Polycaprolactone (PCL) Based Polymer Composites Filled Wheat Straw Flour

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Abstract
In this study, polycaprolactone (PCL) based polymer composites were manufactured through injection moulding machine. Polycaprolactone (PCL) and wheat straw flour was used as polymer matrix and organic filler respectively. The effects of wheat straw flour loading on the mechanical properties of the manufactured composites were investigated. The thermal behaviors (TGA and DSC), mechanical properties (tensile, flexural and impact strength), of manufactured composites were determined. According to test results, the addition of wheat straw into PCL matrix reduced tensile strength, elongation at break and impact strength of composites while improving the tensile modulus, flexural strength and flexural modulus.

Keywords: Wheat Straw, Polycaprolactone (PCL), Polymer Composites, Thermal Properties, Mechanical Properties.

Introduction
Polymer composites based lignocellulosic fiber have been developed in recent years. There has been a tremendous growth of lignocellulosic fiber such as jute, hemp, sisal, wheat straw, rice straw and wood flour in polymer composite manufacturing (Avella et al., 2000; Chen et al., 1998; Digabel et al., 2004). These composites have good mechanical performance, economic and environmental benefits (Averous and Boquillon, 2004; Pan et al., 2009; Aydemir et al., 2015). During the manufacturing of polymer composites, synthetic and biodegradable plastic can be utilized. Synthetic plastic such as polypropylene (PP), polyethylene (PE), polystyrene (PS) are used while biodegradable plastic such as polycaprolactone (PCL), poly(lactic acid) (PLA), polyhydroxy alkanoates (PHA), polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-valerate) (PHB-V) are utilized. Polycaprolactone (PCL) one of the commercially available biodegradable plastics is preferred for its low density, biodegradability, ease of mixing with other plastics (Chen et al., 1998; Arbelaitz et al., 2006; Shibata et al., 2006; Zhao, 2013). PCL is more costly than many other synthetic plastics. For different application areas, the use lignocellulosic filler in PCL matrix were investigated (Ruseckaite and Jimenez, 2003; Mishra and Sain, 2009; Dong and Davies, 2011;
Lignocellulosic filler has several advantages including abundance, low cost and high modulus of elasticity (Hornsby et al., 1997; Velde and Kiekens, 2002). For this purpose some researchers have used various polymer and lignocellulosic fiber (Donmez Cavdar et al., 2011; Kaymakci et al., 2013; Donmez Cavdar et al., 2015). In this study, the effects of wheat straw flour loading on the mechanical properties of PCL based polymer composites were investigated.

Materials and Method

Materials
Polycaprolactone (Solvay, CAPA 6800) and wheat straw were used as polymer matrix and reinforcement fillers in this study. Wheat straws were collected from the local farmers and granulated into flour form using Willey mill. The obtained flours were screened to 60 mesh-size and were dried in oven at 103 °C for 24 hour before compounding.

The Manufacture of Compounding and Composite
During the manufacturing process, PCL and wheat straw were mixed as depending to the formulations in a high intensity mixer to obtain homogeneous blends. The blends were compounded in a laboratory scale single screw extruder at 40 rpm screw speed and in the temperature range of 70-100 °C (Figure 1).

The test samples were prepared with the obtained pellets using HDX-88 Injection Molding. Cooling time was set at 40 seconds in the injection molding (Figure 2). Five different filler loadings for wheat straw were chosen (Table 1). Pure polycaprolactone was also prepared.

Composites Testing
Thermogravimetric analysis (TGA) of the samples was done in a Shimadzu TGA-50 thermal analyzer. Differential scanning calorimeter (DSC) analysis was performed in Shimadzu DSC-60. The mechanical properties of produced polymer composites were conducted in accordance with ASTM standards. The tensile and flexural tests were conducted in accordance with ASTM D 638 and ASTM D 790, respectively using Zwick 10KN testing machine. The impact tests were performed according to ASTM D 256. Ten impact samples for each group were cut from the manufactured composites. The notches were added using a Polytest notching cutter by RayRan™ and notched samples were tested on a HIT5.5P impact testing machine, manufactured by Zwick™.

Data Analysis
Design-Expert® Version 7.0.3 statistical software program was used for statistical analysis. The effects of filler loading on the mechanical properties of the obtained samples were evaluated.
Table 1. Experimental design

| Formulations | Polycaprolactone (PCL) | Wheat straw flour (WF) |
|--------------|-------------------------|------------------------|
| PCL          | 100                     | 0                      |
| PCL-10       | 90                      | 10                     |
| PCL-20       | 80                      | 20                     |
| PCL-30       | 70                      | 30                     |
| PCL-40       | 60                      | 40                     |
| PCL-50       | 50                      | 50                     |

Results and discussion

PCL based composites were manufactured through injection molding method utilizing various amounts of wheat straw flour. TGA and DSC analysis of PCL and wheat straw were performed before manufacturing. TGA analysis revealed that PCL initial degradation was started at around 320 °C and wheat straw started degrading around and 190 °C. The main decomposition temperature for PCL was around 390 °C. For wheat straw, the main decomposition temperature was around 295 °C. Melting temperature of the PCL was around 60 °C. TGA and DSC analysis revealed that during the manufacturing of the composites, extruder temperatures should be over 60 °C to facilitate the melting of the matrix and less than 295 °C to prevent the lignocellulosic material from degrading. Vikman et al. (2000) reported that the melting temperature of the PCL granules was 61.5°C, and increased to 63.5°C after compression molding. Shin et al. (2004) found that the melting temperature and the glass transition temperature of PCL were found to be 59°C and -57°C, respectively, from DSC results. Similar results were also reported by others (Matzinos et al., 2002).

Tensile, flexural strength and impact properties of the obtained composites were investigated and the results were given in Fig 3, 4 and 5, respectively. Statistical analysis showed that wheat straw amount significantly decreased the tensile strength of the composites (P<0.0001). These results may be explained by the lack of adhesion between to hydrophobic plastic and hydrophilic lignocellulosic filler (Mengeloglu and Karakus, 2008).

In the case of tensile modulus, Increasing of the wheat straw loading, improved the tensile modulus (P<0.0001). (Fig. 3). This can be explained by the rule of mixtures. Since lignocellulosic material has higher tensile modulus than plastic, tensile modulus of the composites are improved parallel to the filler loading increase (Matuana and Balatinecz, 1998). Other tensile properties determined were elongation at break values (Fig.1). This value was mostly reduced by the lignocellulosic fiber loading. Addition of filler makes the matrix more...
brittle. (Mengeloglu and Karakus, 2008; Mengeloglu and Karakus, 2012).

Statistical analysis showed that wheat straw amount significantly affected the flexural strength of the composites. Flexural strength was increased with the addition of 30% wheat straw loading however was reduced with addition of wheat straw over the 30% loading (Fig. 4) Flexural modulus was increased significantly with the addition of wheat straw (P<0.0001). This is due to wheat straw has much higher modulus than plastic materials.

In the case of notched impact strength, addition of wheat straw significantly reduced the impact strength values (P<0.0001) (Fig. 5). The addition of lignocellulosic filler into the plastic matrix increases the modulus and makes the composite more brittle which result in reduced impact strength (Mengeloglu and Karakus, 2008).

**Conclusion**

The effect of wheat straw flour loading on the mechanical properties of the PCL based composites was investigated. In conclusion, based on the TGA and DSC studies, processing temperature should be adjusted between 70 °C and 120 °C for PCL and wheat straw flour composites. Addition of wheat straw into the polymer matrix improved the flexural strength and flexural and tensile modulus but reduced the impact strength and elongation at break.

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