

Production of Biocomposites Using Chars Obtained by Co-Pyrolysis of Olive Pomace with Plastic Wastes

Esra Yel, Tabriz Aslanov, Merve Sogancioglu, Suheyla Kocaman, Gulnare Ahmetli

Abstract—The disposal of waste plastics has become a major worldwide environmental problem. Pyrolysis of waste plastics is one of the routes to waste minimization and recycling that has been gaining interest. In pyrolysis, the pyrolysed material is separated into gas, liquid (both are fuel) and solid (char) products. All fractions have utilities and economical value depending upon their characteristics. The first objective of this study is to determine the co-pyrolysis product fractions of waste HDPE- (high density polyethylene) and LDPE (low density polyethylene)-olive pomace (OP) and to determine the qualities of the solid product char. Chars obtained at 700 °C pyrolysis were used in biocomposite preparation as additive. As the second objective, the effects of char on biocomposite quality were investigated. Pyrolysis runs were performed at temperature 700 °C with heating rates of 5 °C/min. Biocomposites were prepared by mixing of chars with bisphenol-F type epoxy resin in various wt%. Biocomposite properties were determined by measuring electrical conductivity, surface hardness, Young's modulus and tensile strength of the composites. The best electrical conductivity results were obtained with HDPE-OP char. For HDPE-OP char and LDPE-OP char, compared to neat epoxy, the tensile strength values of the composites increased by 102% and 78%, respectively, at 10% char dose. The hardness measurements showed similar results to the tensile tests, since there is a correlation between the hardness and the tensile strength.

Keywords—Pyrolysis, olive pomace, char, biocomposite, PE plastics.

I. INTRODUCTION

FIVE types of plastics account for around 75% of all plastic demand in Europe and in the world: polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET). Because of non-biodegradable nature of these synthetic organic structures, plastic wastes should not be disposed of or deposited in the environment. Therefore, other final disposal alternatives different from landfilling have been researched for a long time. The most widely applied alternative is recycling of plastics or recovery of valuable components in the structure of plastics.

The problem of recycling polymeric materials has not yet to be solved at a satisfactory level. Usually only 30% of polymeric wastes have being recycled. Recently,

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environmental, legislative, and consumer pressures have led to an increased interest in using polymeric wastes [1]-[3].

As being one of the thermochemical recycling methods, pyrolysis is extensively studied and applied method. It can be applied extensive types of organics either natural or synthetic. For organics pyrolysis is considered to be an effective technology, by which biomass can be converted to valuable bio-oils, char, and gaseous products. Upon heating in the inert atmosphere, the natural and synthetic polymers tend to decompose and pyrolyse through a self-sustaining combustion cycle. The pyrolysis gas, liquid, and char products are considered as recovered raw materials that can be evaluated at varying processes as feedstock. The most common application is utilization of liquid and gaseous pyrolysis products as fuels, or synthesis of many types of fuels from these fluids.

Char formation is likely the most important condensed phase mechanism to modify the pyrolysis process of polymers [4]. Biomass char represents another potential renewable carbon source, which has attracted significant attention recently.

There are various ways that biomass char can be used e.g. as a material for combustion [5], activated carbon preparation [6], and gasification, such as H₂-rich gas production by steam gasification of biomass char [7]. Some studies in the literature have focused on using char as an adsorbent for the removal of heavy metals and organic pollutants from water and wastewater [8]-[11]. But there are limited studies on the use of biochar in composite preparation, For example, coconut shell char was used in aluminium alloy matrix composites [12]. Ozaytekin and Kar [13] prepared oligo(azomethine) composites using the carbon material (char) derived from the 450 °C pyrolysis of waste PET.

There were limited studies that incorporate pyrolysis char in the composite structure. For example Epoxy resin was used only as a matrix in one of the previous studies of the authors for preparation of epoxy/PET waste char composites [14]. Char has the powdered structure that is suitable to add as additive in composites. Moreover, other physical properties of char particles have potential to affect composite physical properties when used as homogeneously distributed filler in the resin matrix.

OP is the olive oil processing solid waste. It is the residue generated after extracting the oil from olive. Pomace is an important environmental problem. Because, it is in huge quantities, as unaesthetic heaps, and it smells unpleasantly. On the other hand, it is a biomaterial having high organic content. Therefore, it is better not considering it as a waste, instead, applying any recycling/recovery technique. Therefore, in the

present study it was aimed to obtain co-pyrolysis char from co-pyrolysis of PE type plastic waste with OP, to use this char product in the epoxy composite matrix as additive, to investigate the effects of char additive dosage and plastic type on epoxy/char composites. Different char additive weight percentages (10, 30 and 50%) were studied. Chars were produced by the co-pyrolysis of two types of PE plastic wastes, namely HDPE and LDPE.

II. EXPERIMENTAL

A. Materials

Plastic wastes were collected from a local waste collection and separation center. Collected plastic waste samples were separated, HDPE and LDPE type wastes were crushed to less than 8 mm.

OP sample was collected from an olive oil processing plant operated at the Mediterranean coast of Turkey. Pomace sample was utilized directly in the experiments without preprocessing.

Commercially available diluted epoxy resin NPEF 170 called as ER, (Konuray Chemical Co.) was the bisphenol F-type epoxy resin. Some typical properties of the resin are indicated in Table I.

TABLE I
TYPICAL PROPERTIES OF NPEF-170 TYPE EPOXY RESIN

Physical state	Liquid
Epoxy equivalent weight (g/eq)	160~180
Color (Gardner)	3.0 max
Flash point (°C)	150↑
Viscosity (cps, at 25 °C)	2000~5000
Density (g/cm ³ 25°C)	1.16

MNA (methyl nadic anhydride): A mixture of methyl isomers of methylbicyclohept-5-ene-2,3-dicarboxylic anhydride was used as curing agent. The epoxy embedding medium accelerator is a 2,4,6-tris(dimethylaminomethyl)phenol (Sigma-Aldrich).

B. Char Preparation-Pyrolysis

Besides co-pyrolysis of OP with HDPE and LDPE wastes, pyrolysis of OP alone and each plastic alone was also applied for control tests.

All pyrolysis applications were performed at 700 °C, and at inert atmosphere. The inert atmosphere was supplied with nitrogen gas that was passed through the system at the beginning of pyrolysis.

Pyrolysis can be applied at wide range of temperatures. In this study, 700 °C was selected, since this is the temperature at which most of the plastics pyrolysis reactions completed.

C. Composite Preparation

The char samples (particle size < 63 μm) were added to ER mixture at varying portions (10, 30 and 50 wt% of char particles). The mixtures were mechanically stirred at 2000 rpm and room temperature for 3 hours. Then the mixture was ultrasounded for an hour at 60 °C to obtain a good dispersion. Following that, 30 wt% epoxy hardener and 1 wt% epoxy

accelerator were added into the blend. The mixture was degassed for 60 min. at 40°C and transferred into the mould of dumble-shaped. The dimensions of dumble-shaped composite samples were indicated in Fig. 1.

Composite specimens were prepared according to the ASTM D 638 standard. The curing procedure was carried out at 100°C for 24 hours and then the samples were post-cured at 120°C for another 24 hours.

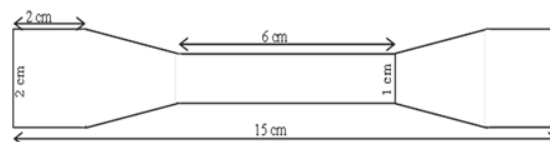


Fig. 1 Schematic representation of the composite sample

D. Analyses and Testing

For characterization and structural check of the specimen, FTIR spectrums were used. The FTIR spectra of the chars were obtained with Bruker-Platinum ATR-vertex70 (Germany) between 500 and 4000 cm⁻¹ wavenumbers at a resolution of 4 cm⁻¹ using an attenuated total reflectance (ATR) accessory.

Scanning electron microscopy (SEM) images were obtained using a Philips XL30 SFEG instrument to investigate the interface between char filler and the epoxy matrix and for surface characterization of chars.

A Shore Durometer TH 210 tester was used for measuring the hardness of the samples. The resistances to stretch properties were determined by Stretch and Pressing Equipment TST-Mares/TS-mxe.

The electrical conductivity measurements of the composites were carried out with an electrometer using a four-point probe technique over a range of 1–10 V. All measurements were obtained at room temperature, and the values were reported as the average of six measurements for each composite.

III. RESULTS AND DISCUSSION

A. Pyrolysis Yields

OP sample was pyrolysed and co-pyrolysed with HDPE and LDPE plastic wastes at 700°C. The pyrolysis of OP alone produced 10.05% solid product (biochar), while HDPE and LDPE pyrolysis produced 2.14 and 6.44% char, respectively (Table II).

TABLE II
CHAR YIELDS AT 700°C PYROLYSIS

Compounds	Char yield, %
OP	10.05
HDPE	2.14
LDPE	6.44
HDPE-OP (in 1:1 wt%)	6.37
LDPE-OP (in 1:1 wt%)	7.26

At the pyrolysis of 50%HDPE+50%OP the produced biochar quantity increased from 2.14 to 6.37% and of 50%LDPE+50%OP biochar increased from 6.44 to 7.26% (Table II). The mixture of equal portions of waste plastic and

OP resulted in pyrolysis char almost at average of the char quantity of each component alone. LDPE resulted in higher quantities of char. Dependingly the co-pyrolysis char of LDPE was also high.

B. Mechanical Properties of Composites

Epoxy resins are used in all known reactive molding techniques. The mechanical properties of epoxy resins depend on the flexibility of the segments and the crosslinking density. For flexibility and adhesive strength, the bisphenol-based epoxy resin is optimal, and the cured resins exhibit low break elongation and increased toughness because of their high crosslinking density. Strength, modulus (related to rigidity or stiffness), hardness and toughness are critical for mechanical performance. Generally, polymer composites show excellent fatigue resistance when compared to most metals. Epoxy-based composites tend to show very good fatigue resistance when compared with both polyester and vinyl ester composites [15].

To investigate the tensile strength, elongation at break, and hardness of the composites, mechanical testing was performed. The results are summarized in Figs. 2-5.

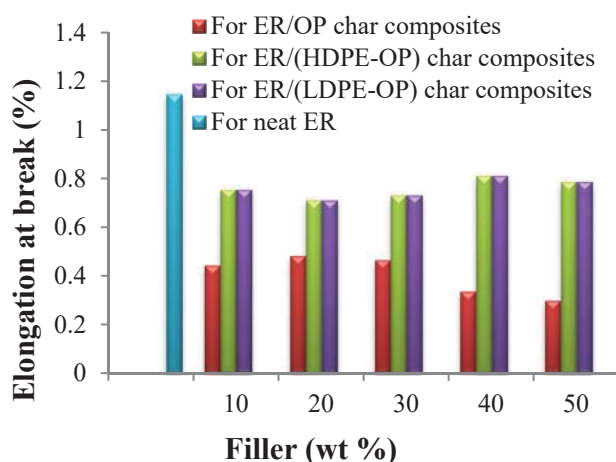


Fig. 2 Elongation percentages of the composites

The mechanical properties of composites depend on the amount and chemical structure of the filler. The neat ER tensile test resulted in a percentage elongation at break of 1.146%, and a tensile strength of 87 MPa. The elongation of neat epoxy decreased in all char contents. PE plastics and OR co-pyrolysis char additive increased break elongations and tensile strengths of the composite as compared to OP char additive. All elongations were lower than the reference composite and all tensile strengths were higher than the reference (Figs. 2 and 3).

The appropriate amount of rigid filler for optimal tensile strength values for composites with OP, HDPE-OP and LDPE-OP chars were determined as 20 wt%, 40 wt% and 40 wt%, respectively. The tensile strength values at these char additive doses were 148 MPa, 288 MPa and 319 MPa.

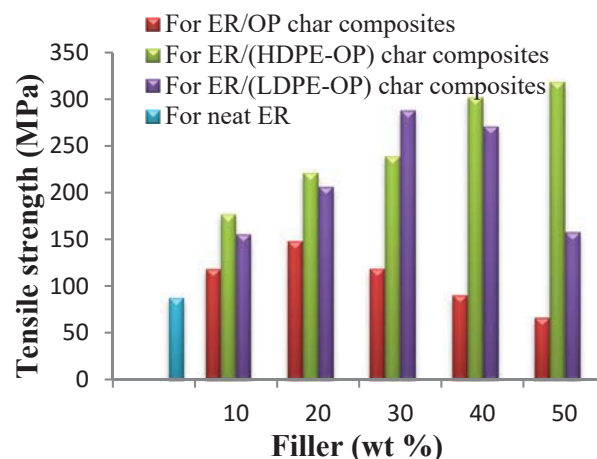


Fig. 3 Tensile strengths of the composites

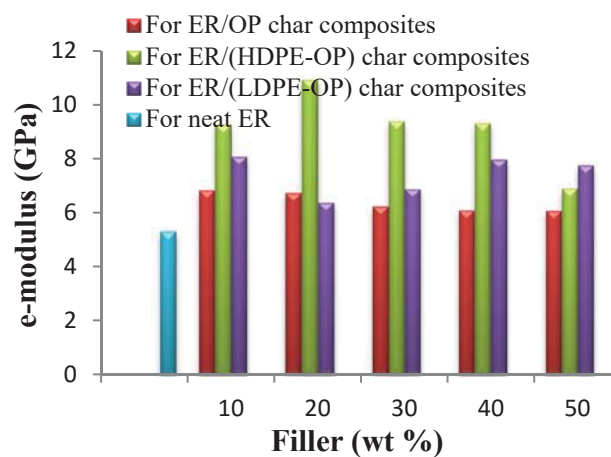


Fig. 4 Young's modulus of the composites

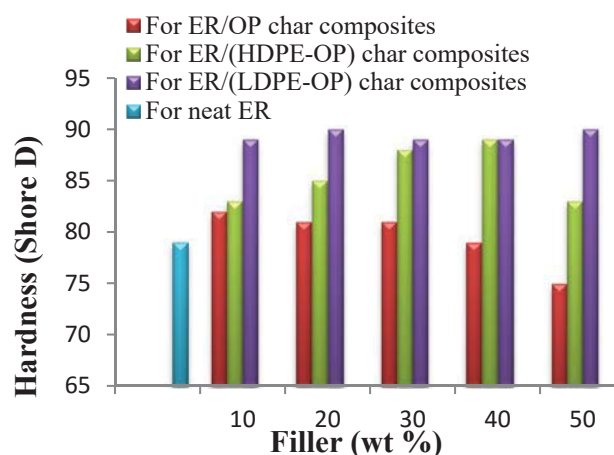


Fig. 5 Hardnesses of the composites

Composites with HDPE-OP chars show higher tensile strength and Young's modulus values than others except 50% additive dose (Figs. 3, 4). However, chars, obtained by co-pyrolysis of PE wastes with OP increased the composites hardness especially LDPE-OP chars as compared to the reference composite (Fig. 5).

C. Electrical Conductivities of Composites

Conductive polymer composites have many advantages over metallic conductors. They can be easily shaped at low cost, are light weight, provide corrosion resistance, and offer a wide range of electrical conductivity [16]. The conductivities of char-filled epoxy composites are given in Table III.

TABLE III.
ELECTRICAL CONDUCTIVITIES (S/CM) OF ER/CHAR COMPOSITES AT ROOM TEMPERATURE

Char (wt%)	Electrical conductivity (S/cm) for filler type of		
	OP char	HDPE-OP char	LDPE-OP char
10	5.54×10^{-8}	2.46×10^{-7}	3.41×10^{-8}
20	6.22×10^{-7}	5.48×10^{-6}	3.44×10^{-7}
30	5.30×10^{-7}	9.35×10^{-5}	2.75×10^{-6}
40	7.79×10^{-5}	4.79×10^{-4}	4.47×10^{-5}
50	2.43×10^{-5}	2.62×10^{-3}	2.03×10^{-4}

Epoxy resin itself is a non-conductive material. As seen from Table III, addition of co-pyrolysis char increased the conductivity, and composites containing 10-50 wt% char filler are considered as semiconductor. The electrical conductivity of ER/char composites continuously increased, up to 50 wt% as the char content increased. The highest electrical conductivities were obtained with HDPE-OP char added composites for all additive dosages.

IV. CONCLUSION

OP biomass was co-pyrolysed with crushed HDPE and LDPE plastic wastes at 700°C. Presence of biomaterial increased the produced char quantity.

Biochars obtained from those pyrolysis runs were used in epoxy based composites as fillers. Mechanical properties of ER/char composites depend on the amount and chemical structure of the filler. The appropriate amount of rigid filler dosage for optimal tensile strength values for composites with OP, HDPE-OP and LDPE-OP biochars were determined as 20wt%, 40wt% and 40wt%, respectively. PE plastics and OR co-pyrolysis char additive increased break elongations and tensile strengths of the composite as compared to OP biochar additive. Higher hardness values were obtained with LDPE-OP char, while higher tensile strength, Young's modulus and electrical conductivity values can be achieved with HDPE-OP biochars filler.

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REFERENCES

- [1] M.V. Gil, J. Feroso, C. Pevida, J.J. Pis, and F. Rubiera, *Fuel Process. Technol.*, 91, 1776 (2010).
- [2] S.H. Rezaeian, P. Jafari, Zahedi, and S. Nouri, *Polym. Composite*, 30, 993 (2009).
- [3] M. Kracalik, L. Pospisil, M. Slouf, J. Mikesova, A. Sikora, J. Simonik, and I. Fortelny, *Polym. Composite*, 29, 915 (2008).
- [4] J. Alongi, F. Carosio, and G. Malucelli, *Polym. Degrad. Stabil.*, 97, 1644 (2012).

- [5] J.W. Mary, H.H. Robert, A.D. Kevin, and Y.C. Nancy, *Twenty-sixth Symposium (International) on Combustion*, The Combustion Institute (1996).
- [6] J.F. Gonzalez, S. Roman, J.M. Encinar, and G.J. Martinez, *Anal. Appl. Pyrolysis*, 85, 134 (2009).
- [7] F. Yan, S.Y. Luo, Z.Q. Hu, B. Xiao, and G. Cheng, *Bioresour. Technol.*, 101, 5633 (2010).
- [8] D. Mohan, Sh. Rajput, V. K. Singh, Ph. H. Steele, and Ch. U. Pittman Jr, *J. Hazard. Mater.*, 188, 319 (2011).
- [9] K. K.H. Choy, and G. McKay, *Chemosphere*, 60, 1141 (2005).
- [10] G. James, D. A. Sabatini, C. T. Chiou, D. Rutherford, A. C. Scott, and H. K. Karapanagioti, *Water Res.*, 39, 549 (2005).
- [11] Y.-N. Chen, L.-Y. Chai, and Y.-D. Shu, *J. Hazard. Mater.*, 160, 168 (2008).
- [12] T.P. Murali, S.V. Prasad, M.K. Surappa, P.K. Rohatgi, and K. Gopinath, *Wear*, 80, 149 (1982).
- [13] I. Ozaytekin, and Y. Kar, *J. Appl. Polym. Sci.*, 123, 815 (2012).
- [14] 19. G. Ahmetli, S. Kocaman, I. Ozaytekin, and P. Bozkurt, *Polym. Compos.*, 34, 500 (2013).
- [15] H.Q. Pham, and M.J. Marks, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley- VCH, Weinheim (2005).
- [16] P. Tsotra, and K. Friedrich, *Compos. A*, 34, 75 (2003).