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ORIGINAL ARTICLE

Thermal and flammability behavior of walnut shell reinforced epoxy composites

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Abstract

In this study, walnut shell particles obtained through the grinding of walnut shells were used as a reinforcing material and pumice powder as a filler for developing epoxy-based composites characterized by reduced flammability. Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), and Underwriters Laboratories (UL)-94 vertical tests were carried out for evaluating the effectiveness of these pumice powder treatments. Under the UL-94 vertical test, composites (S1, S2, S3, S4, S5 and S6) with 20% pumice powder (i.e., by mass content of walnut particles were not self-extinguished, and could not be classified. S7 and S8 composites (40wt% and 50%) assigned a V-2 rating, which was the least flammable composite However, the mechanical tensile tests showed that the pumice powder treated composites increased their tensile strength. The morphological analysis showed an enhancement of the interfacial adhesion of the composites achieved by pumice powder.

Keywords: *thermal properties, walnut particles, pumice, tensile strength, flammability.*

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1. Introduction

With growing environmental awareness, ecological concerns and new legislation, bio-particle reinforced plastic composites have received increasing attention. The important aspect that has impacted favorably on the development of green composite materials is the possibility of incorporating waste agro-waste such as stalks, cereal crops, rice husks, coconut fibers, bagasse, maize cobs, peanut shells, and other wastes product and recycled plastics with the advantage of a positive eco-environmental impact. Due to a worldwide shortage of trees and environmental awareness, research on the development of composite materials using various waste materials is being actively[1].

Walnut (*Juglans regia L.*) is an important crop that is cultivated throughout the world's temperate regions for its edible nuts. Because walnut shell comprises 67% of the total weight of the walnut kernel, 1.5 million tons of walnut shell is left behind each year all over the world. The stone cell of high lignification is the main characteristic of the microstructure of the walnut shell[2]. Several investigators studied different properties of polymer composites using these reinforcements[3]. By Singh[1] studied physico-mechanical characterization and thermal property evaluation of filled with polyester composites walnut shell powder. They prepared the walnut shell based particles reinforced composite materials and also investigated the mechanical behavior of the composite.

Because reinforcement alone does not fulfill the required properties for the applications of composites, a suitable filler is sometimes required to achieve the desired properties. Artificial and natural fillers are used with polymeric matrix composites. Pumice is one of the important natural fillers. Among them, pumice is one of the volcanic based alumina silica, which is composed of 60% of SiO^2. The porous structure of pumice is formed by dissolved gases precipitated during the cooling of lava[4]. Due to its porous structure, it has low density, high thermal insulation, and chemical resistance, which makes it a preferential material for industrial applications. Moreover, pumice powder has a high-temperature resistance and chemical resistance[5]. Pumice powder is cheaper than most traditional particle fillers. The use of pumice powders as a reinforcing material in composites has not been studied in detail in the literature, but there is an increasing trend in using pumice powder as a filler material in composite applications[6].

Sever et al.[5] investigated the effect of pumice powder on the mechanical and thermal properties of PP. Ramesan et al.[7] stated the role of pumice particles in the thermal, electrical, and mechanical properties of poly(vinyl alcohol)/poly(vinyl pyrrolidone) composites. Sahin et al.[6] demonstrated that pumice powder-filled PPS composites can successfully attain mechanical and thermal properties[8]. Montava-Jordá et al.[9] investigated the enhanced interfacial adhesion of polylactide/Poly(ε-caprolactone)/walnut shell flour composites by reactive extrusion with maleinized linseed oil. From an extensive literature survey, many researchers used the walnut shell as a reinforcement, and pumice powder as a filler for

manufacturing composite. It was observed that the filled with pumice powder of natural reinforcement in the composites improves the adhesion between the epoxy/walnut shell and pumice surfaces, resulting in the mechanical anchoring of the blend on the porous structure of the pumice powder. The present developed composite materials containing different walnut particle sizes as the reinforced materials and investigate the tensile strength, thermal, and flammability behavior of composites.

2. Materials and Methods

Purpox® epoxy resin EFLR-0190 (Polikor Inc., Bursa, Turkey) was used as matrix material, which is a solvent free resin with a transparent coating. The density of this resin was 1.00 to 1.10 g/cm^3, the while the viscosity was 300,500 mPa.s. The epoxy resin and hardener were mixed at a weight ratio of 100:50 to produce the composite materials. Composites with 20 wt.%, of pumice powder component were made of all 3 fractions, and %40 -50% wt of pumice powder was made of the 630 μm (Table 1). The preparatory work included separating 400 g of walnut husk particles on a sieve shaker (The Mortar Grinder RM-200 Microtrac Retsch GMBH, (Haan, Germany) for 10 min. The sieve stack was composed of 3 sieves, and their mesh sizes were 1000, 630, and 250 μm from the top to the bottom, respectively.

2.1 Manufacturing of composites

The composite samples were made using 100 wt.% of 1000 μm walnut shell, 100 wt.% of 630 μm walnut shell, and 250 μm walnut shell as well as 80 wt.% walnut particles and 20 wt%40 wt and 50wt% pumice powder proportions and the matrix employing the hand lay-up technique. A metal mold (per ASTM D3039[10] and UL 94[11] was used for composite fabrication.The inner surface of the metal mold was treated with a stripping agent (Polivaks SV-6, İzmir, Turkey) to facilitate easy removal of the samples after fabrication. The slurry was poured into the metal mold; care was taken so that no gaps or air bubbles were formed. A small roller was used during the fabrication process to spread the resin and reinforcement uniformly so that the mold was devoid of voids and agglomeration. The contents of the mold were cured at room temperature for 48 h and then removed from mold for the tests paragraph within a first subsection.

2.2 Tensile test

Composites were subjected to tensile strength tests using a universal testing machine (model BMT 100E, Besmak, Ankara, Turkey). Ten samples of each material were evaluated according to the ASTM D3039[10] standard. The tests were conducted at a crosshead speed of 2mm/min with a 100 kN load cell.

2.3 Flammability (vertical burning) test

The flammability test based on UL- 94[11] was applied to evaluate the fire performance of the materials. The UL- 94 test results are classified by burning rating V-0, V1, or V2; the V-0 rating represents the best flame retardant of polymeric materials. Vertical tests are more rigorous than horizontal burning tests because the vertical specimens are burnt by their lower ends[12-14]. The ignition resistance was investigated at conditioning parameters of 23 ± 2°C, 50 ± 5% relative humidity (RH), for greater than 48 h. The dimensions of the sample were 125 mm x 13 mm x 13 mm for the length, width, and thickness, respectively, according to the UL-94 (2001) standard. Based on the outcome, the samples were categorized as V-0/V-1/V-2 or No Rating (NR)/NC (No Classification). Five samples were tested for each combination and reported.

2.4 Scanning Electron Microscopy (SEM)

A HITACHI TM3030 EDX-BSE (Tokyo, Japan) SEM instrument was employed to examine the topography of the broken surfaces of the composites after tensile testing.

2.5 Thermogravimetry Analysis (TGA)

The thermal stability of walnut shell/epoxy composites and walnut-pumice/epoxy composites was characterized using a thermogravimetric analyzer (SDTQ600, TA, New Castle, USA) at a heating rate of 20 °C/min under Nitrogen (N2) atmosphere from 20 to 900 °C, with, samples with of 10 to 11 mg.

2.6 Differential Scanning Calorimetry (DSC)

A DSC Q2000 (TA, New Castle, USA) instrument with aluminum sample pan was used with an nitrogen (N2) atmosphere with a heating rate of 100°C/min. The pumice powder filled walnut shell/ epoxy composites walnut

Table 1. Composition of walnut husk particles with pumice powder.

Samples Codes	Sieve mesh size of walnut shell (μm)	Walnut shell particles content (wt%)	Filler content (wt%)	Type of filler	Sieve mesh size of pumice powder (μm)
S_1	250	100	-	-	-
S_2	630	100	-	-	-
S_3	1000	100			
S_4	250	80	20	Pumice powder	< 250
S_5	630	80	20	Pumice powder	< 250
S_6	1000	80	20	Pumice powder	< 250
S_7	630	60	40	Pumice powder	< 250
S_8	630	50	50	Pumice powder	< 250

shell/epoxy composites specimens of 5 to 7 mg were scanned over a temperature ranging from 10 to 300°C.

3. Results and Discussions

3.1 Flammability test results

Samples ignition resistance was investigated under a UL-94 vertical burning test. UL 94 vertical is a ranking measurement of the self-extinguishing time of a polymer or reinforced polymer composite The test results are presented in Table 2. The pumice powder is the as it is not sufficient till 20 wt% to reach any V-class. The effect of increasing the wt % pumice powder ratio on UL94 results is promising and the V-2 rating is satisfied except for the sample of 20wt%. During the burning test, after-glowing was observed for all 20wt % samples, and samples were flammable. Thus, all 20wt % pumice powder added specimens failed the vertical burning test. Even though no UL rating was observed for Pumice powder 20wt% the presence of pumice powder of 40wt % and 50% significantly decreased the combustion rate of the specimen. Similarly, studies were also observed[15-17].

3.2 Tensile strength results

Comparisons of tensile strengths of the composites samples are given in Figure 1. The addition of pumice powder as a filler material to the S4, S5, S6, S7 and S8 composite increased tensile strength compared with the control (S1, S2, and S3) samples. The maximum tensile strength was reached in the S8 sample. This may be attributed to the presence of pores of the walnut shell (630 µm particle size) that provide good adsorption capacity for resin,and due to the excellent dispersion of 630 µm particle size larger surface area, and intermolecular interactions between the filler/matrix, which results in stronger bonding between walnut shell particles size and epoxy matrix to improve composite mechanical properties. The low tensile strengths were obtained for the S1 composites according to the other samples. This result can be explained by the walnut shell containing a lower amount of hygroscopic material like cellulose/hemicellulose and a higher amount of hydrophilic material such as lignin. As WSP contains a high amount of lignin this may be the reason behind the decrease in tensile strength of the composites[3], or from the proportion between the particle size and the surface area, which allows obtaining bad dispersion of the filler as well as unproper saturation by the epoxy resin increase in the matrix cross-linking[18] As shown in Figure 1, the tensile strength was found to be low for the composite (S3). This may be attributed to the formation of a fragile surface between the epoxy and pumice powder/ walnut shell size, or poor interface between the epoxy and the pumice powder. As a result, the deterioration of tensile strength properties can be expected, as noted by others[19-22].

3.3 Scanning electron microscopy

The SEM micrographs of the tensile fracture surface of the composites (Figure 2). The micrographs (Figure 2a) show that the walnut particles were not completely covered with the resin. Voids were found on the surface, and their surface was rough to various degrees. Surface roughness impedes its proper wetting by the walnut sheel matrix in the course of processing, thereby contributing to the formation of voids at the interface. This result indicates poor interfacial interactions between the walnut shell and epoxy matrix. SEM images of samples added with 20, 40, and 50 wt.% of pumice powder are given in Figure (b–d). Figure 2c and 2d show a few matrix voids and walnut shell particle pullouts at the tensile fractured surface. At 20, 40, and 50 wt.% pumice powder was uniformly distributed in the matrix and placed between walnut shell and matrix to stop the micro-crack propagation during experiments. Also, in all these SEM images (Figure 2), one can observe that

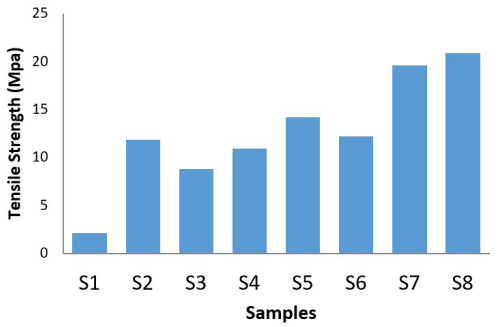

Figure 1. The tensile strengths of the composites.

Table 2. Burning Criteria for UL-94[11]. Vertical Rating.

Samples Code	Combustion up to holding clamp (specimens completely burned)	Cotton ignited	Rating
S_1	Yes	Yes	NR
S_2	Yes	Yes	NR
S_3	Yes	Yes	NR
S_4	Yes	Yes	NR
S_5	Yes	Yes	NR
S_6	Yes	Yes	NR
S_7	No	No	V-2
S_8	No	No	V-2

NR (No Rating).

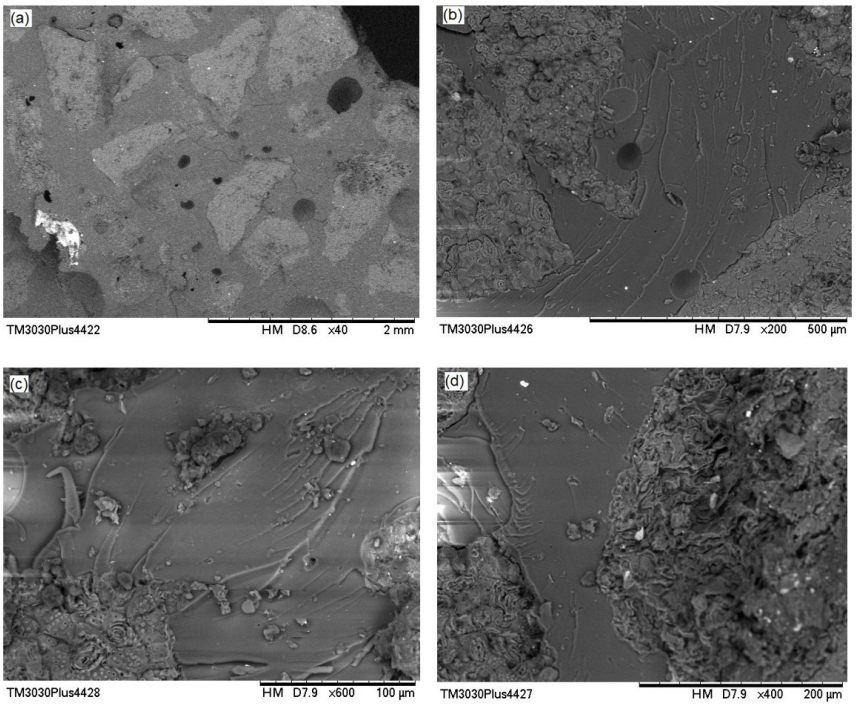

Figure 2. SEM micrograph of tensile fractured surfaces; (a) 100% walnut shell 630µm particle size; (b) 20% pumice powder incorporated composite; (c) 40% pumice powder incorporated composite; (d) 50% pumice powder incorporated composite.

the walnut shell particles were relatively well distributed in the pumice and epoxy, which in turn could support an increase in tensile strength properties at an appreciable level.

3.4 Differential scanning calorimetry

The DSC curve of unfilled and filled composites are presented in Figure 3. the unfilled samples (S2) are two endothermic peaks were observed at 52 °C, to 92 °C respectively. The first endothermic peak at 52°C illustrates the glass trasition temperature (Tg) of composite. The second endothermic peak, at 92°C shows the crystallization peak of the composite. The filled sample (S8) three endothermic peaks were observed at approximately 100°C, and 155°C, and 262 °C respectively. The first endothermic peak was observed at a peak of 103 °C, the peak corresponds to the crystallization peak of the composites. Successively, the other two endothermic peaks, one at 155°C and the other at 262°C, correspond to the decomposition. content. The pumice powder-filled composite was found to have higher crystallization peak temperatures than the unfilled composite. This result shows that the walnut shell particles and pumice powder act as nucleating agents, which increases the crystallization temperature of the composite. A similar study was also observed[2]. According to results obtained from DSC analyses to that the thermal stability of the composite was increased with increased filler.

3.5 Thermogravimetry analysis

The thermal stability and degradation of the selected composites were studied using TGA in air and nitrogen atmosphere. Figure 4 shows the TGA graph of an unfilled and filled composite respectively. Thermal degradation

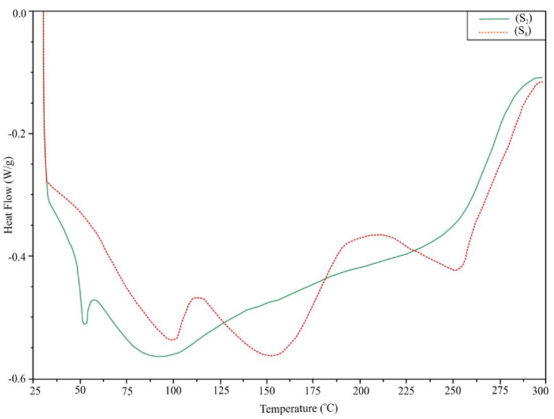

Figure 3. Heating curves of DSC for control composite and composite of filled pumice powder.

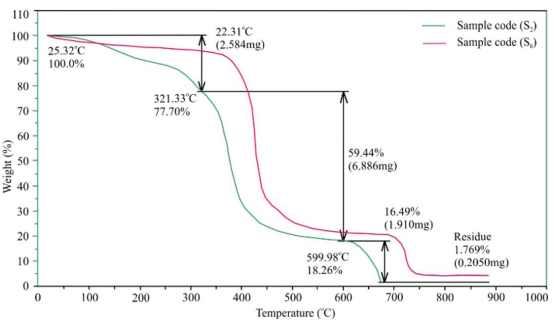

Figure 4. TGA curves of unfilled composite (S_2) and (S_8) pumice powder-filled composite.

(weight loss) of the composites happened in three consecutive phases (unfilled and filled composites). The primary stage of weight loss of filled with temperature is in range of 25-200, the second in 250-321°C, and the third in 321–599°C. The primary stage of weight loss of filled with temperature is in range of 30-350, the second in 450-600°C, and the third in 600-700°C. TGA graph shows an initial weight loss of 25-200 and 30-350°C for (unfilled and filled composites) is due to the evaporation of moisture content surrounding the composite surface, moisture absorbed inside the sample. Maximum weight loss of composites occurs in the second stage of degradation. In the second stage, weight loss occurs because of the elimination of lignin as well as the hemicellulose of a walnut shell. The weight loss occurs in the last stage because of the removal of α cellulose as well as other non-cellulosic materials. Therefore, very minor weight loss could be observed at this final stage[23]. Main components of walnut shell: The TGA curve in the present study is similar of the WS thermogravimetric curves are similar to those presented in the literature and correspond to the decomposition of the three hemicelluloses (210–325°C), a-cellulose (310–400°C), and lignin (160–500°C)[14,24,25].

4. Conclusions

Flame resistance as well as the resulting mechanical properties were considered. samples code S7 and S8 show the best result and reach the V2. But other all samples were not characterized by flammability. The pumice powder filling has improved the tensile strength properties of walnut shell particles reinforced epoxy composites. The pumice powder (50%) filled walnut particles size (630 μm) composites showed maximum improvement in tensile strengths. SEM micrographs of the fracture surface indicated that the walnut shell particles after the pumice powder treatment became better suitability due to the mix of the pumice powder, which resulted in better walnut shell particles-matrix adhesion. Overall, the 50% pumice powder filler loading walnut shell particles the reinforced epoxy composites showed considerably higher and better thermal stability.

5. Author's Contribution

- **Conceptualization** – Göksel Ulay; Menderes Koyuncu.
- **Data curation** – Menderes Koyuncu.
- **Formal analysis** – Göksel Ulay; Menderes Koyuncu.
- **Funding acquisition** – Göksel Ulay; Menderes Koyuncu.
- **Investigation** – Göksel Ulay.
- **Methodology** – Göksel Ulay; Menderes Koyuncu.
- **Project administration** – Menderes Koyuncu.
- **Resources** – Göksel Ulay; Menderes Koyuncu.
- **Software** – NA.
- **Supervision** – Göksel Ulay; Menderes Koyuncu.
- **Validation** – Göksel Ulay.
- **Visualization** – Göksel Ulay; Menderes Koyuncu.
- **Writing – original draft** – Menderes Koyuncu.
- **Writing – review & editing** – Göksel Ulay; Menderes Koyuncu.

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