Kinetic parameters of the thermal degradation of polymers by chemiluminescence

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Today, polymers are everywhere and used for almost everything. The market is still growing year after year to reach a production of 356Mt in 2013, with 20% of the production in Europe, especially in Germany[1]. Although packaging is the major market for plastics, the two other big markets, building-construction and automotive, are more interesting if we consider the lifetime of polymers. There is a lot of suppliers in the plastic industry, but no one is capable to give, with 100% certainty, the lifetime of their plastics or polymers under precise conditions.

It is well known that polymers age by oxidation, and there are three kinds of oxidation processes: photo-oxidation, chemical-oxidation and thermal-oxidation. In our case, we discuss thermal oxidation because polymers are always used in different thermal-conditions and, depending on the temperature of application, the lifetime of polymers can change considerably. If we can find the kinetic parameters of plastics under thermal-oxidation, it will be possible to find the real lifetime of polymers at every possible temperature.

Thermal-degradation of polymers generates hydroperoxydes and peroxy radicals as intermediates in a kinetic chain mechanism[2], and when two radicals react together, there is a light emission. This light emission can be measured by chemiluminescence (CL). Luminescence is defined as the emission of light by a substance which is not resulting from heat, and when the prefix *chemi-* is added it means that the light emission is induced by a chemical reaction. As we have mentioned, oxidation of polymers is accompanied by weak chemiluminescence emission, and that makes the observation of the oxidation processes at various temperatures possible.

To find the kinetic parameters for the thermal-degradation of polymers by chemiluminescence, there are three steps to perform. The first one is to do isothermal measurements on the polymer, in order to obtain at least five CL curves. These curves have then to be fitted in order to find the oxidation rate constant at each temperature. At the end, with the help of Arrhenius law, the activation energy and the pre-exponential factor are found.

This method was used to find the kinetic parameters of polyethylene. The chemiluminescence instrument was an ACL instrument understanding oxidation (Instrument Version 5.0). The isothermal measurements were made at five different temperature, under oxygen environments. We found a value of 94 kJ/mol for the activation energy, and $2.92 \cdot 10^7$ s^{-1} was found for the pre-exponential factor.

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[1] http://www.plasticseurope.org/
[2] Matisová-Rychlá, L.; Rychlý, J., Thermal oxidation of nonstabilized and stabilized polymers and chemiluminescence. *Journal of Polymer Science Part A: Polymer Chemistry* **2004,** *42,* 648-660.