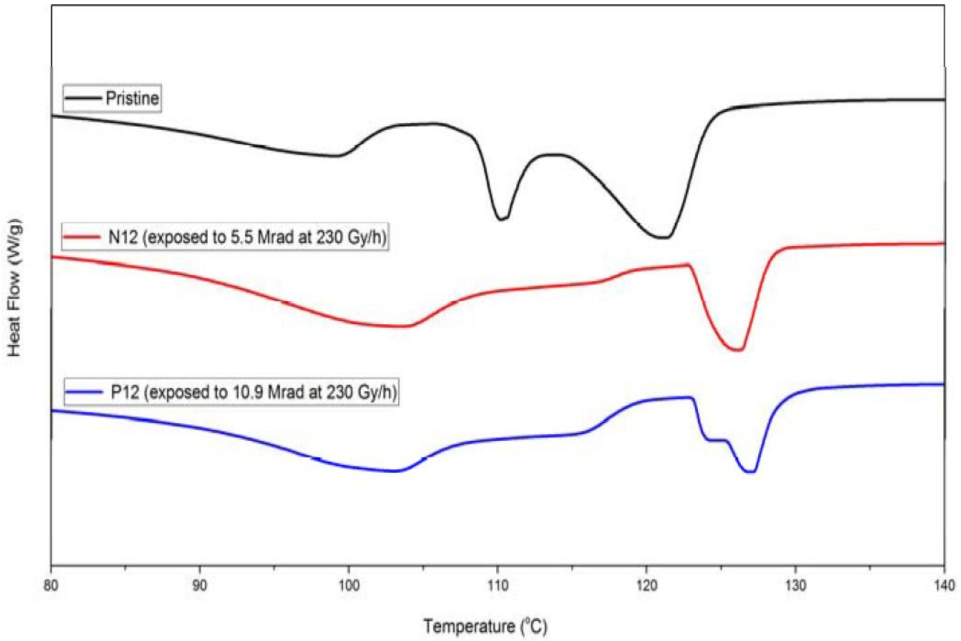

Figure 14. DSC curves for XLPE exposed at 115°C and 230 Gy/h for a series of durations.

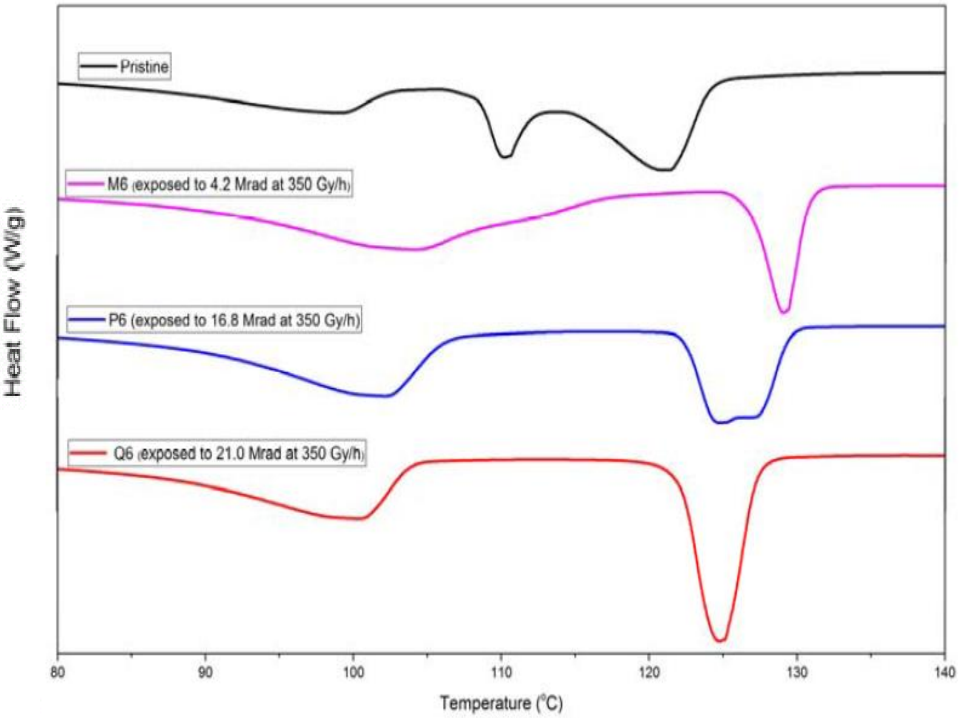

Figure 15. DSC curves for XLPE exposed at 115°C and 350 Gy/h for a series of durations.

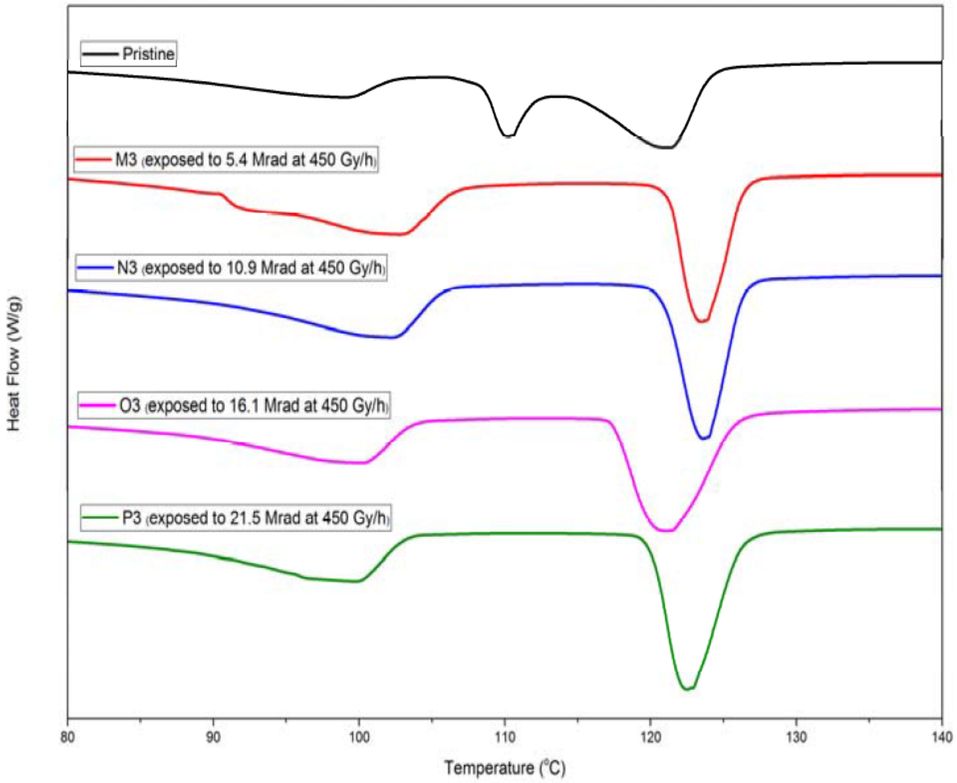

Figure 16. DSC curves for XLPE exposed at 115°C and 450 Gy/h for a series of durations.

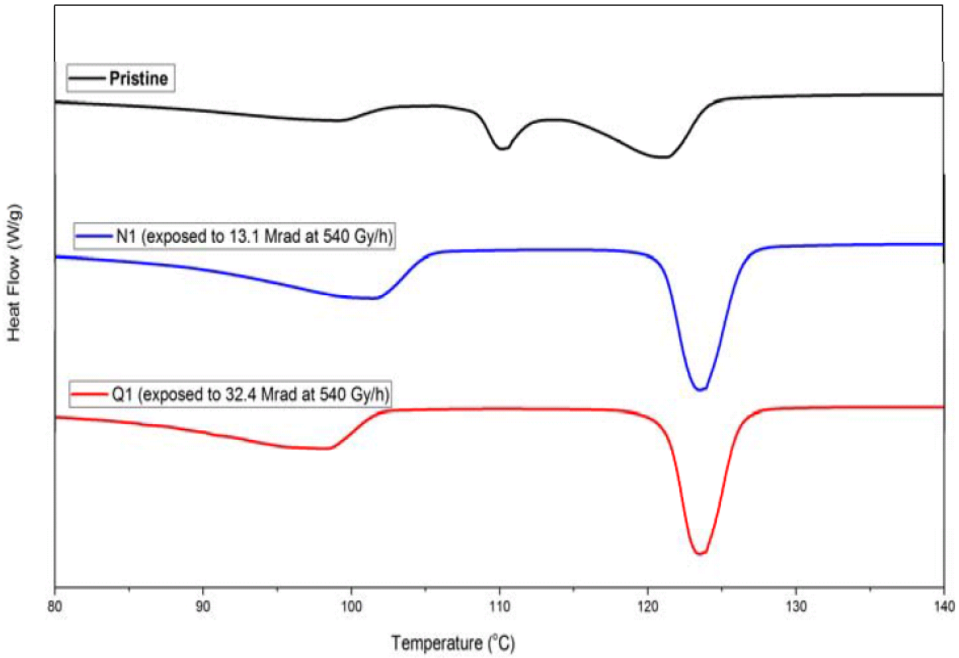

Figure 17. DSC curves for XLPE exposed at 115°C and 540 Gy/h for a series of durations.

A series of XLPE specimens held at 115°C and exposed to gamma radiation at different dose rates are compared as a function of total doses of approximately 5.5 Mrad, 11 Mrad, 16.5 Mrad and 21 Mrad are shown in Figures 18 through 21, respectively. The higher temperature transition in the DSC curves does appear to vary with dose rate and to be composed of two or more distinct transitions in certain samples.

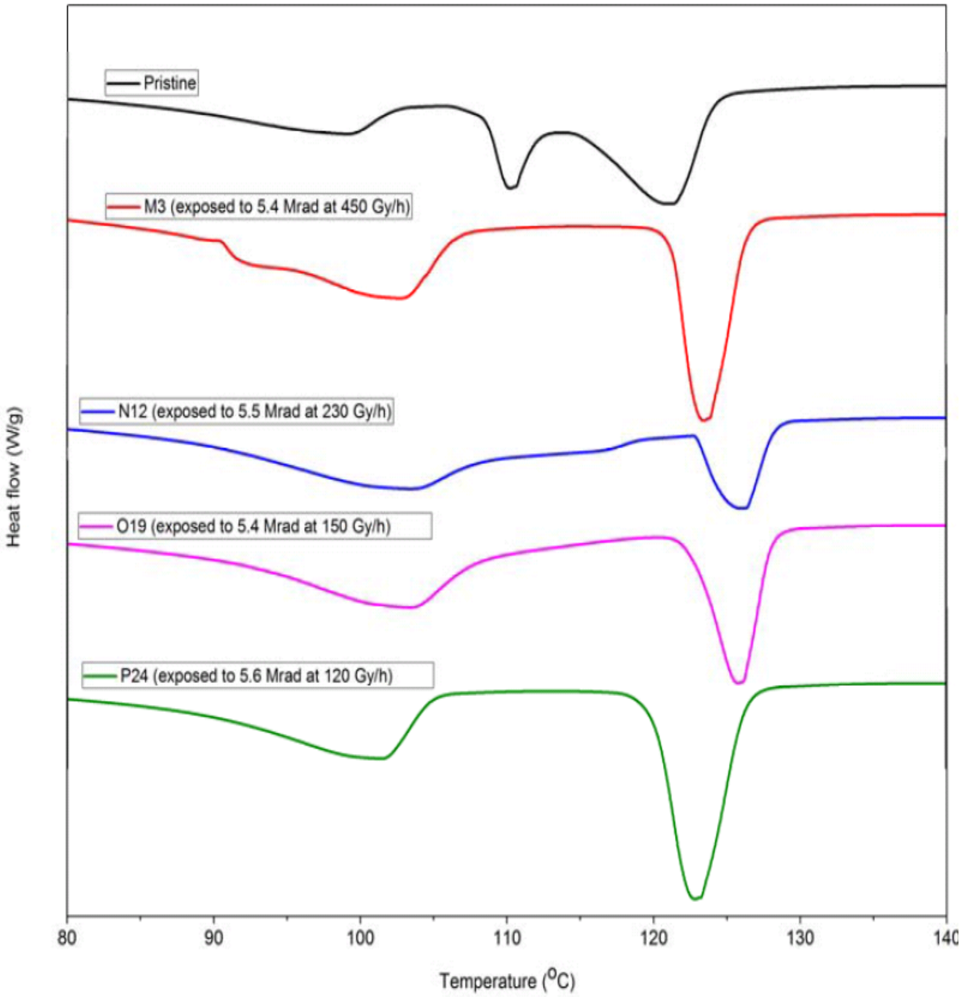

Figure 18. DSC curves for XLPE exposed at 115°C and 5.5 Mrad by a series of dose rates.

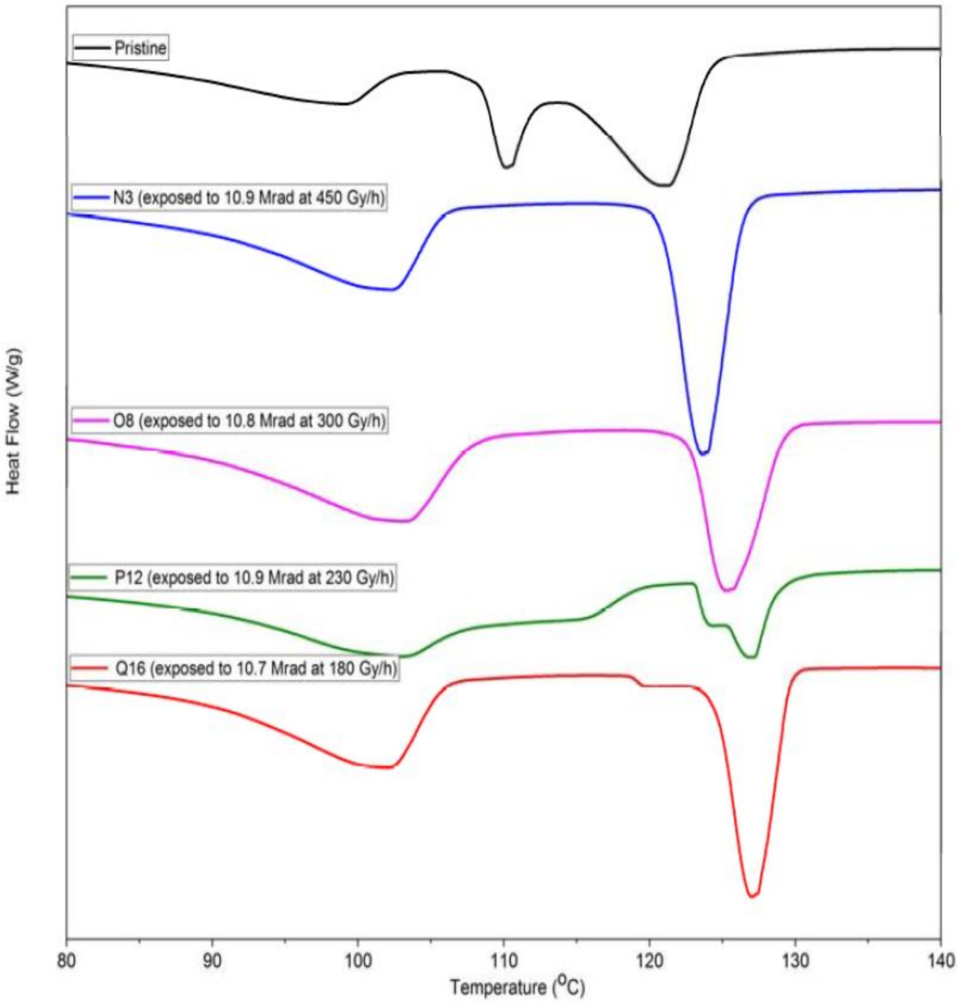

Figure 19. DSC curves for XLPE exposed at 115°C and 11 Mrad by a series of dose rates.

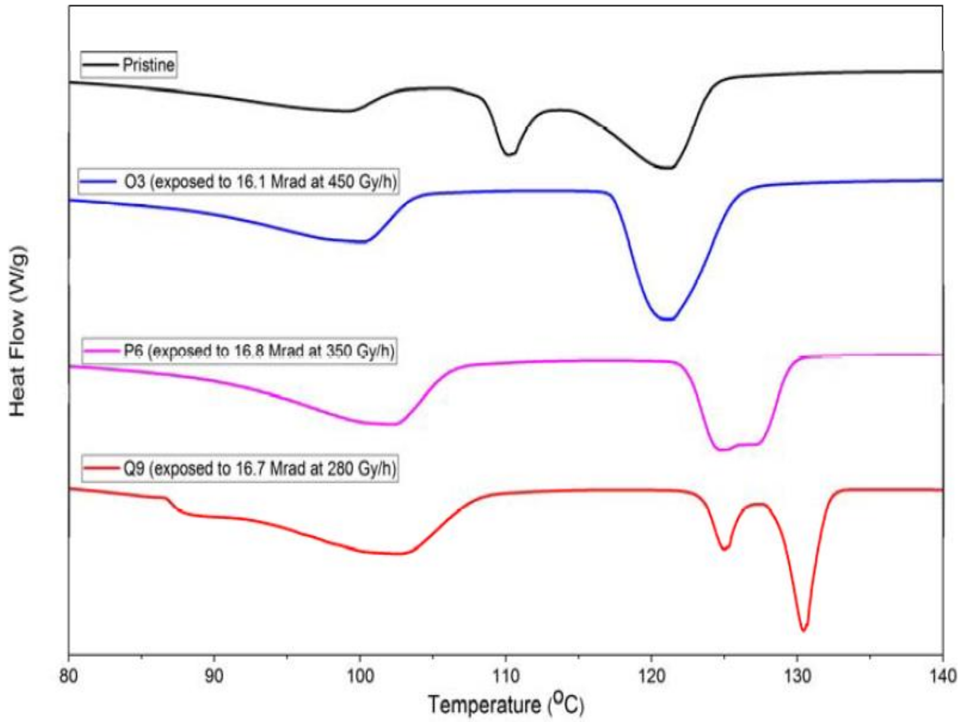

Figure 20. DSC curves for XLPE exposed at 115°C and 16.5 Mrad by a series of dose rates.

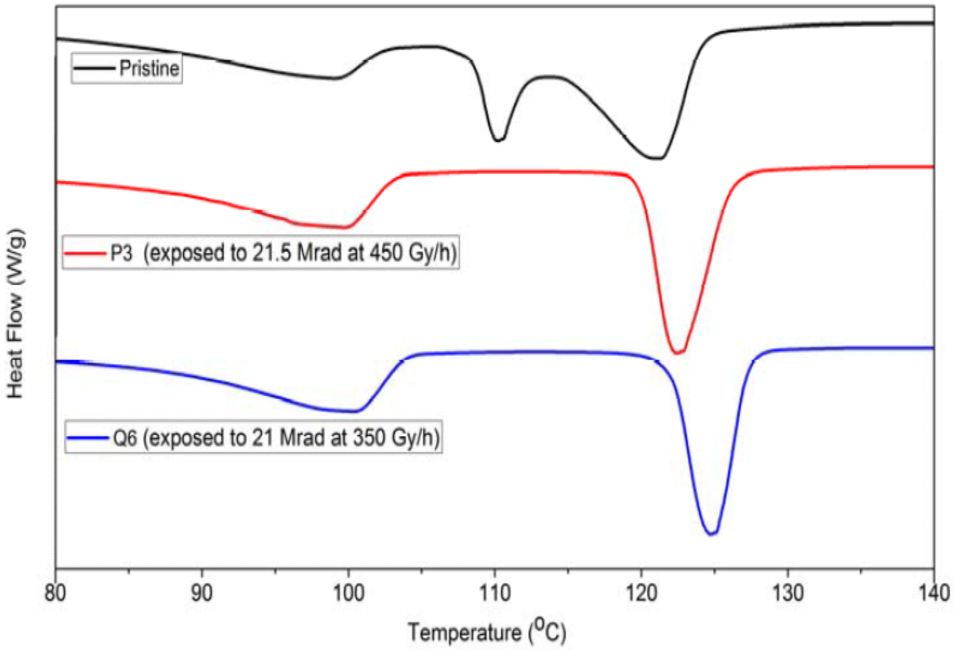

Figure 21. DSC curves for XLPE exposed at 115°C and 21 Mrad by two dose rates.

OIT OF XLPE

OIT experiments were performed on the same XLPE samples, exposed to 115°C and gamma irradiation, as described in the DSC of XLPE section above. For the OIT experiments using the TA Instruments Q2000 DSC, the samples to be tested were heated at 15°C/min to 230°C in helium atmosphere. Upon reaching 230°C, the samples were held for 2 min before carrier gas was changed to oxygen. Each sample was held under these conditions until an exothermic event occurred indicting oxidative reaction. Figure 21 shows the OIT curves for XLPE samples exposed to 115°C for various periods of time without gamma radiation exposure. The time between switching to oxygen gas and onset of the exothermic event is seen to decrease with thermal stress exposure time.

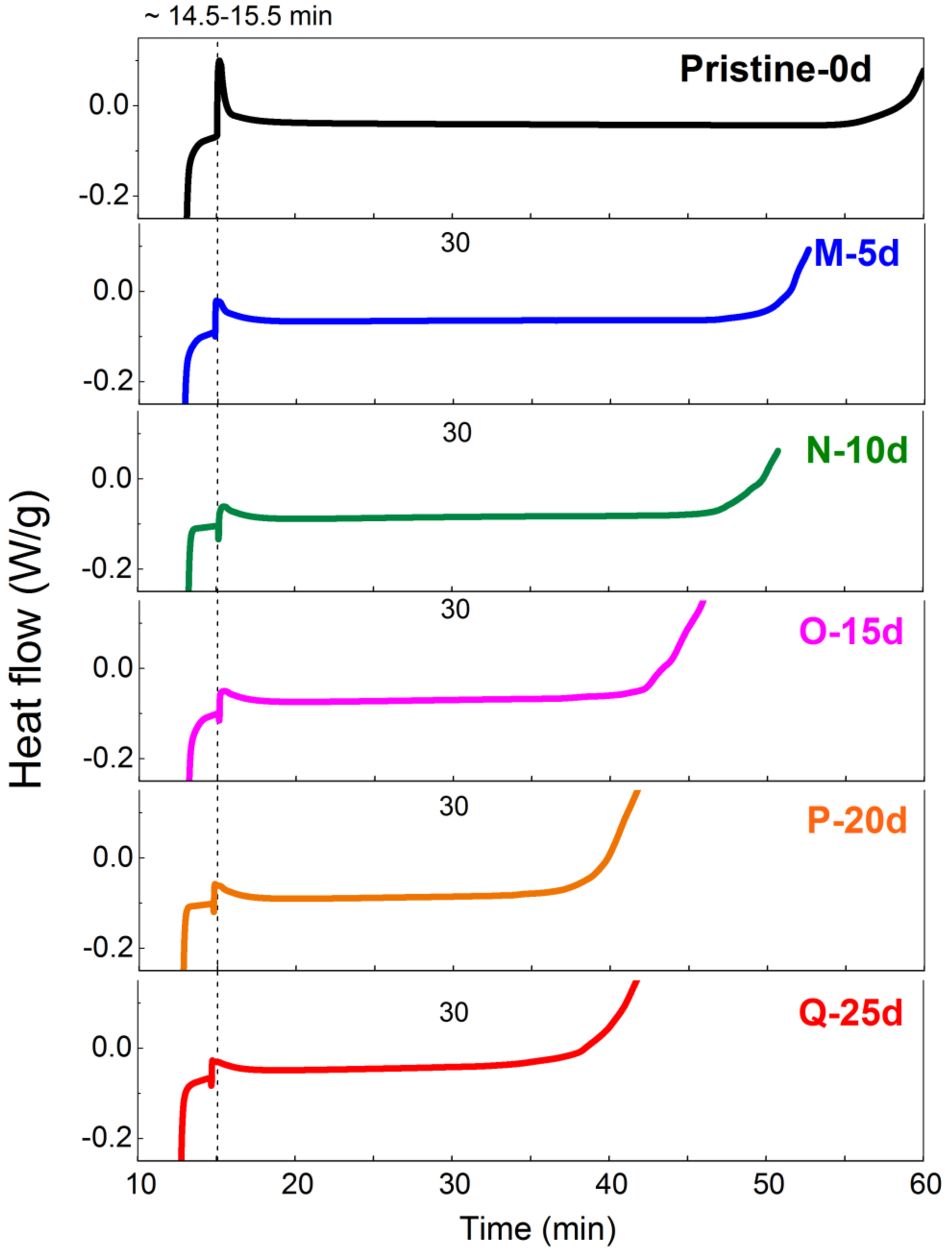

Figure 22. OIT curves of XLPE heated at 115°C for various durations.

OIT curves for XLPE samples heated at 115°C to various total doses at constant gamma dose rates are shown in Figure 23. OIT appears to decrease with total dose at constant dose rates.

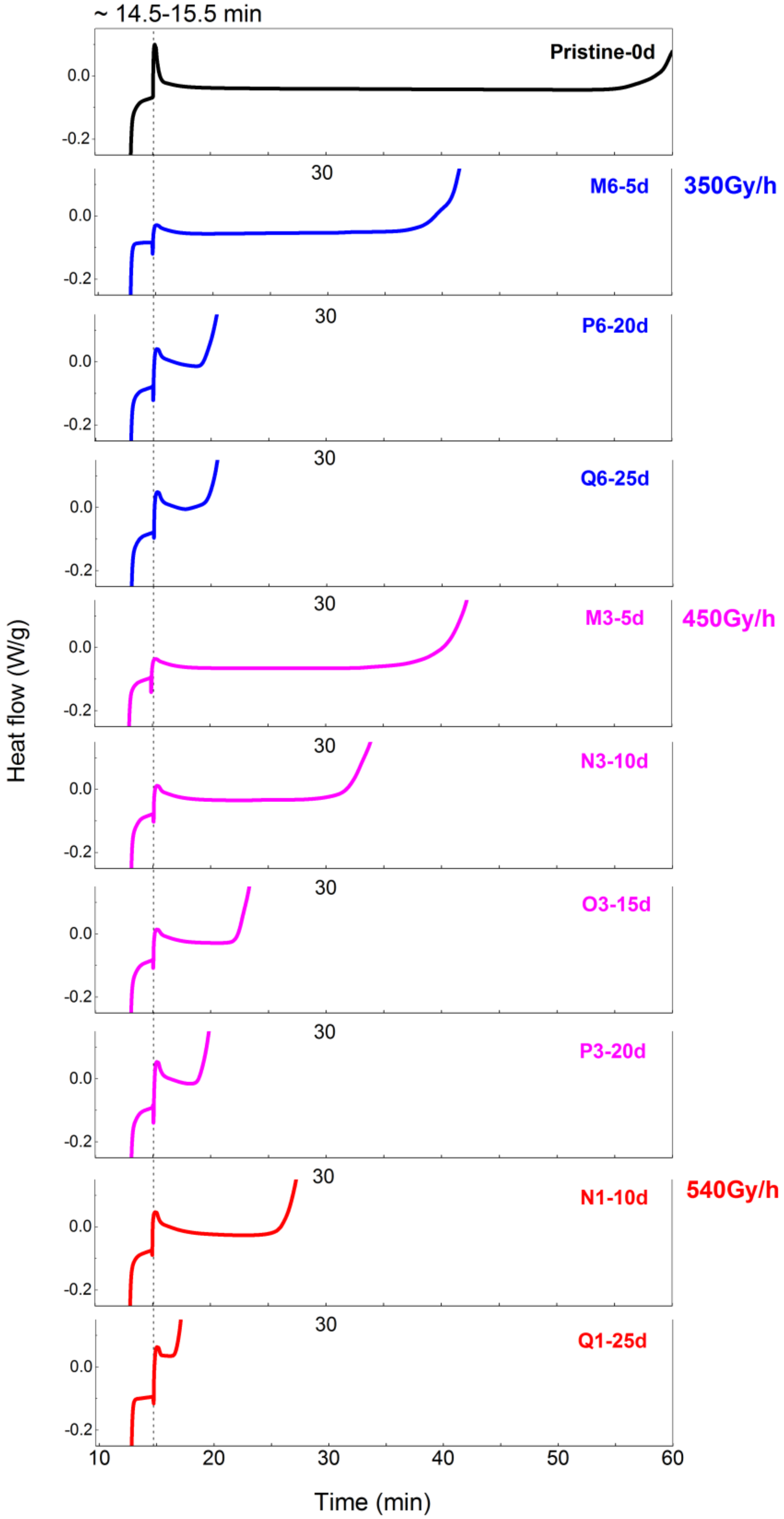

Figure 23. OIT curves of XLPE heated at 115°C to various total doses via constant dose rate.

OIT curves for XLPE samples heated at 115°C to constant total doses via various dose rates are shown in Figure 24. OIT seems to decrease with lower dose rate to constant total dose.

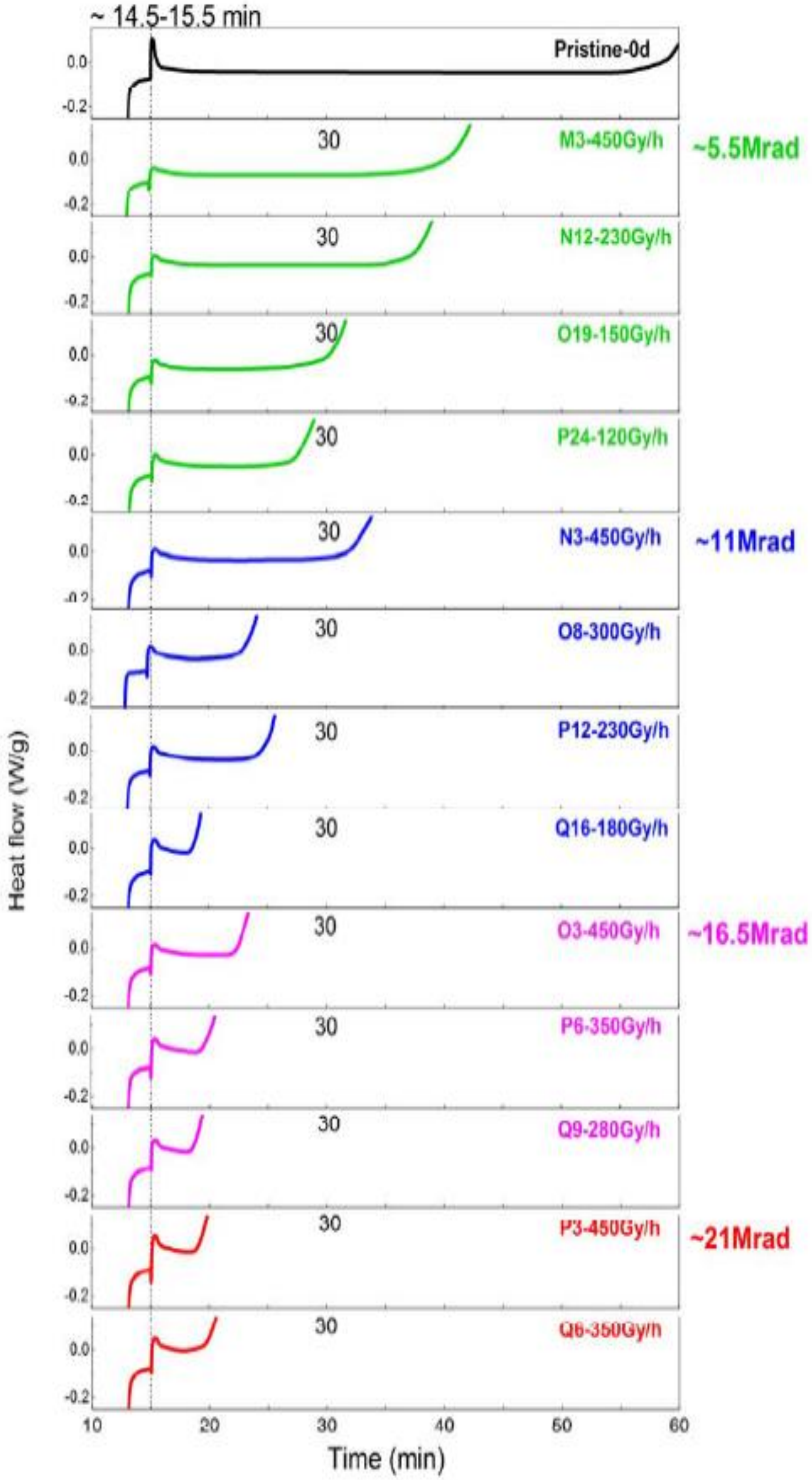

Figure 24. OIT curves of XLPE heated at 115°C to constant total doses via various dose rates.

CONCLUSION

Addressing cable aging knowledge gaps related to thermal stress, gamma radiation stress, and combination of the two such as activation energies, synergistic effects, inverse temperature effects, and dose rate effects will require sensitive and quantitative techniques to measure material changes in cable insulation (NUREG/CR-7153, Vol. 5, 2014). DSC and OIT have been explored as condition monitoring techniques to track changes in crystallinity, antioxidants, and volatile components in cables with aging. International standards organizations have published suggested methods for performing DSC and OIT analyses, including specifically for cable materials.

The DSC and OIT results described above reveal changes in EPR and XLPE materials with exposure to thermal stress and to radiation exposure. In the thermal aging of black, Okonite® FMR-EPR at 140°C experiments described above, two major transitions were observed in the DSC heat flow curves. The lower temperature transition, with peak around 100°C, was well-defined and probably corresponds to the melting point transition of a relatively narrow-range polymer component of the EPR system. It may correspond to the melting of LDPE or paraffin wax in the formulation. In contrast, the higher temperature transition observed in the DSC curves of the FMR-EPR is much broader, initiating around 120°C and extending to around 180°C. This transition is likely due to the melting of the much broader molecular weight-range ethylene-propylene copolymer resin. The area under the curve for the lower temperature transition, indicating the mass of the sample giving rise to the event, is observed to decrease in magnitude with EPR exposure time at 140°C (Figure 11). This behavior may be explained by degradation of the LDPE or wax with aging. The trend of the area under the broad, higher temperature transition in the DSC curves of the FMR-EPR is more complex, first decrease with exposure at 140°C, then increasing to a peak after 600 h of aging, then decreasing again. This trend result requires more investigation and may be due to the way that the ill-defined transitions are analyzed in the Setaram DSC software.

The DSC curves of the Firewall® III XLPE aged at 115°C with no gamma irradiation (Figure 13) exhibit a thermal transition at around 99°C and a larger, sharper transition at ~120°C. The unaged material data has an additional, sharp transition at ~110°C that completely disappears within the first 5d of heating. The persistent, larger peaks are probably melting transitions of polymer components, perhaps smaller and large molecular weight polyethylene species. The small peak that vanishes with thermal aging likely corresponds to a volatile component of the formulation such as a processing aid or antioxidant byproduct from polymer system production. Interestingly, the higher temperature transition resolves into two or more distinct peaks for certain of the aging combinations that include radiation. For instance, in the series of XLPE samples exposed to 115°C and 16 Mrad total dose (Figure 20), the highest dose rate of 450 Gy/h produces a single transition peak at around 120°C, while the at the lower dose rates of 350 Gy/h and 280 Gy/h the peak separates into two peaks. The phenomena may be related to the competition between chain scission and polymer chain cross-linking from oxidative damage as a result of combined thermal and gamma radiation exposure.

The DSC-determined OIT curves of Firewall® III XLPE exhibit a distinct decrease in OIT with exposure of the polymer to 115°C (Figure 22). This trend is likely due to consumption of antioxidant initially present in the XLPE with thermal exposure. The longer the XLPE is exposed, the more antioxidant is consumed, and the shorter the time that is required to produce an exothermic response with heating in the OIT experiment. Similarly, fore XLPE samples held at 115°C at constant dose rates (Figure 23), OIT decreases with exposure. Comparison of this trend with the no dose series and analysis of similar data from exposures at other temperatures will help to elucidate the contributions to this decrease in OIT from thermal exposure and from the radiation. The decrease in OIT did seem to proceed differently at the 350 Gy/h, 450 Gy/h and 540 Gy/h dose rates explored in this work. For XLPE samples held at 115°C to similar total doses via different dose rates (Figure 24), total dose definitely seemed to correspond to short OIT. However, longer exposures to the thermal stress were required to reach higher total dose. Future temperature studies using similar dose rates and total doses will similarly help to illuminate the relative contributions of gamma and thermal aging on XLPE low voltage cable insulation.

As demonstrated in the experimental results described above, characterization of the oxidation of cable insulation materials using DSC techniques including OIT is useful for investigation of material changes with aging. Careful selection of exposure conditions, controlling variables of temperature, exposure sequence, dose rate and total dose, will enable analysis of the relative roles of these aging factors in cable polymer degradation due to oxidation. Combining DSC techniques with complimentary condition monitoring methods to explore multi-factor aging in the most relevant cable materials will address knowledge gaps for electrical cable and cable system longevity in nuclear power plants. Addressing these gaps will support cable aging management and long-term plant operations.

REFERENCES

ASTM International. *Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry*. ASTM D3895-14. 2014.

ASTM International. *Standard Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry*. ASTM E1858-08 (Reapproved 2015). 2015.

IEC/IEEE 62582-4. *INTERNATIONAL STANDARD: Nuclear power plants – Instrumentation and control important to safety –Electrical equipment condition monitoring methods –Part 4: Oxidation induction techniques*. IEC Central Office/Institute of Electrical and Electronics Engineers, Inc. 2011.

Gillen, K.T., R.A. Assink, and R. Bernstein. *Nuclear Energy Plant Optimization (NEPO) Final Report on Aging and Condition Monitoring of Low-Voltage Cable Materials*. Sandia National Laboratories. SAND2005-7331. 2005.

Gillen, K.T. and R. Bernstein. *Review of Nuclear Power Plant Safety Cable Aging Studies with Recommendations for Improved Approaches and for Future Work*. Sandia National Laboratories. SAND2010-7226. 2010.

Hashemian, H.M. and K.-S. Kang. *Results of IAEA Project on Cable Condition Monitoring and Ageing Management*. Presented to EPRI Cable User Group, Columbia Marriott Hotel South Carolina. Wednesday, August 5, 2015.

Menczel, J.D. and R.B. Prime, Editors. Thermal Analysis of Polymers: Fundamentals and Applications. John Wiley and Sons. 2009.

NUREG/CR-7153, Vol. 5. *Expanded Materials Degradation Assessment (EMDA) Volume 5: Aging of Cables and Cable Systems*. 2014.

R.T. Vanderbilt Company, Inc. The Vanderbilt Rubber Handbook, 14th Edition. 2010.