Polycaprolactone (PCL) Based Polymer Composites Filled Wheat Straw Flour

***Kadir KARAKUS[1], Fatih MENGELOGLU[2]**

[1]Kahramanmaraş Sütçü İmam Üniversitesi, Orman Fakültesi, Orman Endüstri Mühendisliği Bölümü, Kahramanmaraş,
[2]Kahramanmaraş Sütçü İmam Üniversitesi, Fen Bilimleri, Malzeme Mühendisliği Bölümü, Kahramanmaraş
*Corresponding author: karakus@ksu.edu.tr

Recieved Date: 10.03.2016

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.

Buğday Sapı Unu Katkılı Polikaprolakton (PCL) Esaslı Polimer Kompozitler

Özet

Bu çalışmada polikaprolakton (PCL) esaslı polimer kompozitlerin üretimleri enjeksiyon kalıplama yöntemi kullanılarak gerçekleştirilmiştir. Polimer matris olarak PCL ve organik dolgu maddesi olarak buğday sapı unları kullanılmıştır. Üretilen kompozitlerin mekanik özellikleri üzerine buğday sapı unu oranının etkileri araştırılmıştır. Elde edilen örneklerin termal davranışları (TGA ve DSC), mekanik özellikleri (çekme, eğilme ve darbe direnci testleri) belirlenmiştir. Test sonuçlarına göre PCL matrise buğday sapı unu ilavesiyle çekme direnci, kopmada uzama ve darbe direnci azalırken çekmede elastikiyet modülü, eğilme direnci ve eğilmede elastikiyet modülü değerleri iyileşmiştir.

Anahtar Kelimeler: Buğday sapı, Polikaprolakton (PCL), Polimer Kompozitler, Termal Özellikler, Mekanik Özellikler.

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; Arbelaiz 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).

Figure 1. Single screw extruder

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.

Figure 2. Injection molding machine

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).

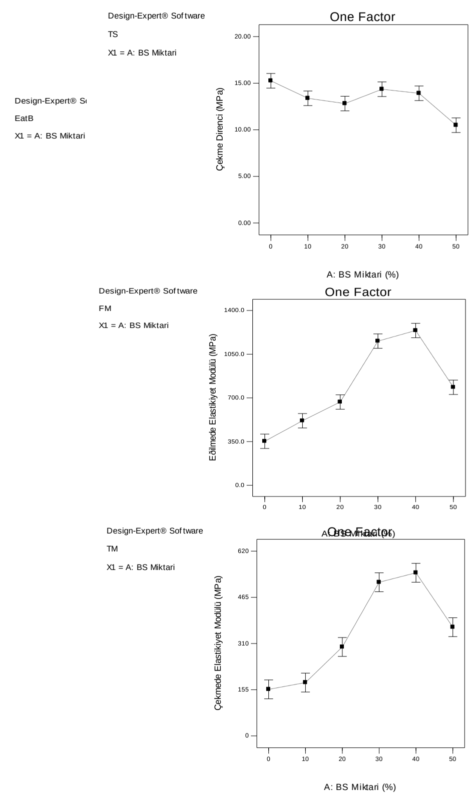

Figure 3. Tensile properties of the obtained composites

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.

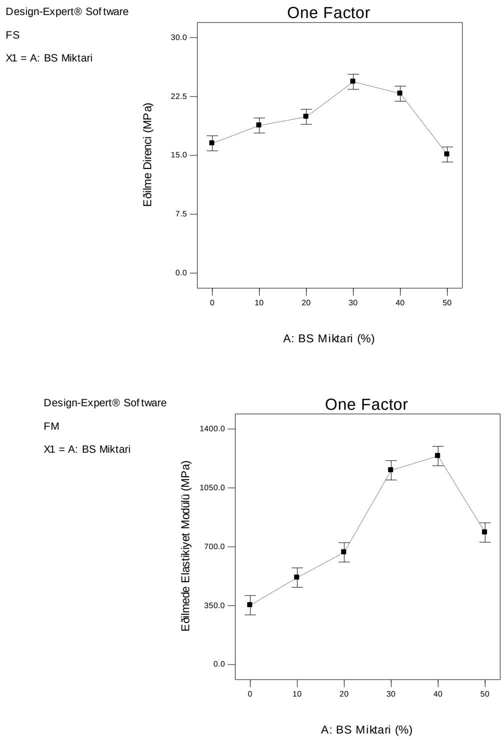

Figure 4. Flexural properties of the obtained composites

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).

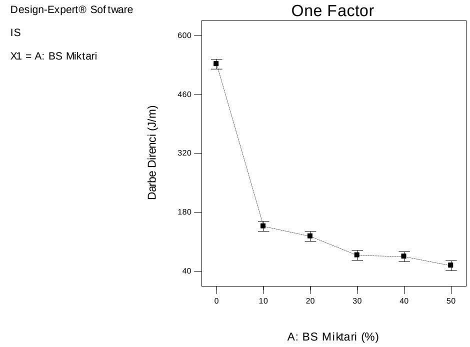

Figure 5. Impact strength of the obtained composites

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.

Acknowledgements

This research was partially supported by The Scientific & Technological Research Council of Turkey (Project number: 107O830).

References

Arbelaiz A., Fernandez B., Valea A., Mondragon I. 2006. Mechanical properties of short flax fiber bundle/poly(-caprolactone) composites: influence of matrix modification and fiber content, Carbohydrate Polymers, 64 (2), 224-232.

Avella M., Rota G.L., Martuscelli E., Raimo M., Sadocco P., Elegir G., Riva R. 2000. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fibre composites: thermal, mechanical properties and biodegradation behaviour, Journal of Materials Science, 35 (4), 829-836.

Averous L., Boquillon N. 2004. Biocomposites based on plasticized starch: thermal and mechanical behaviours, Carbonhydrate Polymers, 56, 111–122.

Aydemir D., Kızıltas A., Kızıltas E.E., Gardner D.J., Gunduz G. 2015. Heat treated wood–nylon 6 composites, Composites: Part B, 68, 414-423.

Chen X., Guo Q., Mi Y. 1998. Bamboo fiber-reinforced polypropylene composites: A study of the mechanical properties, J. Appl. Polym. Sci., 69 (10), 1891-1899.

Digabel L., Boquillon F., Dole N., Monties P., Averous L. 2004. Properties of thermoplastic composites based on wheat-straw lignocellulosic fillers, Journal of Applied Polymer Science, 93 (1), 428-436.

Dong C., Davies I.J. 2011. Flexural properties of wheat straw reinforced polyester composites, American Journal of Materials Science, 1 (2), 71-75.

Donmez Cavdar A., Kalaycıoğlu H., Mengeloğlu F. 2011. Tea mill waste fibers filled thermoplastic composites: The effects of plastic type and fiber loading, Journal Reinforced Plastics and Composites, 30, 833–844.

Donmez Cavdar A., Kalaycıoğlu H., Mengeloğlu F. 2015. Technological properties of thermoplastic composites filled with fire retardant and tea mill waste fiber, Journal of Composite Materials, DOI: 10.1177/0021998315595113.

Hornsby P.R., Hinrichsen E., Tarverdi K. 1997. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres: Part I Fibre characterization, Journal of Materials Science, 32 (2), 443-449.

Kaymakci A., Ayrilmis N., Gulec T., 2013. Surface properties of polypropylene composites filled with agricultural flour, Bioresources, 8, 592-602.

Matuana L.M., Balatinecz J.J. 1998. Effect of surface properties on the adhesion between PVC and wood veener laminates, Polym. Eng. Sci., 38 (5), 765-773.

Matzinos P., Tserki V., Kontoyiannis A., Panayiotou C. 2002. Processing and characterization of starch/polycaprolactone products, Polymer Degradation and Stability, 77, 17-24.

Mengeloglu F., Karakus K. 2008. Thermal degradation, mechanical properties and morphology of wheat straw flour filled recycled thermoplastic composites, Sensors, 8 (1), 500-519.

Mengeloglu F., Karakus K. 2012. Mechanical properties of injection-molded foamed wheat straw filled HDPE biocomposites: The effects of filler loading and coupling agent contents, Bioresources, 7 (3), 3293-3305.

Mishra S., Sain M. 2009. Commercialization of wheat straw as reinforcing filler for commodity thermoplastics, Journal of Natural Fibers, 6 (1), 83-97.

Pan M., Zhang S.Y., Zhou D. 2009. Preparation and properties of wheat straw fiber-polypropylene composites. Part II. Investigation of surface treatments on the thermo-mechanical and rheological properties of the composites, Journal of Composite Materials, 114 (5), 3049-3056.

Ruseckaite C.R., Jimenez A. 2003. Thermal degradation of mixture of polycaprolactone with cellulose derivatives, Polymer Degradation and Stability, 81 (2), 353–358.

Shibata S, Fukumoto I, Cao Y. 2006. Effects of fiber compression and length distribution on the flexural properties of short kenaf fiber-reinforced biodegradable composites, Polymer Composites, 27, 170-176.

Shin B.Y., Lee S., Shin Y.S., Balakrishnan S., Narayan R. 2004. Rheological, mechanical and biodegradation studies on blends of thermoplastic starch and polycaprolactone, Polymer Engineering and Science, 44(8),1429-1438.

Velde V.D., Kiekens K. 2002. Biopolymers: overwiev of several properties and consequences on their applications, Polymer Testing, 21 (4), 433–442.

Vikman M., Hulleman S.H.D., Zee V.D., Myllarinen P., Feil H. 1999. Morphology and enzymatic degradation of thermoplastic starch–polycaprolactone blends, Journal of Applied Polymer Science, 74 (11), 2594–2604.