An innovative method for the recycling of carbon-based ashes wastes as reinforcing fillers and catalysts for different polymers

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In this study, carbon-based ashes have been produced by the wooden biomass pyro-gasification plant CMD ECO20. CMD ECO20 is a micro-scale combined heat and power system powered with biomass, under development by the Italian company Costruzioni Motori Diesel S.p.A. (CMD). It is an integrated system combining a downdraft gasifier, syngas cleaning devices, a spark ignition internal combustion engine and an electric generator, and it is able to produce electric and thermal power up to 20 kW_e and 40 kW_{th}, respectively [1,2]. Two different types of fillers were produced from ashes: the first type was obtained by dry ball milling of the ashes (DBA), while the second one included water induced oxidation of the milled particles (oDBA). Both fillers have been characterized by several techniques including Wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), Multi-angle light scattering (MALS), Energy Dispersive X-ray (EDX) Spectrometry, Organic Elemental Analysis (OEA) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).Each filler has been added to different polymers with the to verify the effect of the ashes on the transport properties of the matrix. Firstly, the ashes were added to an epoxy resin in an amount equal to 1, 3, 5 and 10 wt % and they have been tested as possible catalyst for the crosslinking of the resin, as already observed for oxidized carbon black [3]. This study has been mainly conducted by rheometry and Differential Scanning Calorimetry (DSC). The curing agent (22phr) has been added to the resin that has been cured for 1h at 60 °C and 2 h at 150 °C [4,5]. The results obtained indicate the potential improvement brought by the addition of carbon based waste ashes, which allow to both increase the flexural properties and the glass transition temperature of the epoxy resin and reduce the curing time, acting as a catalyst for the crosslinking reaction of the epoxy resin. In detail, the elastic modulus of the epoxy resin containing an amount of fillers of 1 and 5 wt% is higher in comparison to that of the neat epoxy. The flexural strength of the epoxy resin containing an amount of DBA of 1 and 5 wt% is also higher than that of the neat epoxy.

Furthermore, the ashes fillers, tested as possible catalysts for the crosslinking of the epoxy resin with amines, by means of rheological and calorimetric analysis, evidencing that the oxidised filler significantly reduce the gel time of the epoxy resin (Table 1).

These data suggest a catalytic activity of the oxidised filler on the epoxy crosslinking.

Table 1. Gel time (**t_{gel}**) measured as the cross point of the G' and G'' curves of either the neat resin and composites mixtures.

Name	**t_{gel}**
Neat epoxy	81.3±1.1

Epoxy_DBA_3	79.0±0.92
Epoxy_oDBA_3	53.3±0.86

The same fillers were also added to a commercial maize starch in an amount of 35 wt.%. The presence of the waste carbon ashes allows to improve thermal and durability performances of the thermoplastic starch (TPS) films. They reduce the water absorption of starch matrix and strongly decrease the deterioration of starch, independently of the fillers amount, enhancing the lifetime of the TPS films in outdoor conditions (Table 2). In addition, the waste carbon ashes/maize starch films present an additional advantage in comparison to those of neat starch; they can biodegrade, releasing the plant nutrients contained in the ashes into the soil. For this reason, this approach for recycling carbon waste ashes increases the efficiency of industrial waste management, along with a reduction of its negative effects on the environment and population.

Table 2. DSC and TGA values of thermoplastic starch (TPS) and thermoplastic recycled carbon ashes/maize starch (TPAS) films.

Sample	T_g **(°C)**	$T_{DSCPEAK}$ **(°C)**	ΔH_m **(J g^{-1})**	***Water loss*** **(%)**	***Solid residue (%)***
TPS	97.70	167.51	219.14±1.30	14.96±1.87	7.74±0.07
TPAS7	146.37	191.95	217.73±0.85	12.03±0.86	13.62±0.13
TPAS14	146.23	187.18	212.51±2.00	11.54±0.61	20.30±0.19
TPAS21	146.25	179.48	217.52±3.25	9.30±0.53	23.55±0.11

Finally, the ashes were added to a conductive polymer, PEDOT:PSS with the aim to increase its thermal and electrical conductivity and to verify their suitability to be used for the production of electronic circuits by an innovative 3D printing technique, such as aerosol jet printing. The preliminary results obtained show that the presence of the ashes does not modify the rheological properties and the wettability of the PEDOT, allowing their printability, with the same process parameters used for PEDOT. Further analyses are in progress to verify the increased conductivity of the composites containing ashes respect to that of the neat matrix.

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