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Polymer composites containing different types of Biochar: novel fire retardant systems

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Introduction

The ease of flammability is one of the most serious issues for the polymers. In fact, if not appropriately flame retardant, these materials burn very vigorously when exposed to an irradiative heat source or to a flame. In addition, potential toxic smoke can be generated during the combustion, thus increasing the hazards of fire. To overcome this problem, flame retardants (FRs) were developed and added to the plastics, in order to protect the polymer matrix slowing down or even stopping the combustion. In recent years, the use of bio-sourced and environmentally friendly products has been exploited for the design of effective and 'green' alternatives to common flame retardants. Among them, biochar (BC), which is a solid product obtained from the thermo-chemical conversion of biomasses in an oxygen-limited environment, is attracting great interest as a low-cost carbon source for flame retardant applications [1]. In this work, different types of biochar obtained by pyrolysis of various sources, reported in tab.1, were used as a filler for Ethylene-Vinyl Acetate (EVA) copolymer. BC/EVA compounds at different bulk concentration, namely 20 and 40 wt.%, were prepared using a co-rotating twin-screw extruder. Compression and injection molding processes were utilized for preparing the specimens for the following tests. In addition, the BC-T compounds were used to prepare specimens with a 500 µm thick layers of EVA-BC-T (BC loading: 3 and 6 wt.%) molded on specimens of unfilled EVA. Finally, the obtained composites were fully characterized by SEM, DSC, TGA, cone calorimetry and tensile tests.

Table 1: sources used for obtaining BCs.

Source	**BC name**
Soft woods	Low
Oil seed rape	Medium
Rice husk	High
Tetra Pak®	BC-T

Results and discussion

SEM observations performed on EVA/BC compounds showed a good distribution of the particles within the polymer matrix. Their size was substantially micrometric, though some bigger aggregates (not exceeding 100 microns) were clearly visible. These findings indicate that the experimental conditions adopted for compounding were suitable for obtaining an homogeneous dispersion of the fillers, regardless of their type and loadings. DSC analyses revealed that the presence of BC, irrespective of its type and loading, didn't affect the melting temperature and the crystallizzation temperature (about 85 and 65°C, respectively), while the degree of crystallinity was slighty reduced with respect to the unfilled polymer. The thermal and thermo-oxidative stability of the composites was analysed through thermogravimetric analyses. From an overall point of view, it is worthy to note an increase of the characteristic temperatures, i.e. T_{onset} and T_{max}, compared to neat EVA due to the presence of BCs, coupled by a significant increase of the residue at the end of the test. In detail, the tests performed in air enhanced the differences between composites and unfilled EVA: T_{onset} reached 322 °C and T_{max} 354°C for the composites with 40 wt.% BC, compared to 304 °C and 337°C, respectively for T_{onset} and T_{max} of EVA. The residues exhibited by the composites were up to 16 wt.% while that of EVA was negligible. These findings indicate the barrier effect of the BC particles on oxygen diffusion in the polymer, resulting in enhanced thermal stability of the composites.

The combustion behavior of composites was investigate using the cone calorimeter based on oxygen consumption principle. The standard heat flux used for tests was equal to 35 kW m^{-2}; the HRR vs time curves of 40 wt.% BC composites compared to EVA are presented in figure 1.

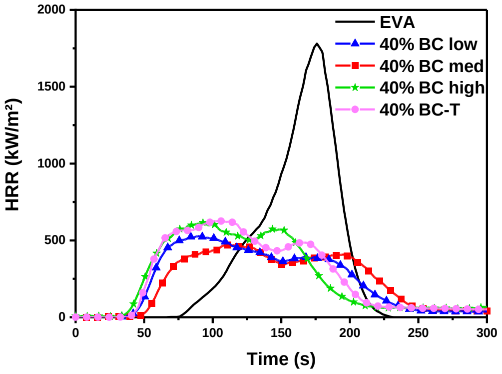

Figure 1: Heat Release Rate (HRR) vs time curves for EVA and its composites filled with 40 wt.% of different types of biochar.

It is worthy to note that the incorporation of BC decreases the peak of heat release rate (pkHRR) of the specimens: this effect is more markable when the filler loading increases. Indeed, the pkHRR values of the composites decrease by 43 to 75% depending on type of BC and loading, compared to unfilled EVA. The highest decrease is observed when BC medium is incorporated into EVA. As a consequence of pkHRR decrease, also FPI (pkHRR/TTI ratio, where TTI is Time to ignition) and FIGRA (pkHRR/time to peak) show a notable lowering for the specimens containing the BC medium. Also the total heat release (THR) values remarkably decrease for the compounds containing BC low, medium and BC-T and the residues after tests are significantly increased (up to 27 wt.% of the initial mass). Finally, the incorporation of BC promotes the reduction of such smoke parameters as total smoke release (TSR) and specific extinction area (SEA) values. All these findings are clear evidences of the formation of a stable char, which protects the polymer matrix from the exposure to the irradiative heat flux. In fact, during the combustion, a protective surface layer resulting from recession of the polymer from the surface by pyrolysis is created by the accumulation of BC particles. This structure seems to enhance the performance of the char through structural reinforcement, acting as thermal and mass transfer barrier, slowing down the escape of volatile products generated during the material decomposition.

Due to the anticipation of TTI values of the composites compared to EVA, cone calorimetry tests have also been performed on the surface-coated samples with BC-T. By comparing the times to ignition of the specimens, the scenario is considerably different between bulk incorporation and surface dispersion of BC. Indeed, the resulting TTIs were delayed with respect to the unfilled EVA. Specifically, the specimens with 3 wt.% of BC-T delayed TTI up to 112 s, while the TTI of EVA was 74 s. Furthermore, the coated-samples showed higher time to peak values with respect to unfilled EVA.

Finally, to evaluate the effect of the biochars on the mechanical behavior of EVA, tensile tests were performed on EVA and its bulk composites. Figure 2 shows, as example, the typical behavior of stress-strain obtained curves of EVA/BC-T bulk specimens. As expected, the incorporation of BCs, irrespective of the type and content, increases the stiffness and lowers the ductility of EVA copolymer. Moreover, the ductility is significantly decreased only at the highest filler loading (i.e. 40 w.t.% BC content). In particular, the values of tensile modulus increase up to 246 MPa for specimens containing 40 wt.% of BC-T, i.e., more than four times higher than that of unfilled EVA [2,3].

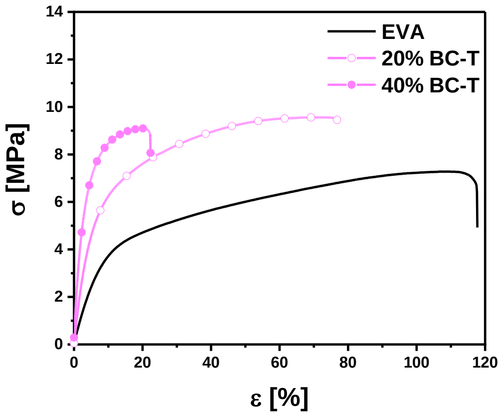

Figure 3: stress-strain curves for EVA and its composites filled with different concentration of BC from Tetrapak.

Conclusions

In this work, the thermal, mechanical, and fire behavior of an EVA copolymer compounded with various loadings of different selected biochars was thoroughly investigated. BC was incorporated into bulk EVA at 20 and 40 wt.% loadings or applied to unfilled EVA matrix as a surface coating (at 3 and 6 wt.%).

SEM images highlighted a good distribution of the fillers with aggregates not exceeding 100 µm.

DSC analyses showed a slight decrease of the degree of crystallinity for all the composites due the presence of BC.

The thermal and thermo-oxidative stability of composites were enhanced, hence indicating a protection effect provided by the BC filler.

Cone calorimetry tests were exploited for assessing the combustion behavior of the designed compounds. In this context, the bulk approach promoted a significant decrease of peak of heat release rate (up to 75%) and of total heat release, combined with a remarkable increase of the residues at the end of the tests, compared to unfilled EVA. Conversely, the surface approach was only capable to delay the time to ignition (+38 s) and the time to peak of HRR (+48 s), depending of the BC concentration.

Finally, the incorporation of BC negatively affected the ductility of EVA, making the composites, at the same time, stiffer.

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