Mechanistic Understanding of Distearyl Thiodipropionate as an Antioxidant in the Cross-Linking of Polyethylene

Charles Winslow, Fiaz Mohammed, Mark Conley, Harris Eldridge, Pamela Pollet, Charles Liotta, Charles Eckert

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA

Cross-linked polyethylene (XLPE) is used as insulation in high and medium voltage electric cables. It is primarily synthesized through the free- radical induced crosslinking of polyethylene (PE) using organic peroxides as the radical initiator. One such initiator which is commonly used is dicumyl peroxide (DCP). However, during the processing of the PE, a small percentage of DCP undergoes homolytic cleavage into its cumyloxy radicals which subsequently causes premature cross-linking, or scorch. Scorching affects the ability of the PE to be processed and also reduces the physical and chemical properties of the final end product. To prevent scorching, different antioxidants and stabilizing additives are used to inhibit the free radicals produced during the processing stage. This ensures that uniform cross-linking will occur and the XLPE will have enhanced inductive properties. A frequently used additive is the secondary antioxidant distearyl thiodipropionate (DSTDP). However, despite its use in conjunction with other primary antioxidants, a detailed investigation of PE blends using only DCP and DSTDP has not been proposed in literature to the best of our knowledge. This work therefore explores the underlying chemistry of the thermal decomposition of DCP in the presence of DSTDP to determine how this antioxidant prevents scorch.

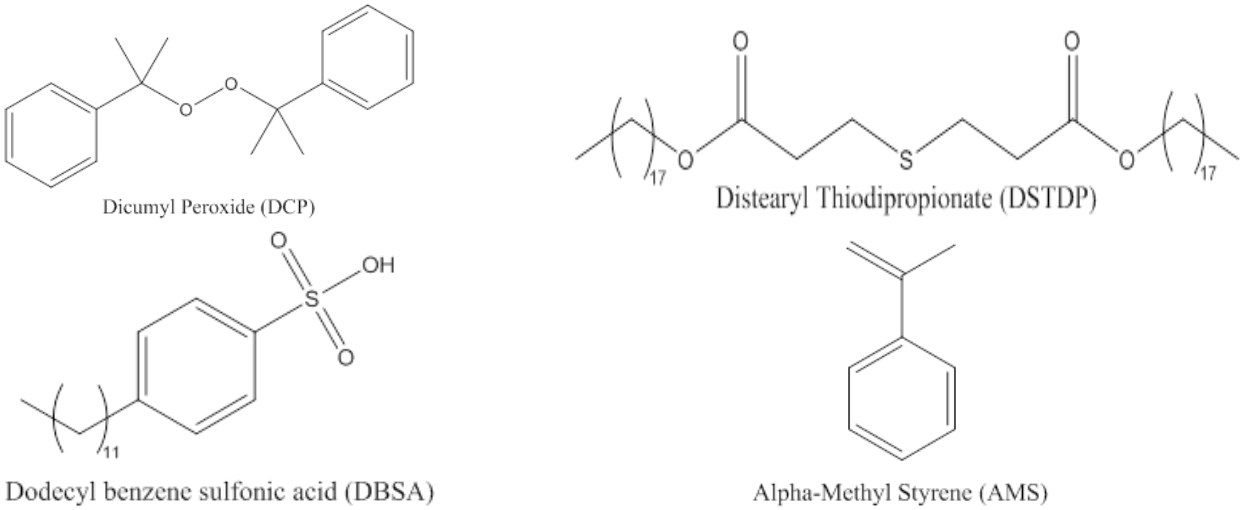


Figure 1: Main Species Used in Studies

The work was primarily performed in a liquid system using dodecane as a solvent to simulate polyethylene. A temperature range from 70 °C to 140°C was used for kinetic studies and to determine the overall effects of temperature on our system. The temperature most commonly used was 120°C, a temperature where thermal degradation of DCP was still relatively slow but the significant chemistries between DCP and DSTDP were accelerated. At this temperature, experiments were performed in both

inert environments and environments open to the air with varying concentrations of DSTDP as well as its oxidized derivatives (DSTDP-sulfoxide and DSTDP-sulfone). A series of acid studies were also performed where low concentrations of dodecyl benzyl sulfonic acid (DBSA) were introduced into the DCP and DSTDP environments under argon. Species identification and quantification were determined using proton NMR, GCMS and HPLC.

By tracking DCP concentrations over the reactions of varying DSTDP concentrations in an environment open to air, it was observed that the rate of DCP decomposition increased with the concentrations of DSTDP until a maximum rate was observed at .25 molar equivalents of DSTDP. Furthermore, the rate of DCP degradation decreased as the oxidation level of DSTDP increased. However, under argon, this rate was comparable to the rate that DCP degrades by itself under a similar environment and temperature; this was also observed with DSTDP's oxidized derivatives. When DBSA was introduced into the inert environments, though, the rate of DCP degradation was comparable to that of the above DSTDP and DCP system that was open to air. Another important observation is the presence of α-methyl styrene (AMS) was observed only in the systems where DSTDP was present in air or the acid was present under argon. .

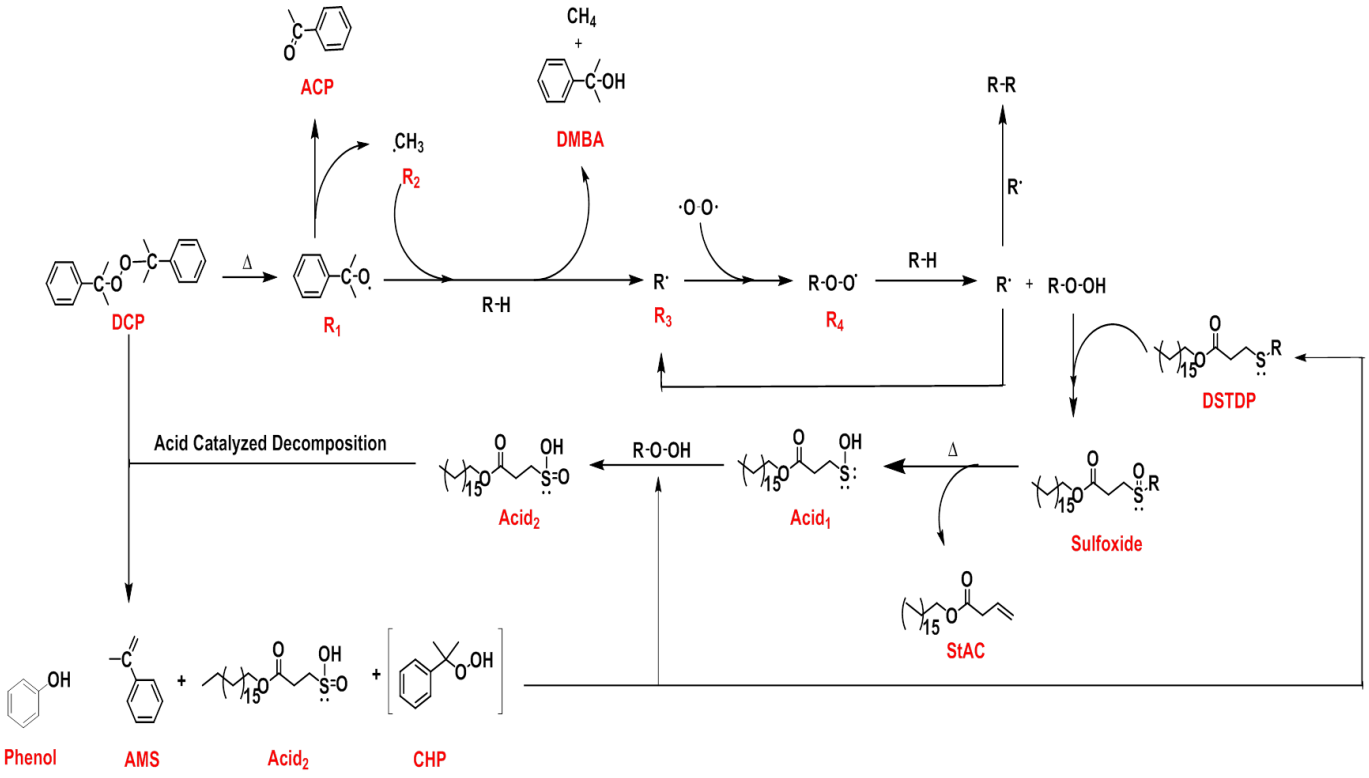


Figure 2: Working Mechanism for Reaction of DSTDP and DCP in Air

These observed effects can be explained through a detailed mechanism, shown in Figure 2, by which alkylhydroperoxides, formed when alkyl radicals reacted with triplet oxygen in the air, oxidize DSTDP into DSTDP-sulfoxide. The in-situ DSTDP-sulfoxide can then go under a retro-michael addition at the processing temperature, forming a hyposulfenic acid and a subsequent acrylate. It is conjectured that the hyposulfenic is then further oxidized into a sulfenic acid, subsequently catalyzing the decomposition of

DCP into cumene hydroperoxide (CHP) and AMS. As a reactive intermediate, CHP contributes to the oxidization of DSTDP into DSTDP-sulfoxide, forming an auto-catalytic cycle as more hyposulfenic acid is formed by the retro-michael of the newly formed DSTDP-sulfoxide. Lastly, the AMS, formed from both acid-catalyzed decomposition of DCP and the dehydration of cumyl alcohol, could then dimerize through both cationic and radical pathways to form a known radical sink.

In conclusion, the study of DCP and DSTDP has led to a working mechanism by which DSTDP is oxidized before undergoing a retro-michael addition and decomposing DCP into AMS and CHP. This AMS formed can quench the cumyloxy radicals by dimerizing and acting as a radical sink, thus preventing premature cross-linking, which improves the processing efficiency of XLPE.