

## Article

# Recycling of Wastes Deriving from the Production of Epoxy-Carbon Fiber Composites in the Production of Polymer Composites

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**Abstract:** The formulation of composites reinforced with shredded epoxy-carbon fibers wastes is investigated. Poly (buthylene terephthalate) PBT was selected as the matrix for the composites. In order to increase the interaction between the epoxy resin still coating the carbon fibers and the PBT matrix, polycarbonate (PC) was added either to the matrix formulation or as a waste coating. The flexural strength, impact strength, and dynamic-mechanical analysis of the new composites was investigated, as well as their microstructure by scanning electron microscopy. Experimental results show that the recycled fibers can be dispersed in both pure PBT and in its blend, enhancing the mechanical properties of the composites. An increase in the investigated properties is found specifically in the elastic modulus below 50 °C and in the impact strength. The extent of the increase depends on the obtained microstructure.

**Keywords:** composites; poly (buthylene terephthalate); polycarbonate; recycling; waste carbon fiber



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## 1. Introduction

Carbon fiber reinforced composites are a worldwide growing market. A large number of wastes deriving both from the production (partially from reacted pre-pregs and manufacturing cut-off) and from the end-of-use of carbon fibers composites are produced every year. In order to avoid damping, different forms of recycling have been proposed and developed [1,2]. This waste has still high mechanical properties and can potentially be used in the formulation of new composites. The main routes to recycling are either mechanical processes, mainly aiming at shredding the composite to obtain a small size filler [3–5] which will have lower mechanical properties than the pristine material, or fiber reclaiming, where the surrounding matrix is either pyrolyzed [6,7] or chemically removed in different ways [8–10]. Mechanical recycling is possibly the simplest method, while reclaiming implies more complex thermal and/or chemical treatments, which may result in an energy or environmental drawback. A possible alternative is to employ the waste as it is, that is without any treatment aiming at depriving the carbon fibers of the matrix. Although this recycling route has been proposed in ceramic alkali-activated composites [11–13], organic polymers may be selected to formulate new composites. Among those, PBT composites are largely employed in industry and are an object of large scientific interest [14–17]. Accordingly, carbon fiber/epoxy scrap PBT composites have been formulated without performing any chemical or high-temperature treatment on the waste. The challenge being the obtainment of the most efficient interaction between the epoxy coating and the matrix, an attempt is made to improve the chemical affinity between the phases. Indeed, matrix–fiber interaction in composites is a crucial topic in literature. Different strategies have been applied, like the use of silane agents [18–20], environmentally sustainable agents [21,22], or nanoparticles [23]. In the present research, a small amount of PC was added either to the matrix or as a waste coating. PC/PBT blends have been extensively investigated [24–26], and, at the same time, PC shows a higher affinity

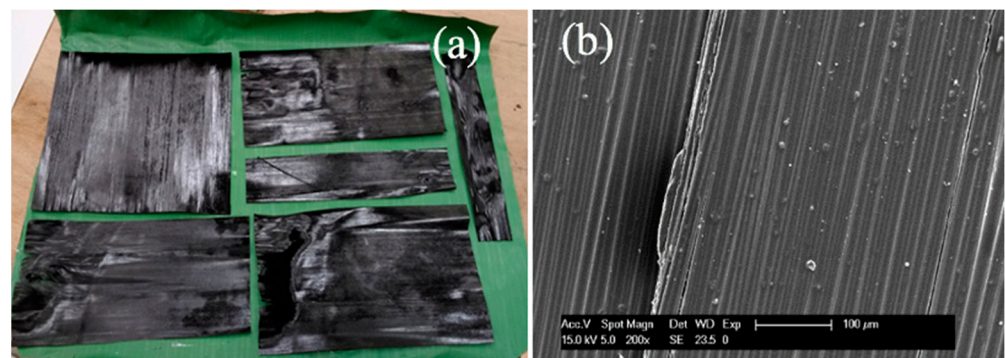
to the epoxy network [27–31], possibly providing a better interaction with the reinforcement. The presence of PC at the interphase between the waste and the matrix can improve the stress transfer from the matrix to the fibers. The mechanical properties of the derived composites are analyzed and compared to the ones of the bare matrix.

## 2. Materials and Tests

### 2.1. Materials

#### 2.1.1. Waste Epoxy Impregnated Carbon Fibers

Single layer waste epoxy impregnated carbon fibers (CF/EP) were supplied by Reglass, Italy. Figure 1 reports the macroscopic and high magnification image of the material layers. Figure 1b was obtained by scanning electron microscopy after gold sputtering of the layers by means of a XL20 SEM, FEI (FEI, Hillsboro, Oregon, USA). The amount of epoxy resin in the composite, derived from thermogravimetric analysis (TA Q50 model, nitrogen atmosphere), is of  $31 \pm 5$  wt%. In order to get, as far as possible, an almost equal thermal history for the material, scraps of cured or partially cured sheets of epoxy-carbon fiber were submitted to a thermal treatment at  $140$  °C for 1 h. The density of the scraps was  $1.53$  g/cm<sup>3</sup>. Afterwards, the sheets were cut to obtain squared specimens with lateral dimensions of  $5 \times 5 \pm 0.2$  mm.



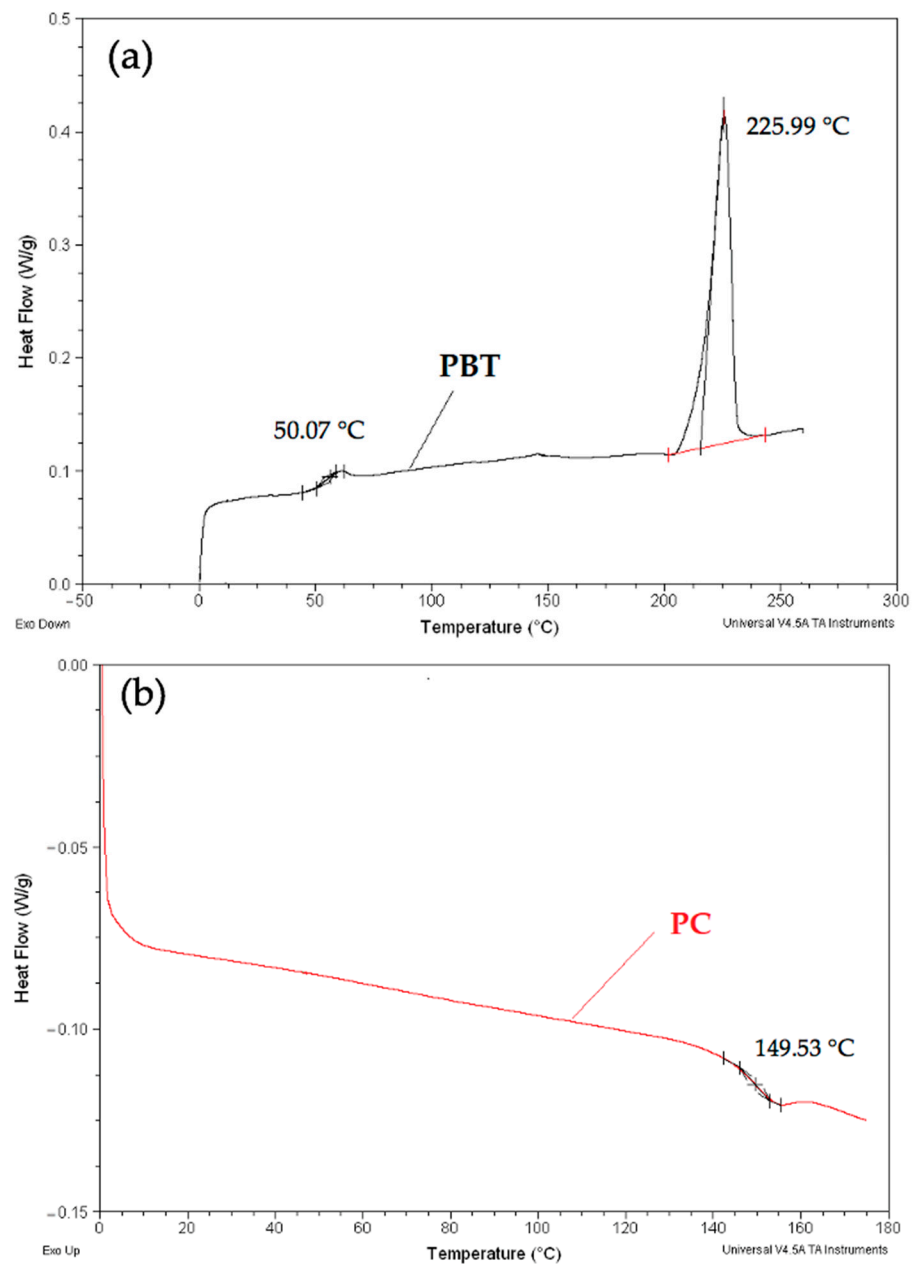
**Figure 1.** Morphology of the waste: (a) scraps layer and (b) high-magnification photo of the surface.

#### 2.1.2. Matrix and Coupling Polymer

Poly (butylene terephthalate) (PBT) chips were used as the composites matrix. The polymer has an intrinsic viscosity  $[\eta]$  of  $0.65$  dL g<sup>-1</sup> measured in chloroform at  $30$  °C.

Polycarbonate (PC) powders were used as a coupling polymer. The polymer has an intrinsic viscosity of  $1.13$  dL g<sup>-1</sup> in a 40/60 (*w/w*) measured phenol/1,1,2,2-tetrachlorethane mixture at  $25$  °C.

Figure 2a shows the thermogram of PBT, while Figure 2b shows that of the PC, obtained by a Q10 DSC instrument, in a nitrogen flow at a scanning rate of  $5$  °C/min.



**Figure 2.** Thermograms of (a) PBT and (b) PC.

## 2.2. Mixing Procedures and Compositions

The mixing process was performed by means of a Brabender mixer (Model PL2000, Duisburg, Germany). Materials in the form of chips, powders, or scraps were mixed at 240 °C and 30 rpm. The investigated batches and the mixing sequence is the following: (a) plain PBT mixed for 5 min to match the same thermo-mechanical history of the composite matrix; (b) carbon fibers/epoxy resin mixed with PBT (hereafter defined as CF/EP\_PBT) for 5 min; (c) PC and PBT mixing for 5 min to create a blend followed by the fibers/epoxy addition and further mixing for 3 min (hereafter defined as CF/EP\_Blend); (d) CF/EP mixing with PC, and the final addition of PBT (hereafter defined as CF/EP/PC\_PBT) so that the PC should remain mainly surrounding the waste. Table 1 summarizes the weight percentage composition of the investigated materials. In the last column, the volume amount of carbon fiber is reported.

**Table 1.** Composition (wt%) and codes of the investigated materials.

Sample Code	PBT	PC	CF/EP	CF <sup>1</sup>
PBT	100	0	0	0
CF/EP_PBT	90	0	10	4.60
CF/EP_Blend	83	7	10	4.57
CF/EP/PC_PBT	83	7	10	4.57

<sup>1</sup> Estimated % volume amount of carbon fibers from the average waste composition.

### 2.3. Characterization

The different compounds obtained with the Brabender were compression-molded between Teflon sheets at 240 °C by means of a Carver molding machine, applying 350 kPa of pressure. Different types of specimens were obtained: (a) rectangular prisms (length of 80 mm, width of 10 mm, and thickness of 2 mm) to be submitted to flexural tests; (b) small-sized bars (length of 33 mm, width of 8 mm, and thickness of 2 mm) for DMA characterization; (c) 80 × 10 × 4 mm for Charpy tests.

#### 2.3.1. Mechanical Tests

Flexural tests were performed on five samples for each composition by an INSTRON 5966 dynamometer equipped with a 10 kN load cell (test speed 5 mm/min; room temperature of 21 ± 2 °C; 65 ± 5% of relative humidity).

Impact strength was evaluated by the Charpy method on unnotched specimens according to ASTM at 23 ± 1 °C and 65 ± 5% RH.

The dynamic mechanical properties were measured by using a Rheometric Scientific DMTA IV dynamic mechanical thermoanalysis (DMA) instrument with a dual cantilever testing geometry. A heating rate of 2 °C/min at 1 Hz of frequency was applied.

#### 2.3.2. Microstructure

The fracture surface of specimens submitted to the flexural test was gold sputtered in vacuo with a coater (Quorum 150R ES, Quorum Technologies, East Sussex, UK) and submitted to morphological analysis by means of an XL 20 (FEI) scanning electron microscope under a tension of 15 kV.

## 3. Results and Discussion

The DMA results are summarized in Figures 3 and 4, where the real part ( $E'$ ) of the modulus and the dissipation factor ( $\tan\delta$ ) are shown as a function of temperature. The waste addition increases the modulus of the materials (Figure 3) at low temperatures (<50 °C). Afterwards, the large drop deriving from the glass relaxation of PBT starts. At higher temperatures, all the reinforced composites still have a higher modulus than PBT. As to what concerns Figure 4, all the plots present a maximum corresponding to the glass transition of PBT. A further relaxation than the one deriving from the segmental motions of the PBT chains takes place in the reinforced materials, as evidenced by a second maximum in  $\tan\delta$ . This relaxation takes place at lower temperatures for CF/EP\_PBT (100–125 °C) than for CF/EP\_Blend (120–170 °C). The origin of this relaxation, absent in the PBT matrix, could be related to the matrix–reinforcement interphase movements. Indeed, the position of the peak (higher temperatures and intensity) can be explained with a better interaction between the epoxy coating and the blend. In the CF/EP/PC\_PBT samples, the second relaxation takes place at even higher temperatures (about 160 °C). In this last case, the origin should be related to the glass transition of the PC layer surrounding the wastes. Indeed, after this relaxation, the modulus ( $E'$ ) decreases rapidly since the relaxed phase (PC) separates the matrix from the reinforcing phase. A second relaxation, linked to the crystallites melting, starts in all materials at higher temperatures (about 200 °C).

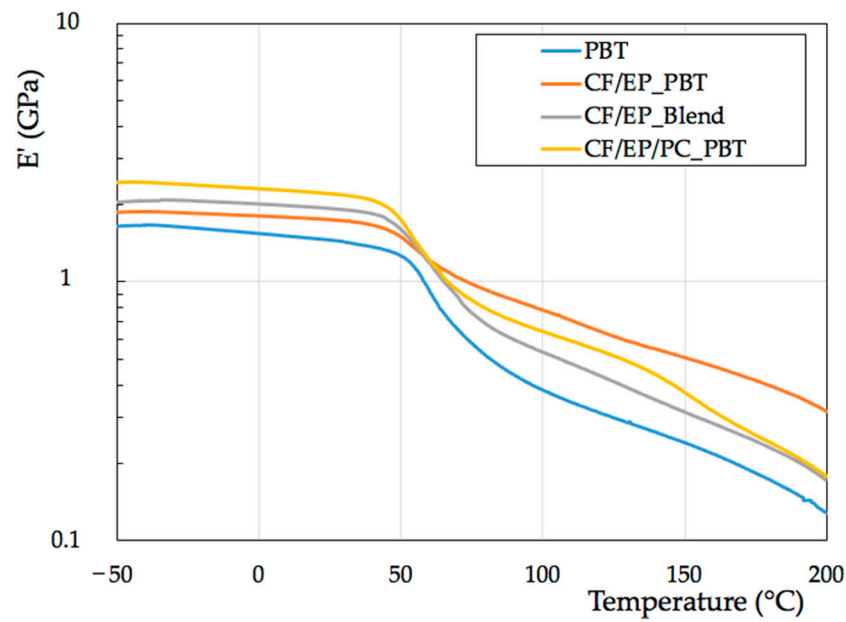


Figure 3. Elastic modulus ( $E'$ ) of the investigated materials.

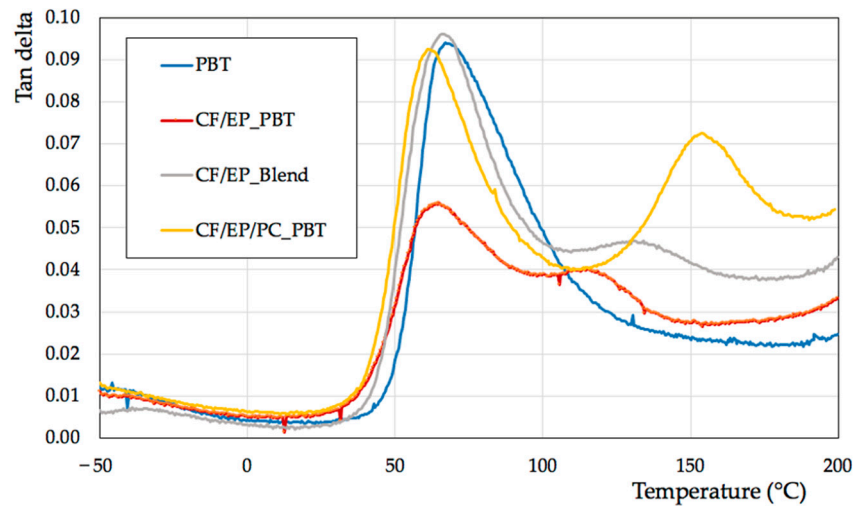


Figure 4. Loss factor ( $\tan\delta$ ) of the investigated materials.

Table 2 shows the results of the flexural tests. In all the cases, the waste addition increases the value of elastic modulus and flexural strength. The best results are obtained in the CF/EP/PC\_PBT samples. Moreover, the unnotched values of the impact strength are summarized in Table 3. In this case, the reinforcing effect of the carbon fibers is stronger, leading to an increase over the 100% in all composites.

Table 2. Flexural properties of the investigated materials.

Sample	Young Modulus (MPa)	Standard Deviation (MPa)	Flexural Strength (MPa)	Standard Deviation (MPa)
PBT	2290	79	71	2.5
CF/EP_PBT	2850	83	79	6.1
CF/EP_Blend	2956	98	82	5.8
CF/EP/PC_PBT	3550	97	99	9.3



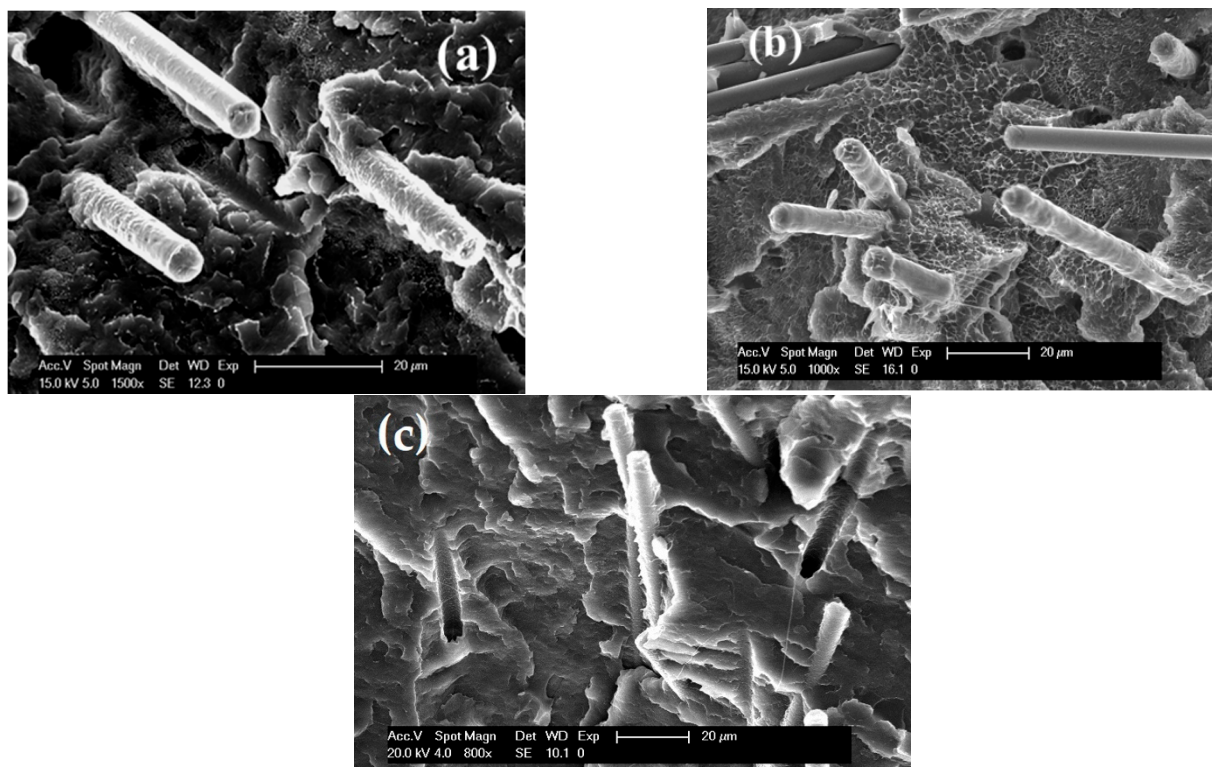
**Table 3.** Charpy unnotched impact strength of the investigated materials.

Sample	Impact Strength (kJ/m <sup>2</sup> )	Standard Deviation (kJ/m <sup>2</sup> )
PBT	47	3.7
CF/EP_PBT	84	4.2
CF/EP_Blend	113	4.4
CF/EP/PC_PBT	109	5.2

The morphology of the fracture surfaces of the composites after the flexural tests are summarized in Figure 5. A uniform random dispersion of the single fibers is detected in all samples. Almost all of them are still covered by the surrounding matrix, and thus the presence of bare fibers is rare. The interphase between fibers and matrix is a key parameter in determining the mechanical properties [32,33]. Accordingly, the link between the fibers and the original epoxy layer seems to be the ruling interphase determining the stress transfer to the matrix. Indeed, this is consistent with the values of the Young modulus reported in Table 2. Assuming a modulus of 250 GPa for the isotropically dispersed volume amount of carbon fibers, the esteemed value of the composite modulus ( $E_c$ ), derived from the classical Equation (1):

$$E_c = v_m \cdot E_m + \nu \cdot v_f \cdot E_f \quad (1)$$

where  $E_m$  is the matrix modulus,  $E_f$  is the fiber modulus,  $v_m$  is the matrix volume fraction,  $v_f$  is the fiber volume fraction, and  $\nu$  is a corrective parameter, should reach a theoretical value above 6 GPa, assuming a corrective parameter  $\nu$  of 0.375, as suggested in the literature [34].

**Figure 5.** Morphology of the fracture surfaces of flexural tests: (a) CF/EP\_PBT; (b) CF/EP\_Blend; (c) CF/EP/PC\_PBT.

Thus, the addition of the epoxy-coated fibers provides a lower reinforcement than the one deriving from virgin ones. Nevertheless, considering the environmental gains deriving from this recycling route, since no chemical treatments are performed before application, the properties of the derived materials are remarkable.

#### 4. Conclusions

Composites have been formulated through the direct recycling of epoxy-carbon fibers cut-off without any previous treatment. Although to a lower extent than the one obtainable with virgin fibers, the wastes can increase the mechanical properties of the PBT matrix, particularly the Young modulus and the impact strength. It is also possible to modulate the mechanical properties of the materials by acting on the affinity of the epoxy resin surrounding the carbon fiber and the selected matrix.

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