



# Effect of nitroxyl-based radicals on the melt radical grafting of maleic anhydride onto polyethylene in presence of a peroxide

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## ABSTRACT

The effect of a nitroxyl-based radical scavenger (tetramethyl piperidino radicals, TEMPO or indolynoxyl radicals, DPAIO) on the course of the melt radical grafting of maleic anhydride (MA) onto polyethylene has been explored. The reaction was conducted at 160 °C in a mini-extruder with 2,5-dimethyl-2,5-di(tertiobutylperoxy)hexane (Luperox 101-C<sub>16</sub>H<sub>34</sub>O<sub>4</sub>; L101) as hydrogen abstractor. Optimal experimental conditions were defined by varying both L101 concentration and L101/nitroxide molar ratio. The degree of grafting of MA was determined by infra-red spectroscopy and was as high as 0.26 wt.% and 0.34 wt.% in presence of TEMPO and DPAIO respectively.

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## 1. Introduction

Environmental concerns have triggered many efforts in the development of friendly processes. In this very demanding context, the field of polymer modification in the melt has gained great importance allowing obvious advantages such as solvent free process (thus reducing or eliminating the emission of Volatile Organic Compounds), continuous processing (starting from monomer and resulting in polymer or furnished products) and control over residence time. For many polymer surfaces, the compatibility with other substrates should be improved by either chemical modification of the polymer with functional groups or modification of the surface topography, reducing the interfacial tension, preventing excessive coalescence of disperse phase during mixing and annealing, and improving adhesion between dispersed and continuous phases. Effective chemical modifications include

changes in chemical group functionality, surface charge, hydrophilicity, and wettability. For example, the compatibility of polyolefins based polymer blends can be improved by the addition of suitable emulsifying agents at the interfaces. The grafting of maleic anhydride (MA) to the polyolefin backbone [1–3] opened the way to modified polyolefins acting as an efficient compatibilizer for a large number of blends [4–6]. Maleation of polyethylene (PE), as a polymer exhibiting a higher grafting efficiency towards reaction with MA comparing to the other polyolefins [7,8] can be conducted by many methods, including grafting with the aids of free-radical initiator in solution [9–11] or in the melt [12–15] and radiation grafting [16–18]. Maleic anhydride (MA), because of its poor homopolymerization characteristics toward free radicals, is a suitable grafting agent for the modification of PE substrates [19]. Free-radical melt grafting of MA is the most important method from the economical and environmental points of view but the use of free-radicals which act as both hydrogen abstractors and initiators, are generally carried out at high temperature (up to 200 °C), rendering

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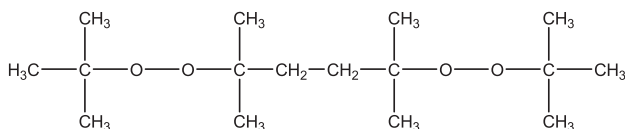
E-mail address: [beyou@univ-lyon1.fr](mailto:beyou@univ-lyon1.fr) (E. Beyou).

the reactions non-selective. As initiator, dialkyl peroxides are most commonly used and the decomposition mechanism involves initial O–O bond homolysis to generate the corresponding alkoxy radicals that can add to the grafting monomer, which would lead to homopolymers as undesired by-products [20–24]. Alkyl radicals formed by decomposition of the primary radicals are known to preferably add to the monomer. However, under typical grafting conditions, i.e. high temperature and low monomer concentration, the kinetic chain length for homopolymerization is much lower than in typical vinyl polymerizations and degrees of polymerization are relatively low [25]. Grafting, branching, cross-linking and degradation set boundaries of the desired grafting reaction and their extent of grafting depends on the type of polymer and nature/type of chemicals used [26]. Primary and secondary radicals are reported to give more easily the coupling reaction than the tertiary ones which instead undergo  $\beta$ -scission reactions or disproportionation reactions. Moreover, transfer reactions to the polymer backbone can be observed thus producing additional tertiary macroradicals which lead again to  $\beta$ -scission [27–29].

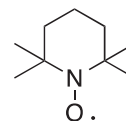
The occurrence of these side reactions can severely damage the macromolecular structure with poor control of ultimate properties. Therefore, an optimization has been carried out for ensuring MA grafting over the undesirable side reaction. The reactant parameters (type and amount

formation. Moreover, Chandranupap and Bhattacharya [32] examined the effect of the presence of comonomers on the grafting reaction of MA onto PE and showed that the use of styrene can lead to a higher degree of grafting and less crosslinking. In addition, Chaudhary et al. [33] showed that the reaction of carbon-centered radicals with nitroxides and its derivatives can control the extent of crosslinking in the reaction of polyethylene with peroxides. In the polymer field, it has to be mentioned that nitroxyl free radicals are usually utilized as light stabilizers (HALS) [34,35] or radicals scavengers in the controlled radical polymerization [36,37].

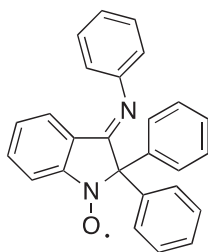
In order to improve the MA grafting degree by limiting secondary reactions such as crosslinking, in this study, we decided to focus our attention on the use, at 160 °C, of 2,5-dimethyl-2,5-di(tertiobutylperoxy)hexane (i.e. Luperox 101, **1**) as peroxide initiator in the presence of low density polyethylene (LDPE), maleic anhydride as grafting agent and tetramethyl piperidino radicals (i.e. TEMPO, **2**) or indolynoxyl radicals (i.e. DPAIO, **3**) as radical scavengers. We studied MA grafting reactions in regards with both L101 concentration and L101/nitroxide molar ratio. Blank experiments using mixtures of LDPE, L101 and nitroxyl radicals allowed us to define optimal experimental conditions for MA grafting. The formed products were analyzed by rheology, GC/MS, and  $^1\text{H}$  NMR and the MA grafting degree was determined by IR spectroscopy.



Structure 1. LUPEROX 101



Structure 2. TEMPO



Structure 3. DPAIO

of peroxide [1,2,13,15,30], MA concentration [1,2,31] and PE structure [8]) on MA grafting degree and the extent of chain-branching/crosslinking side reactions occurred during the maleation of PE have been studied. For example, Gaylord and coworkers [1,2,14] showed that in contrast to other monomers, MA intensifies the chain-branching/crosslinking reaction by the mechanism of MA excimer

## 2. Experimental

### 2.1. Materials

The polymer used is a low density polyethylene (LDPE,  $d \approx 0.9$  g/mL) of number average molecular weight and weight of about 21,000 and 84,000 g/mol, and a

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