

# KINETIC MODELING OF A POLYMER BLEND THERMAL AGEING

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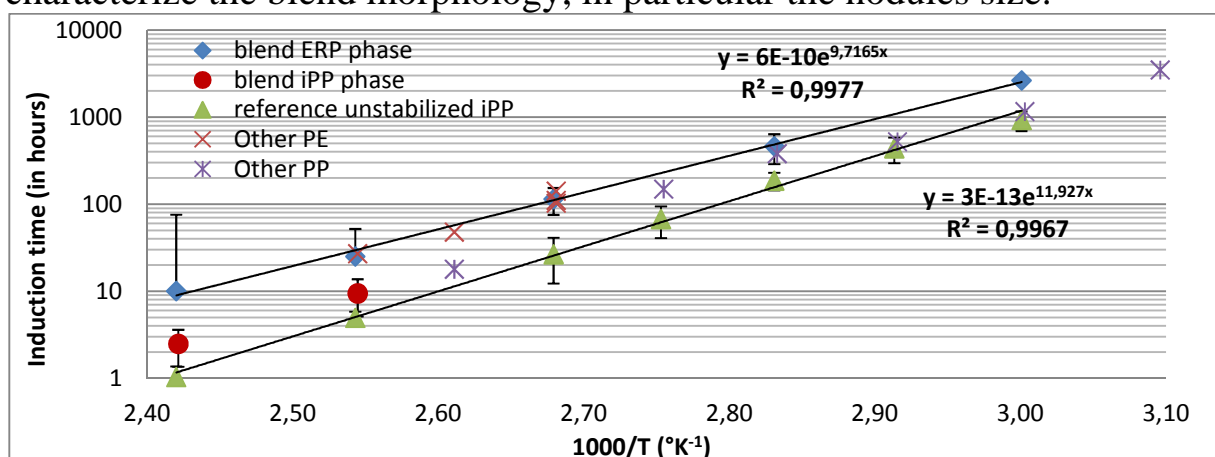
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As reviewed by Pospíšil<sup>1</sup>, polymer blends generally oxidize with a different rate than their elementary constituents because of the existence of cooxidation reactions at the interfaces. In certain cases, however, cooxidation reactions would be negligible, as evidenced by microscopy analyses (such as TEM-EDX, AFM or SEM) focused on nodules changes in PE/PP blends, even if few heterogeneities were reported in PP matrix<sup>2</sup>. The aim of this communication is to check this last assumption from a kinetic modeling approach.

## Methods

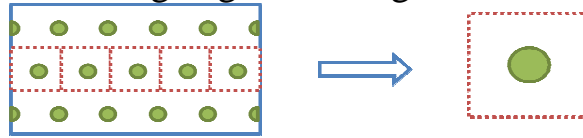
The experimental approach consists in fractionating the blend to study the ageing of each polymer phase separately (cf. figure 1). Blend fractionation was performed by solvent extraction and the fraction of soluble ethylene rich phase (ERP) was determined by mass loss. Ethylene fraction in ERP was also determined by NMR and FTIR using the classical Wei's law that leads to quite consistent results. At least, S-TEM analyses were made to characterize the blend morphology, in particular the nodules size.



**Figure 1 : Arrhenius plot of OIT determined in air for ERP and PP phases. ERP behaves similarly as PE because of its high ethylene content. The degradation kinetics of both phases are sufficiently different to envisage a two-steps degradation kinetic for the corresponding ERP/PP blend.**

## Kinetic modeling

For a sake of simplicity, the blend was represented by a series of ERP nodules regularly spaced in a PP matrix. The corresponding elementary cell used for kinetic modeling is given in Figure 2.



**Figure 2: Schematization of an ERP/PP blend and the corresponding elementary cell.**

In a first approach, it was assumed that each polymer phase degrades independently, i.e. that cooxidation reactions are negligible at the interface. Their thermal oxidation kinetics was simulated by a general kinetic model established for pure PP<sup>3</sup> and pure PE<sup>4</sup> in previous studies. This model considers only one type of reactive site: methyne group in PP and methylene group in ERP phase. Moreover, the oxygen concentration was determined by the classical Henry's law in PP and by a continuity equation in ERP phase:

$$C_{O_2}^{PP} = s_{O_2}^{PP} \cdot P_{O_2} \quad \text{and} \quad C_{O_2}^{ERP} = C_{O_2}^{PP} \cdot \frac{s_{O_2}^{ERP}}{s_{O_2}^{PP}}$$

with  $s_{O_2}^{PP}$  and  $s_{O_2}^{ERP}$  the respective oxygen solubility coefficients in each phase and  $P_{O_2}$  the oxygen partial pressure in the environment.

As a result, the overall blend oxidation rate corresponds to the average value of phase oxidation rates:

$$r_{ox}^{blend} = X \cdot r_{ox}^{ERP} + (1 - X) \cdot r_{ox}^{PP}$$

with X the volume fraction of nodules in the PP matrix:  $X = \omega_{ERP}^{blend} \frac{\rho_{blend}}{\rho_{ERP}}$ .

It will be shown that this kinetic model allows to simulate a wide range of thermal oxidation behaviors by varying only one parameter: X. These simulations will be compared to experimental results in order to decide on the need to introduce interface effects in the kinetic model.

1. Pospíšil et al, Polymer Degradation and Stability 65 (1999) 405-414
2. Manabe et al, Journal of Applied Polymer Science 100(3) (2006) 1831-1835
3. Colin et al, Radiation Physics and Chemistry 79 (2010) 365-370
4. Khelidj et al, Polymer Degradation and Stability 91 (2006) 1598-1605