The Chestnut Shell/Kaolin - Reinforced Hybrid Polyester Composite: Preparation, Characterization

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Abstract

The developing world comes to face with unconscious consumption and waste formation as a result of industrialization and urbanization. Urban and food factories bulky food waste is a very heterogeneous material flow usually destined to landfill. Many researchers have been changing their research direction is to improve the end-of-life and disposal of the complex products. Many food processing wastes are suitable to treatments to increase the quantity and quality of recovered materials with highest environmental impact. In this work, one such industrial food waste, chestnut shell fiber and 2 different kind of kaolin were tested comprehensively for their potentiality as reinforcement in polyester matrix to optimize the mechanical properties. Samples not only with chestnut shell and without kaolin but also with kaolin and without chestnut shell exposed for many tests to determine the effect of chestnut shell/kaolin contents on the mechanical, microstructural, thermal and water absorption properties of polyester composites. The polymer composites were characterized by scanning electron microscope, thermogravimetry analysis

Keywords: Chestnut shell waste, Kaolin, Polyester Composite, Thermo-Mechanical Properties, Characterization

1. Introduction

In the globalized world, with the impact of industrialization and urbanization, the unconscious use of natural resources has resulted in wastes, especially in food waste [Gunduzalp and Guven, 2011]. For this reason, the collection of waste and the use of it in the production of new products are important for human health, environmental pollution and national economy [Yagci *et al*., 2006]. The production of composite materials is increasing day by day in order to evaluate existing resources more efficiently and to meet the new needs that are emerging over time with reasonable costs [Avci, 2013]. Natural fibers have been used as reinforcing materials for many years. Being low cost, having high physical and mechanical resistance because of its advantages, plastic-composite materials are produced by mixing with plastics at various ratios. Compared to wood fibers and glass fibers, it provides a significant advantage as it provides significant reductions in composite weight. For this purpose in the plastic industry, many materials such as wheat stalks, hemp and various lignocellulosic industrial wastes have been tested. Besides these, in the composite industry, non-wood forest products such as chestnut shell, pine cone and tree bark are also evaluated [Bektas, 2014]. Underutilized agro-waste are most importantly rich resources of lignocelluloses materials, some typical example are millet, rice, wheat, corn straw, cocoa husk, corncobs and fiber [Abba *et al*., 2013]. Chestnut wastes are usually used as biomass/biochar source. Nature proposes, and Man disposes; we have to find or create/ alter new forms of chestnut wastes to increase their value and environmental issues. Kaymakci and Ayrilmis, they evaluated dimensional stability and some mechanical properties of polypropylene composites filled with chestnut shell flour (CSF). To meet this objective, CSF was compounded with polypropylene with and without coupling agent in a twin screw corotating extruder and then were manufactured by injection molding process. The thickness swelling and water absorption of the samples increased with increasing CSF content. The flexural and tensile modulus improved with increasing CSF content, while the flexural and tensile strengths of the samples decreased. The use of maleic anhydride polypropylene had a positive effect on the dimensional stability and mechanical properties of the polypropylene composites filled with CSF. This work showed that the composites treated with maleated polypropylene could be efficiently used as decking products, due to high-dimensional stability and satisfactory mechanical properties of the composites [Kaymakci and Ayrilmis, 2014]. Kaolinite ($Al_4(OH)_8Si_4O_{10}$) is a clay mineral which is a major component of the industrial clay kaolin [Strengl *et al*., 2014]. The production of clay-polymer nanocomposites is an active area of research which benefits from the high surface area of nanoclay particles to greatly improve the thermo mechanical properties of the polymer matrix, even with low filler contents. Polymers are used as a matrix in these types of composites, and clay minerals act as reinforcement material [Ayyasamy *et al*., 2014]. Leong *et al*. in their work three type of mineral fillers-talc, calcium carbonate ($CaCO_3$), and kaolin (10-40 wt% filler loadings)-were compounded with polypropylene (PP) with a twin-screw extruder. The composites were injection-molded, and the effects of the filler loading on the mechanical, flow and thermal properties for the different types of filled composites were investigated. The results that the filler matrix interactions are strongest for talc-filled PP, followed by those for kaolin-filled PP composites and $CaCO_3$-filled PP composites [Leong *et al.*, 2003]. Al-Asade and Al-Murshdy in their work studied addition of kaolin into unsaturated polyester matrix to prepare particulate composites. Addition of kaolin to an unsaturated polyester resin in the 3-9% (this considered relatively low percent) shows that kaolin act as binder and as particulate reinforcement results in improvement in the mechanical properties of the unsaturated polyester via the resulting composite [Leong and Al-Murshdy 2008]. Kaolin can be classified according to their use. They can be classified according to their physical properties as aluminous, siliceous, ferrous, kaolin-like mineralogical composition, oily, hard, cast, soft, plastic kaolin, and refractory kaolin. It is mostly used in filling and paper industry. It is followed by plastic and ceramic industry. The thermal stability of polymer composites depends upon various factors. Knowledge of the thermal decomposition process in polymers and their blends on heating is highly essential for developing many end products out of them [Schmidt *et al.*, 2004]. In this paper, composites were manufactured using of waste chestnut shell flour and kaolin as filler and polyester as polymer matrix. Using chestnut and two different kaolin increasing ratios; the mechanical properties of chestnut shell flour/kaolin ratio in polyester composite formation were tried to be revealed. The thermal stability of the blends of chestnut shell flour / kaolin polyester composites was studied by TGA.

2. Material and Methods

2.1. Materials

The polyester resin (Polipol383-G) was used as the matrix that was obtained from the Poliya Composite Resins and Polymers Inc. The mixing ratio used was 100g of polyester resin with 0.625ml accelerator (2% Cobalt naphthenate solution), 3ml hardener (Methyl Ethyl Ketone peroxide, MEKP, Akzo Nobel Products) and 0.5ml Polyethylene graft maleic anhydrite (Sigma Aldrich) as coupling agent. The filling material of discarded chestnut shells was obtained from the chestnut candy company in Bursa/Turkey. Two kind of the kaolin was added as reinforcement materials with chemical composition show in Table (1). This table shows the result of XRF analysis of kaolin. The samples were placed in the XRF machine for elemental analysis. The machine (XRF PANalytical, AXios mAX minerals) was operated at 50 KV. The theoretical densities and volumes belonging to the ground chestnut shell, kaolin were determined by using a Micromeritics brand AccuPyc II 1340 model Helium-gas pycnometer (Table 2). Figure 1. shows the whole process of the experimental composite specimen preparation. The predetermined amounts of filler, polyester were mixed together in a suitable beaker with a magnetic stirrer. When the process was finished, all agents, including the hardener, accelerator and coupling agent, with a determined ratio, were added to the previous filler/polyester mixture. An aluminum mold (Figure 1) of the required dimensions (10mm x 4 mm x 100 mm) was used for the making of samples. The mold was covered with a mold-releasing agent so the samples could be easily removed. The completed mixture was poured into the mold (Le and Huang, 2015).

2.2. Preparation of composites

The three fillers i.e., Chestnut shell flour (C), White kaolin (W), Grey kaolin (G) in the powder forms were properly mixed according to the each experiment run given in Table 3. After proper mixing of these fillers, six compositions of hybrid fillers were prepared.

Table 1. Chemical composition of kaolin.

Oxides	Grey kaolin	White kaolin	Oxides	Grey kaolin	White kaolin
Na_2O	0.039		Cr_2O_3	0.137	
MgO	0.196	0.236	Fe_2O_3	4.340	2.326
Al_2O_3	20.259	44.294	NiO	0.038	0.014
SiO_2	59.077	44.749	CuO	0.050	
P_2O_5	2.014	2.770	ZnO	0.009	0.039
SO_3	0.157	0.057	SrO	0.106	0.065
K_2O	6.545	3.420	ZrO_2	0.195	0.088
CaO	1.722	0.759	PbO	0.042	0.274
TiO_2	5.074	0.691			

Table 2. Filling materials theoretical density and volume

Sample	Mean Density (g/cm^3)	Mean Volume (cm^3)
Chestnut shell	1.4714± 0.0018	1.3547± 0.0016
White kaoline	2.5999± 0.0040	1.0211± 0.0016
Grey kaoline	2.5008± 0.0013	2.3833± 0.0013

Table 3. Mixture volume proportion of composites

Filler/ Polyester	Composite codes and ratio by volume					
	C1P	C2P	C3P	C4P	C5P	C6P
C[a*]	3	4	6	7	9	10
P[b*]	97	96	94	93	91	90
	C1WP	C2WP	C3WP	C4P	C5WP	C6WP
C	3	4	6	7	9	10
W[c*]	3	3	3	3	3	3
P	94	93	91	90	88	87
	C1GP	C2GP	C3GP	C4GP	C5GP	C6GP
C	3	4	6	7	9	10
G[d*]	3	3	3	3	3	3
P	94	93	91	90	88	87

a*C: Chestnut shell flour; b*P: Polyester; c*W: White kaolin; d*G: Grey kaolin

2.3.Experimental studies

The flexural properties of the material were determined by 3 point bending test (Fig. 2). The test specimens were with dimensions 10 x 4 x 100 mm. A test speed of 2mm min-1 and Shimadzu AG IC100 kN test device was used. Results were gathered compliant to the equations given below, by calculating the mean of the five samples.

Flexural strength (N/mm^2) = $(3LP)/(2bd^2)$ E1

Flexural modulus (MPa) = $(L^3m)/(4bd^3)$ E2

Where L is the support span (mm), P is the maximum load (N), b is the width of the composite sample (mm), d is the thickness of composite sample (mm), m is the slope of the initial straight line portion of the load–displacement curve. The indentation hardness of the material was measured by Shore D. the izod impact test was conducted with the device DVT CD, Devotrans Quality Control Test Instruments Ltd., Turkey.

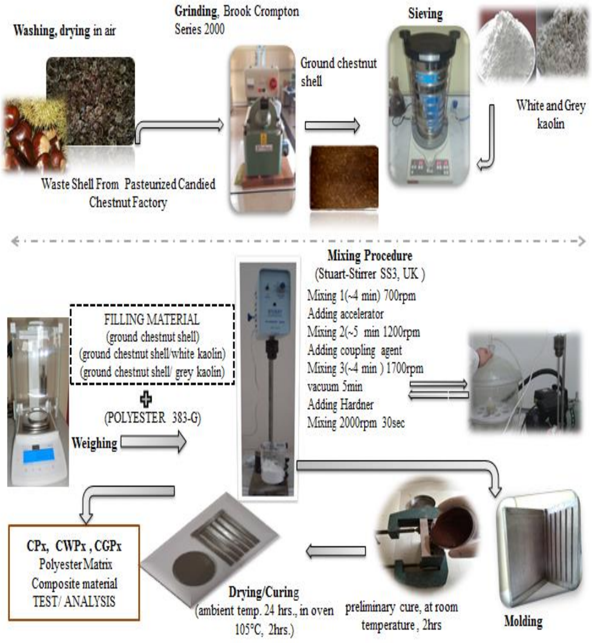

Figure 1. Graphical illustrations for manufacturing process of polyester composites

Figure 2. Application of the three point bending test

The densities of the composite materials were determined by weighting method. A kit of analytical scale and a weighting jig was used for weighting a specimen of the material in air and fluid. The density is determined by equation: water absorption, bulk density and % open porosity values were calculated.

$$A, \% = (W_D - W_K) / W_K * 100 \quad \text{E3}$$

$$B = [W_K / (W_D - W_A)] * \rho_w \quad \text{E4}$$

$$P, \% = [(W_D - W_K)/(W_D - W_A)]*100 \quad \text{E5}$$

Here A is Water absorption, B is Bulk density, P is Apparent porosity W_K is dry weight, W_D is specimen weight in air, W_A is specimen weight in fluid, and ρv is density of the fluid. Scanning Electron Microscope (SEM., Zeiss Supra 40VP, Germany) was used to obtain microstructural images which were taken from a cracked surface of composites. Thermal behaviors of the composite samples were investigated using Seteram LabSys Evo analyzer. 7–11 mg of accurately measured powdered composite of specimen was kept in alumina crucible. The process is done under nitrogen atmosphere with a flow rate of 20 ml/min by raising its temperature from 20° C to 800° C in steps of 20° C/min.

3. Results and Discussion

Table 4 shows the variation in flexural strength of composites with increase in volume fraction of chestnut shell flour. The flexural strengths of chestnut shell-filled composites decreased with increase in filler volume fraction (Kaymakci and Ayrilmis, 2012 and Wu *et al.*, 2014). Similar results were also obtained with the use of palm kernel shell, sugarcane bagasse and pineapple chaffs hybrid polyester composites by Adeosun *et al.* (2016). Addition of kaolin to filler content influenced to flexural strength as reinforced.

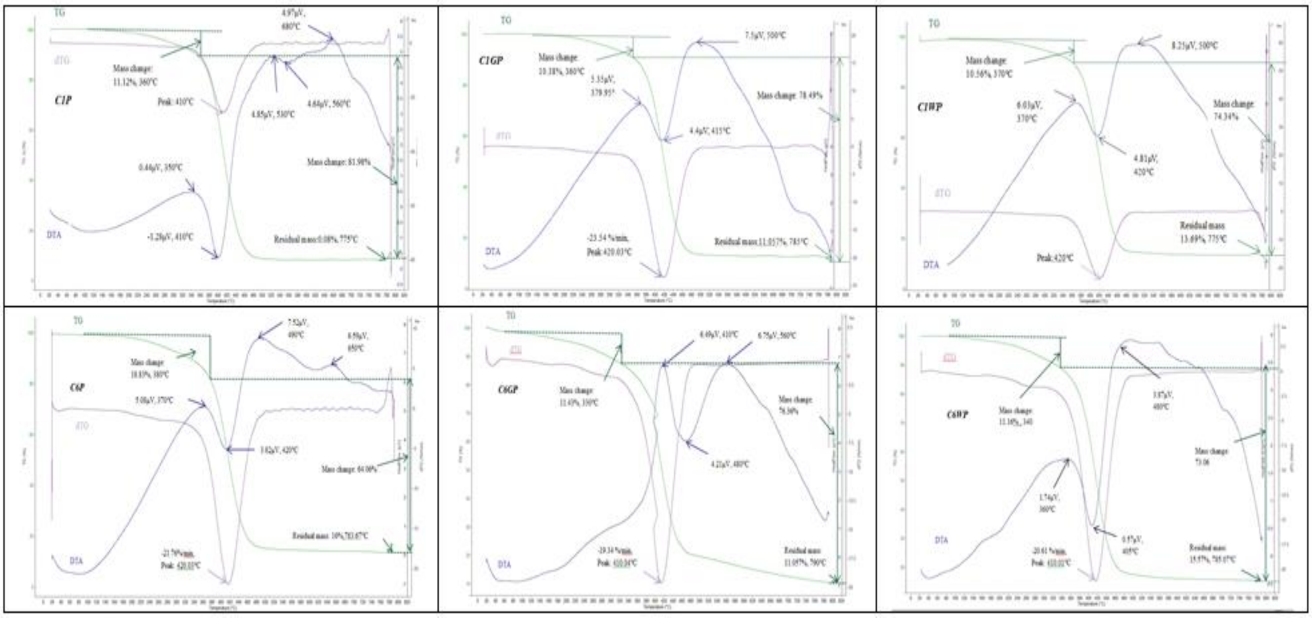

Figure 6. TG, DTG and DTA curves of composite samples

The flexural modulus of chestnut shell-filled composites increased with increasing of chestnut shell flour. In Table 4, the hardness was decreased with an increase in Chestnut shell flour amount for all polyester composites but the addition of kaolin fillers were improved hardness of composites. We believed that it must have been stronger matrix/filler interfacial bond. The CP composite series has the highest percentage of water absorption in other composite samples. The percentage of water absorption in composite samples increased with the amount of cellulose in the chestnut shell and the percentage of open porosity (Table 4). The kaolin clay has reduced the amount of open porosity and improves the coalescence of the matrix and fillings as seen in SEM images.

Table 4. The effect of chestnut shell flour content on bending and the dimensional stability properties for CP, CWP and CGP composites

Composite Samples	Flexural Strength (N/mm^2)	Flexural modulus, (MPa)	Hardness, Shore D	Water absorption, (%)	Open porosity,(%)	Bulk Density
C1P	55.21	4,356.82	85.25	0.805	0.955	1.187
C2P	53.38	4,430.69	85.75	0.915	1.088	1.189
C3P	51.81	4,653.77	85	0.921	1.105	1.190
C4P	51.78	4,848.32	85.75	1.038	1.239	1.193
C5P	49.07	5,113.52	86.25	1.212	1.447	1.195
C6P	49.30	5,119.64	85.75	1.273	1.512	1.190
C1WP	62.19	4,132.19	86.000	0.707	0.876	1.240
C2WP	57.10	4,371.91	86.750	0.847	1.053	1.243
C3WP	54.22	4,791.48	87.750	1.005	1.228	1.235
C4WP	53.79	5,025.93	88.000	1.019	1.264	1.240
C5WP	53.51	5,002.15	87.750	1.037	1.287	1.240
C6WP	52.61	5,097.28	88.250	1.128	1.385	1.228
C1GP	55.57	4,630.31	87.250	0.797	0.986	1.237
C2GP	54.98	4,969.10	87.500	0.807	1.075	1.237
C3GP	54.71	5,323.13	87.750	1.135	1.135	1.244
C4GP	53.46	5,325.22	88.500	1.136	1.407	1.238
C5GP	51.06	5,525.18	87.750	1.166	1.439	1.234
C6GP	50.62	5,474.99	88.750	1.171	1.446	1.235

This is supported by Adeosun *et al*. The scanning electron microscopy (SEM) images of chestnut shell flour, the two types kaolin powders as fillers and fractured surfaces of different composites are shown in Figure 5. Electron micrographs of the structure of kaolin filler (White and Grey) should help illustrate the basic idea contains well developed books of pseudo-hexagonal platy kaolinite cluster. When the chestnut shell fiber content is increased to 10 vol% the bonding characteristics gets distorted due to insufficient matrix contact with the fiber and the formation of voids leading to reduced mechanical properties (Nagarajan *et al*.,2013). Thermal stability results of composite samples by TG, DTG and DTA analysis are presented in Figure 6. The top one is the TG, the bottom one is the DTA and the middle one is the DTG curve of composite samples. Minor weight loss occurred up to 100°C-140°C in all composites, which is due to the evaporation of water absorbed in pores and on the surfaces. The lighter substances are removed initially and then heavier materials are removed. The TG curve shows that major degradation occurs in one stage. Thermal stability of the composites are ensured up to 330°C -360°C and chestnut shell and kaolin burn out occurred at around 480°C which is reasonably a high temperature for polymer composite processing and intended composite applications. DTA curves of composites shows endothermic.

4. Conclusions

In the present work, the discarded, chestnut shell is tested for its potentiality as reinforcement for polymer composite. The influence of fiber content on the mechanical properties, such as flexural strength, impact strength and hardness are significant decreases with fiber content up and with addition of kaolin as reinforced due to improper to chestnut shell polyester composite mechanical features. Chestnut shell and kaolin with together as a filler has been able to withstand sufficient temperature without any serious issues enables it to be used as a potential reinforcement for polymer composites. It is expected that the present behavior may be improved more by changing manufacturing type as use extruder and with injection molding.

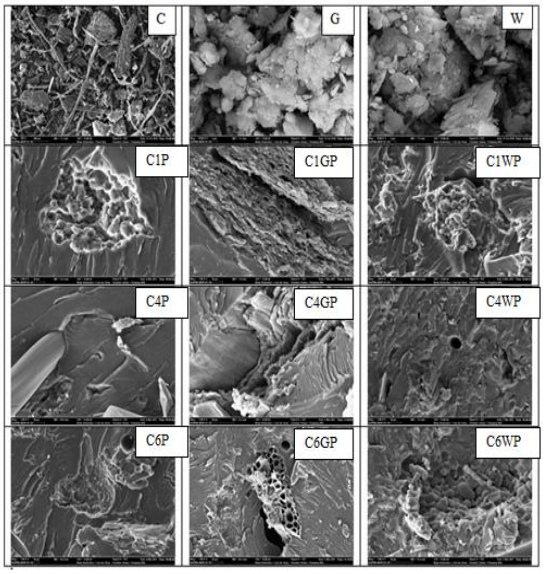

Figure 5. SEM images showing the morphology of fillers (Chestnut shell flour, grey kaolin, white kaolin), polyester composite samples

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