Aliphatic polyesters are among the most interesting candidates for biodegradable materials in agricultural and sanitary fields as well as in packaging applications. Such materials, during their normal use, are exposed to sunlight and hence their photo-aging becomes a real concern. Historically, poly(hydroxyalkyls) were the first products introduced industrially, whereas more recently poly(butylene succinate), PBBS, and poly(butylene adipate-co-terephthalate) (PBBS-co-TPA) have appeared on the market under the trade name of Bionolle in the present work. PBBS, PBBS-co-TPA, and Bionolle films were subjected to photo-aging and the photo-oxidation products were analyzed by Matrix Assisted Laser Desorption Ionization-Time of Flight-M.S. (MALDI-TOF).

In the present work, synthetic PBSu (Scheme 1), contrary to the oligomers shown in Fig. 2, which are immediately subject to variation. Remarkably, the induction period for the appearance of the oxidation products from the hydroperoxide decomposition is 24 hours (Fig. 4a).

In Fig. 3a is shown the MALDI spectra (mass range of 1,220-14,000 Da, after desorption) of the PBSu sample irradiated for 48 hours. The mass change with respect to the sample irradiated for 24 hours (Fig. 3b), is given by the appearance of a new peak at 1374 Da, which structure (Species B) suggests that the well known 1,6-end group abstraction process (Scheme 2) is already active. MALDI spectra (after desorption) of the PBSu sample irradiated for 150 hours is reported in Figure 3b. In addition to the oligomers present in the previous spectra, several new compounds can be identified in this spectrum. Among them, the peak at 1,274 Da (Species D), having a bulky formate and succinic acid as the chain end, is diagnostic for the occurrence of the Norrish 2 cleavage reaction, as reported in Scheme 3. The Norrish 1 cleavage reaction, yields oligomers with end groups such as butyl formate, ethyl formyl butyl ester, malonic acid, that correspond to peaks at 1,108, 1,274, 1,288, 1,300, and 1,360 Da. The other peaks appearing in Fig. 3b have not been assigned to oligomers bearing end groups that can derive from all the processes in Scheme 1 and consequently are not unequivocally connected to a specific photo-oxidation reaction.

Photo-oxidation Procedure:
- Photo-decomposition of PBBS via the hydroperoxide mechanism.
- Photo-decomposition of PBBS via the hydrogen abstraction.
- Photo-decomposition of PBBS via the oxygen abstraction.

In Fig. 4 are reported the kinetic trajectories of some oxidation products identified by MALDI-TOF MS after an induction period (72 hours). The evolution of the oligomers shown in Fig. 2, which are immediately subject to variation. Remarkably, the induction period for the appearance of the oxidation products from the Norrish 2 reaction (Species E) is the same, whereas the induction period for the appearance of the oxidation products from the hydroperoxide decomposition is 24 hours (Fig. 4b).