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# Improvement of the photo-stability of polystyrene-blockpolybutadiene-block-polystyrene through carbon nanotubes



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#### ABSTRACT

The photo-stability of Polystyrene-Polybutadiene-Polystyrene (SBS) based nanocomposites containing bare multi-walled carbon nanotubes (CNTs) and carbon nanotubes bearing carboxylic functional groups (CNTs-COOH) in comparison to that of pristine SBS has been studied. The photo-oxidation of pristine SBS occurs through crosslinking reactions and oxidized species formation and both these processes begin at early stage of exposure. The formation of crosslinking, formerly in polybutadiene phase, assessed by spectroscopical (FTIR), mechanical, dynamic mechanical and rheological analysis, leads to occurrence of internal mechanical stresses in the solid state and the SBS samples become prematurely unable to stretch. SBS-based nanocomposites showed a significant improved photo-stability to the respect to pristine matrix, due to the presence of CNTs and even more, of CNTs-COOH, that are able to protect efficiently SBS against UVB exposure. All obtained results suggest that the used nanotubes are able to delay the degradation process because of their acceptor-like electron properties and their ability to shield UV-light. Besides, the CNTs act as radical traps, hindering the crosslinking and slowing down the oxidation process. The presence of carboxylic functional groups onto CNTs outer surface enhances the protection ability of CNTs due to the presence of a larger amount of surface defects, that improves their radical scavenging activity.

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### 1. Introduction

Carbon nanotubes (CNTs) are one of the most promising candidates for design of novel high performance polymer-based nanocomposites [1,2], as these nanoparticles are able to improve the electrical, thermal, mechanical and optical properties of the host polymeric matrices [3–5]. Unfortunately CNTs show tendency to aggregate and/or agglomerate, and this feature makes very difficult their uniform dispersion into polymer matrices [6-8], that is a key issue to obtain enhanced properties [9,10]. Furthermore, according literature, the dispersion of CNTs can significantly affect the stability against thermal degradation of CNTs polymer-based nanocomposites [11]: an interesting paper by Seo at al. [12], addressed to the study of thermal degradation of multiwalled carbon nanotubes (MWCNTs) reinforced polypropylene-based composites, found that the activation energies of the thermal degradation increase with increasing MWCNTs content. Also the presence of functional groups onto the outer surface of CNTs, affecting the interfacial bonding between the nanofillers and the polymeric matrix, influences the thermal degradation of CNTs based nanocomposites. For instance, the presence of amino- and poly(L-lactide)- functional groups onto CNTs surface enhances thermal stability of polyamide 6 [13] and poly(L-lactide) [14] based nanocomposites, respectively. Besides, it is documented that the thermal stability could be affected by the formation of a protective layer, that acts as a heat shield [15].

Concerning the thermo-oxidation behavior of CNTs basednanocomposites, few studies documented that CNTs can act as anti-oxidants due to their acceptor-like electronic properties [16,17]. In particular, their anti-oxidant ability is carried out through a radical scavenging mechanism that is exacerbated by the presence of structural defects onto the CNTs outer surface [18,19]. The same mechanism can be invoked to explain the protective action of CNTs against photo-oxidation [20]. CNTs photo-oxidative protection ability is related also to an inner filter action: CNTs, similar to carbon black, absorb the UVB irradiation, decreasing the oxidation rate of polymer. This beneficial effect, however, is related to a homogenously CNTs dispersion in the host polymeric matrix. Indeed, their UV-protection efficiency is compromised by the formation of agglomerates that, increasing locally the temperature,

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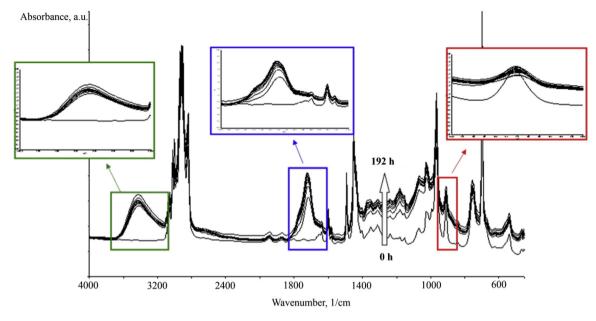


Fig. 1. FTIR spectra of SBS block-copolymer at different exposure time.

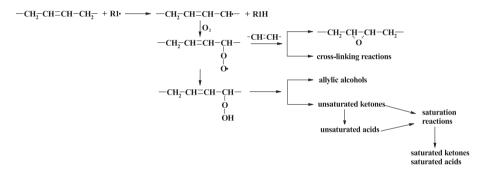


Fig. 2. Photo-oxidation pathway for butadiene segments in SBS copolymer [28].

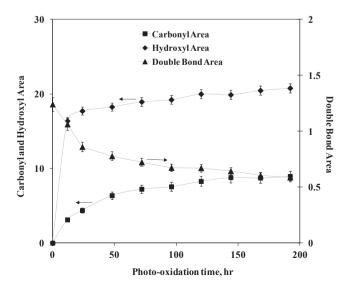


Fig. 3. Carbonyl, hydroxyl and double bond area of SBS block-copolymer as a function of the exposure time.

accelerate the degradation process at the interface between the fillers and polymeric matrix [21]. The latter, in some case, could overlap the CNTs protective action, resulting in a pro-degradant action for the polymeric matrix. Additionally, the CNTs upon UV light are able to physisorbe the oxygen molecules which, being strongly bonded on the walls of carbon nanotubes, are not available for the oxidative phenomena [22].

However, the effect of the CNTs on the photo-degradation behavior of CNTs elastomeric-based nanocomposites has not been extensively studied yet, although thermoplastic elastomers has been widely used in various outdoor applications, such as adhesive, asphalt, tread, plastic modifies, etc [23].

Diene elastomers, bearing unsaturated carbon–carbon bonds, are very sensitive to photo-oxidative aging and many effort have been made to deeply study the degradation mechanism in order to assess an efficient strategy to provide protection during lifetime [24,25]. Particularly, the photo-oxidative degradation pathway of polystyrene-polybutadiene (SB) copolymer has been investigated and documented in literature [26–29]. It is generally admitted that the photo-degradation of SB occurs by two simultaneous events: formation of oxidized species, mainly in the polystyrene units, and crosslinking process taking place in the polybutadiene phase. It was

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