Waste Biomass Valor (2017) 8:1855–1862
DOI 10.1007/s12649-017-9856-6

ORIGINAL PAPER

Effect of Marble: Pine Cone Waste Ratios on Mechanical Properties of Polyester Matrix Composites

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Received: 1 May 2016 / Accepted: 6 February 2017 / Published online: 25 February 2017

Abstract There is ongoing research interest in finding alternative sources of materials for composite manufacturing. Therefore, alternative non-wood based materials may play an important role in the forest product industry. Natural fibers have many advantages compared to synthetic fibers such as low density, lower cost, acceptable specific properties and being renewable and biodegradable. Natural fiber composites show high strength and stiffness, as well as good thermal and insulating properties. In this study, polymer matrix composites were manufactured using pine cone and marble waste and ATH powder as filler and polyester as matrix material with the casting method. Methyl ethyl ketone peroxide as hardener for cross-link network structure and cobalt naphthenate as accelerator were used to produce polyester matrix composites. Marble: ATH filler ratio was kept constant and polyester: filler (pine cone + marble + ATH) ratios were changed. Mechanical properties of composite materials were investigated and the final product tested to determine flexural strength, flexural modulus and hardness as well as some physical features such as bulk density, % total porosity and % open porosity. The experimental results showed that flexural strength and hardness of the composite materials decreased with the increase in pine cone: marble + ATH ratio.

Keywords Polymer matrix composites · Marble wastes · Pine cone wastes · Polyester · Mechanical properties

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Introduction

Composites have some excellent properties such as light weight, specific strength and stiffness and these properties make them preferable to conventional materials like metals, woods etc. [1]. Polymers used in composite materials cannot provide the desired features singly. Therefore fibers are reinforced with polymer composites [2]. Natural fibers are gaining much interest in composite materials due to their potential for use instead of conventional glass fibers. In recent years, the strong emphasis on environmental consciousness worldwide has brought much interest in the production of recyclable and environmentally sustainable composite materials [3]. Researchers focused on the use of natural fibers in composite manufacturing over the past few decades. Natural fiber composites have many advantages compared to synthetic fibers such as glass fibers; low density, cheaper cost, availability and biodegradability [4, 5]. The advantages of using this type of bio-resource are multifunctionality, flexibility and ability to be supplied extensively worldwide without damaging the environment. Several recently conducted studies on this subject are available. Bending properties of macadamia nutshell/polyester composites have been investigated by Dong, C. et al. It was concluded that flexural modulus increased with the weight fraction of macadamia nutshell particles (10, 20, 30 and 40%) while it decreased with increasing void content. The study also showed that flexural strength decreased with increasing void content [6]. Guru and colleagues have studied fly ash and marble powder addition in the production of the composite polymer matrix. Mechanical properties of composite materials were examined. Optimal three-point bending strength and hardness values were found to be 30.42 N/mm^2 and 98 Shore D, respectively [7]. In the study of Arrakhiz et al. various amounts

of pine cone and clay were melt mixed with the polypropylene. Tensile and hardness tests were carried out for these composites to obtain the impact of the hybrid effect. According to the test results, hardness properties decreased with high clay content. The mechanical test results showed that the Young's modulus had increased for a gain of 80% but tensile strength remained stable with the increasing amount of both fillers [8]. Tensile strength of the natural reinforced coconut fiber composites was investigated by Wei and Gu. The tensile modulus of the specimens has been calculated and the average value has been found as 115.3 MPa. They also concluded that the optimum fiber volume fraction for composites was 60%. According to experimental results, the addition of lower or higher than 60% of the fiber reduced the tensile strength of the composites [9]. Prasad and Nao studied the mechanical properties of natural fiber reinforced polyester composites such as Jowar, sisal and bamboo. They found that jowar fiber has a tensile strength of 302 MPa and a modulus of 6.99 GPa. It was concluded that bamboo composite has similar tensile strength values to jowar fiber composites. Sisal composite has 11 and 45% greater tensile modulus than bamboo composites. According to the results of this study using jowar fibers as reinforcement in polyester matrix could develop a composite material in the way of high strength for light weight applications when compared to conventional sisal and bamboo composites [10]. Tensile and flexural properties of snake grass natural fiber reinforced isophthallic polyester composites were investigated in the study of Sathishkumar et al. In the results of their study, increasing the ratio of volume fraction of grass fiber increases the mechanical properties of composites such as tensile, flexural strength and modulus [11]. Besides using natural fiber alone, Ramesh et al. researched the combination of natural and glass fiber composites. Mechanical properties such as tensile strength, flexural strength and impact strength of sisal–jute–glass fiber reinforced polyester composites were investigated. The results indicated that the jute composite material shows maximum tensile strength and can achieve strengths up to 229.54 MPa. The maximum value for the impact strength obtained for the sisal fiber composite was 18.67 joules [12].

In this study a mix of pine cone, marble waste and ATH was chosen as filler for polyester composite production. Pine cone, a renewable resource, has not been used effectively. It is collected, dried to facilitate seed release, and generally discarded or burned in stoves in winter. Also, cone collection does not involve extra costs. The total area covered by stone pine woodlands is about 380,000 ha and 75% of these cones are found in Spain, 9% in Portugal, 9% in Turkey, 5% in Italy and lower percentages in Greece, Lebanon and France [13, 14]. Turkey has 54,000 ha of stone pine forests that produce 3500 tons of pine cone annually [15]. This value has significant importance to evaluate pine cone waste in manufacturing composites to provide sustainability. The other filler chosen in this study was marble waste. During the cutting process in marble factories about 25% of the original marble mass is lost in the form of dust. In Turkey marble dust is settled by sedimentation and in summer it forms a dust that damages both agriculture and public health and also results in environmental pollution. Therefore, utilization of the waste marble dust in composite production would protect the environment [16]. Filler amount is a significant property when considering the cost of a product and is as important as the mechanical and physical properties of composites. To keep the resin amount lower can lead to a decrease in the costs because resin is more expensive when compared to other kinds of fillers. In accordance with this approach, ATH was chosen as a filler to decrease the amount of polyester used in composite production and also to provide good mechanical properties when combined with other filler materials [17].

In this study, polymer matrix composites were manufactured using pine cone, marble waste and ATH (alumina trihydrate) as filler and polyester as polymer matrix with the casting method. Butanox as hardener and cobalt naphthenate as accelerator were used to produce polyester matrix composites. Some mechanical and physical properties of the composite material were investigated.

Materials and Methods

Materials

Polyester resin (Polipol 383-G, Poliya Composite Resins and Polymers Inc.) was used as the matrix in all tests. Methyl ethyl ketone peroxide (MEKP, Butanox™ M-60, AkzoNobel Products) catalyzes the crosslinking reaction of the polyester resin, which leads to hardening. Cobalt (1% solution) was used as an accelerator in the curing of polyester resins. Pine cone fibers and marble waste and ATH were used as reinforcement (Fig. 1). The pine cones were dried at ambient conditions before the manufacturing process. Finally, pine cones and marble waste were ground in the hammer mill (Brook Crompton Series 2000). Waste marble powder was again grinded with Fritsch-Pulverisette9 to convert into dust form. Pinecone and marble dust were sieved by Fritsch, Analysette 3. ATH (Aluminum trihydrate) was provided by Poliya Composite Resins and Polymers Inc. ATH was added to polyester resin to cheapen the end product and to enhance technical properties of the end products. Polyester matrix was combined with marble dust, ATH and pinecone powder at different particle size content.

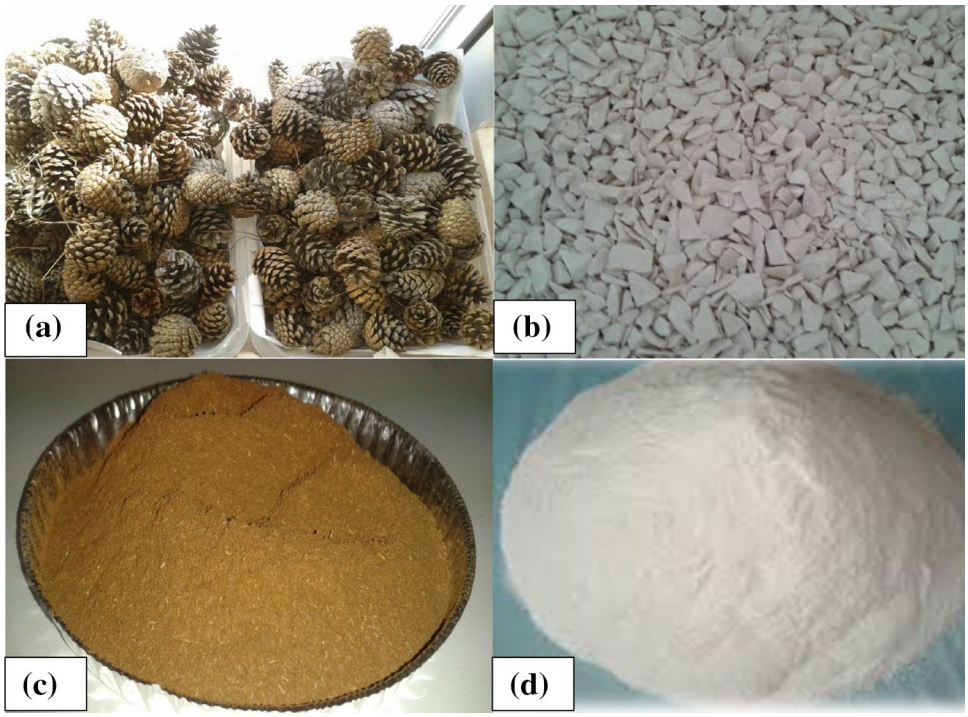

Fig. 1 Photographs **a** the Pine cone plants, **b** marble wastes, **c** powder of cones, **d** powder of marble wastes

Table 1 Mix proportions designation of composite samples by volume

Recipe codes	Polyester, %vol.	Pinecone powder, %vol.	Marble dust, %vol.	ATH, %vol.
P0	100.0	0.0	0.0	0.0
P1	61.3	0.8	29.5	8.4
P2	64.6	2.7	25.5	7.2
P3	68.4	4.7	21.0	5.9

Composite Preparation

The filler mixture used in this research consisted of three different materials: marble waste (as industrial inorganic waste), ATH (as noninflammable commercial filler material), and pine cone (as natural organic waste containing fiber). In this paper, the Marble/ATH ratio was kept fixed at four by weight and three different prescriptions were prepared by adding pinecone powder at increasing amounts and by decreasing the marble and ATH amounts (provided that the ratio between them was maintained). The physical and mechanical properties of composites obtained were solely mixed with the polyester. The prescriptions belonging to the compositions prepared are given by volume and weight in Tables 1 and 2 by using the mixture rule. The density values belonging to the materials used in the study for volumetric calculations and which were determined with the gas pycnometer are shown in (Micromeritics the AccuPyc II 1340 model) Table 3.

Primarily, the filler substances and polyester resin were (Stuart scientific mechanical stirrer SS3, UK) mixed with the mechanical mixer at the amounts given in Table 2. After the first mixture, a second mixing was made by adding the accelerator and following this, the vacuum was applied for 5 min. The third mixing was conducted by adding hardener to the second mixture. The rate of third mixing applied was selected as 500, 1000 and 1500 rpm, respectively and the

Table 2 Mix proportions designation of composite samples by weight

Recipe codes	Filler			Polyester, %wt	Total	Marble/ATH	Polyester/Filler
	Pinecone powder, %wt	Marble dust, %wt	ATH, %wt				
P0	0	0	0	100	100		
P1	0.7	46.0	11.5	41.8	100	4.00	0.7
P2	2.3	41.4	10.3	46.0	100	4.00	0.9
P3	4.3	35.7	8.9	51.1	100	4.00	1.0

Table 3 Density of the raw materials of composites

Raw materials	Density (g/cm^3)
Pine cone	1.450
Marble	2.750
Polyester	1.200
ATH	2.420

mixing procedure was maintained for 5 min for each of them. The final mixture was molded and curing was provided at ambient temperature for 1 h and in the drying oven (Binder, Germany) at 60 °C for 2 h.

Experimental Method

Determination of the mechanical properties of polyester composites in the form of rectangular bars (100 mm × 10 mm × 4 mm; length x width x thickness) were used for measurement, particularly flexural modulus and flexural strength. The three composite bars of each group were tested with a material testing machine (Shimadzu AG-IC Test Machine) at room temperature (23 ± 2 °C) and the crosshead speed of 2.0 mm/min. The flexural strength (σ, N/mm^2) and flexural modulus (*E*, MPa) of the composite were calculated using the Eqs. 2.1 and 2.2, respectively. The arithmetic mean values for each group of composites were calculated and reported as the "average value".

$$\sigma = \frac{3FL}{2WD^2} \tag{2.1}$$

$$E = \frac{L^3}{4WD^3}m \tag{2.2}$$

where F_{max} is the applied load (N) at the highest point of the load–deflection curve, L is the span length (60.0 mm), W is the width of the specimens perpendicular to the loading direction (mm), D is the depth of specimens tested in parallel to the loading direction (mm), and M is the slope of the tangent to the initial straight-line portion of the load–deflection curve (N/mm) of deflection.

Durometer Hardness was used to determine the relative hardness of composite samples. A sample 8 cm in diameter of the composite specimen was first placed on a hard flat surface to establish firm contact between the durometer point and the specimen. The indentor for the instrument was then pressed into the specimen making sure that it was parallel to the surface. The Shore D hardness was read within 1 s. Five replicates of each composite formulation were tested to determine averaged hardness. Density measurements of the composite specimens were made according to the Archimedes' Principle. To determine the porosity of the composite specimens the bulk volume, which is the sum of the grain and pore volumes, was measured. In Eq. 2.3 bulk density, and in Eq. 2.4 open porosity calculations are shown.

$$\text{Bulk Density} = \frac{W_1}{W_3 - W_2} \times \rho_{water} \tag{2.3}$$

$$\%\ \text{Open Porosity} = \frac{W_3 - W_1}{W_3 - W_2} \times 100 \tag{2.4}$$

where W_1 is weight of clean, dry sample (g); W_2 is weight of saturated sample, immersed in water (g); W_3 is weight of saturated sample in air (g).

The fracture surfaces of the flexural test specimens were characterized with high resolution field emission scanning electron microscopy (SEM, Zeiss Supra 40VP, Germany). The SEM was operated to determine their fracture surface, microstructure, and fiber orientation characteristics. Samples of image analysis and SEM study were prepared from the edges of the three point bending test specimens. The granulometry and electron and optical microscope (Nikon Eclipse LV 150, Japan) images belonging to the filler materials used are given in Fig. 2.

Results and Discussion

Characterization of Raw Materials

It was seen that the marble waste powder (Fig. 2a) consisted of partially equiaxial and both fine and coarse grains. At the same time, it was determined that the granulometry of marble waste powder varied between 1 and 50 μm and maximum grain size increased up to 50 μm. In SEM examination, it was seen that ATH grain size was ≤20 μm (Fig. 2b). In SEM examination and Optical microscope examination of ground pinecone powder, it was determined that the granulometry varied between 10 and 500 μm and there were mostly coarse grains having a mixed geometry that were equiaxial and fiber-like shapes (Fig. 2c–d).

It was seen that the pinecone powder had the lowest surface area due to its coarse-grained and fibrous structure while the marble waste powder and ATH had the largest surface area among the filler materials. The fibrous structure of pinecone played a significant role in the increase of viscosity of the mixture due to the lock on during the preparation of composite mixture [18]. ATH and marble powder had a more positive effect on the decrease of viscosity due to its grain size, distribution and shape compared to the pinecone. Therefore, the inorganic addition had positive effects on mechanical properties even while partially but distinctively decreasing the composite cost [17].

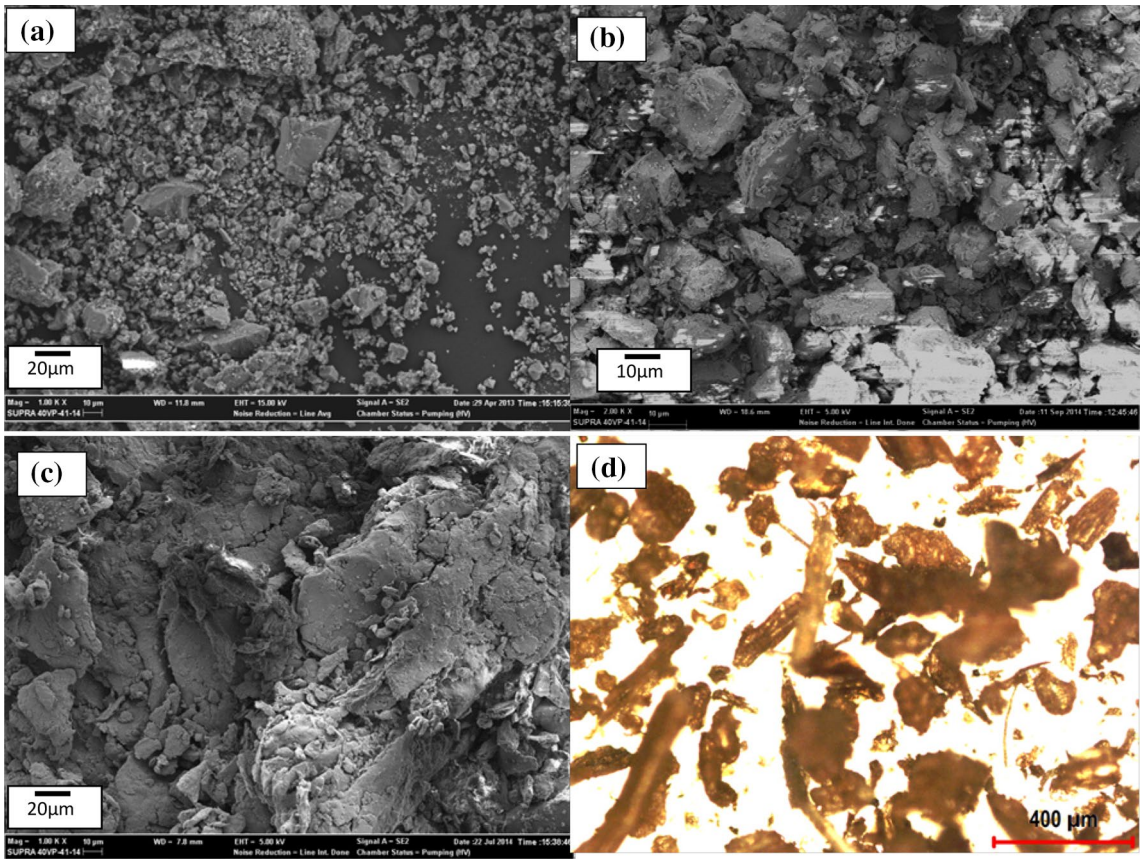

Fig. 2 SEM Images of the filler materials **a** marble dust, **b** ATH, **c** Pine cone powder and **d** Optic Microscope photograph of pine cone powder

Microstructural Characterization of Composite Samples

When the microstructure images taken from the electron microscope belonging to the composite samples were reviewed, it was seen that the distribution was homogenous at the structure of Fig. 3a, b. The pinecone was not seen very much in the current image because pinecone was used in very small quantities in P1 composite prescription. It was seen that the grain size of marble waste reached levels of 150 microns. It is thought that this was because the grain agglomerates were not broken before the mixing. The cracks seen in the grains of marble waste did not show an adverse effect at the stage of determination of mechanical properties (see Fig. 5).

When the images given in Fig. 3c, d were reviewed, it was seen that the structural homogeneity of P2 prescribed composite decreased compared to P1 composites. The poor interface interaction seen between the matrix and pinecone and the marble waste and matrix adversely affected the mechanical and physical properties as well as the fact that the grains of pinecone did not completely distribute homogenously [1] (see Figs. 4, 5). It was seen in the microstructure that the waste grain size reached the level of 100 microns and the pinecone grain size reached the level of 200 microns. When the images of Fig. 3e, f were reviewed, it was seen that the structure homogeneity of P3 composites was similar to the homogeneity of P2 composites.

Physical Properties of Composites

In Fig. 4, the bulk density, total porosity and open porosity belonging to the composite prescriptions prepared respectively are shown graphically. It was determined that the bulk density value decreased as the inorganic substance (marble and ATH) amount decreased at the composite prescriptions and both pinecone and polyester amount increased. P1 prescription had the highest inorganic volume amount and the bulk density value had the highest value through 1.73 g/cm^3. In spite of that, P3 prescription decreased to 1.58 g/cm^3, which was the lowest density value due to the highest polyester and pinecone content. When total porosity values were reviewed, it was seen that the viscosity of composite mixture increased due to the fibrous structure of pinecone although P3 prescription had the lowest filling phase by

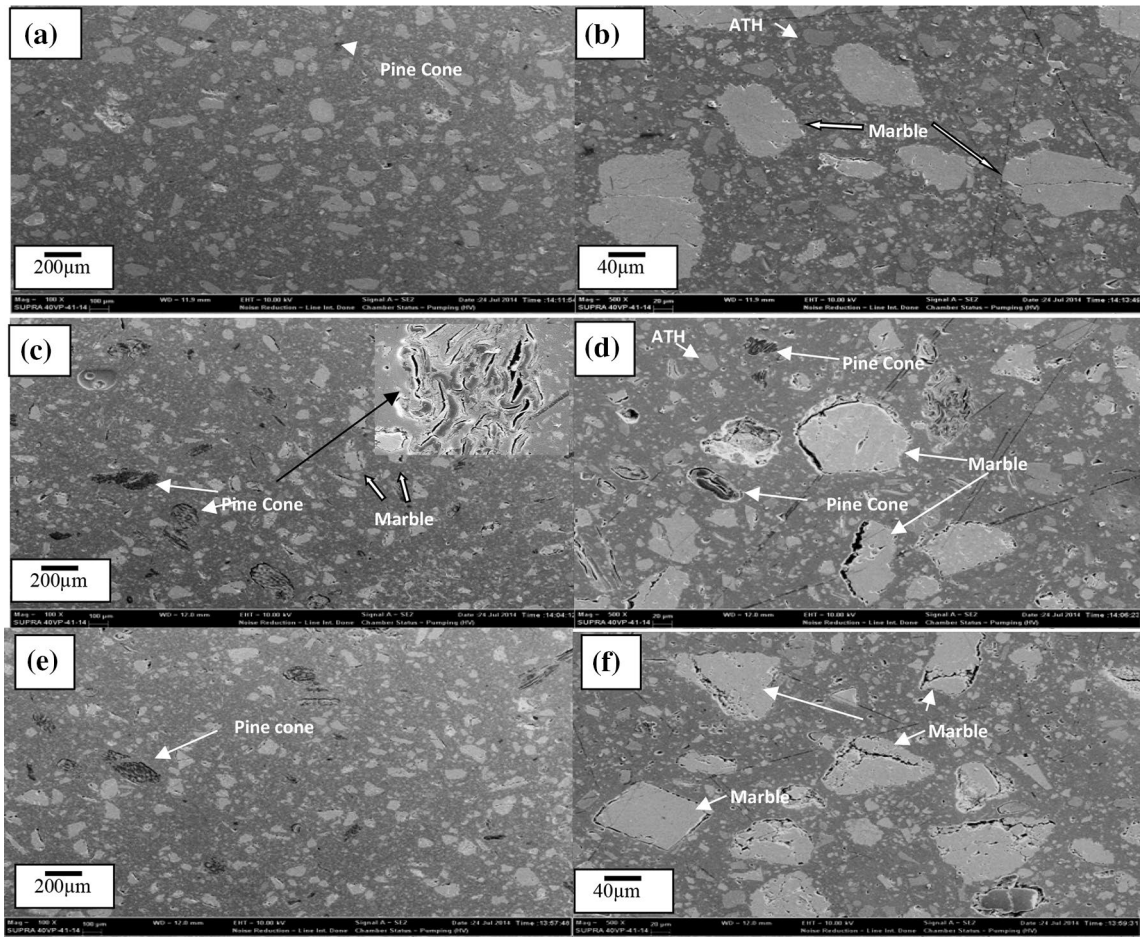

Fig. 3 100× and 500× magnified SEM images of the composite samples **(a)** and **(b)** P1, **(c)** and **(d)** P2, **(e)** and **(f)** P3

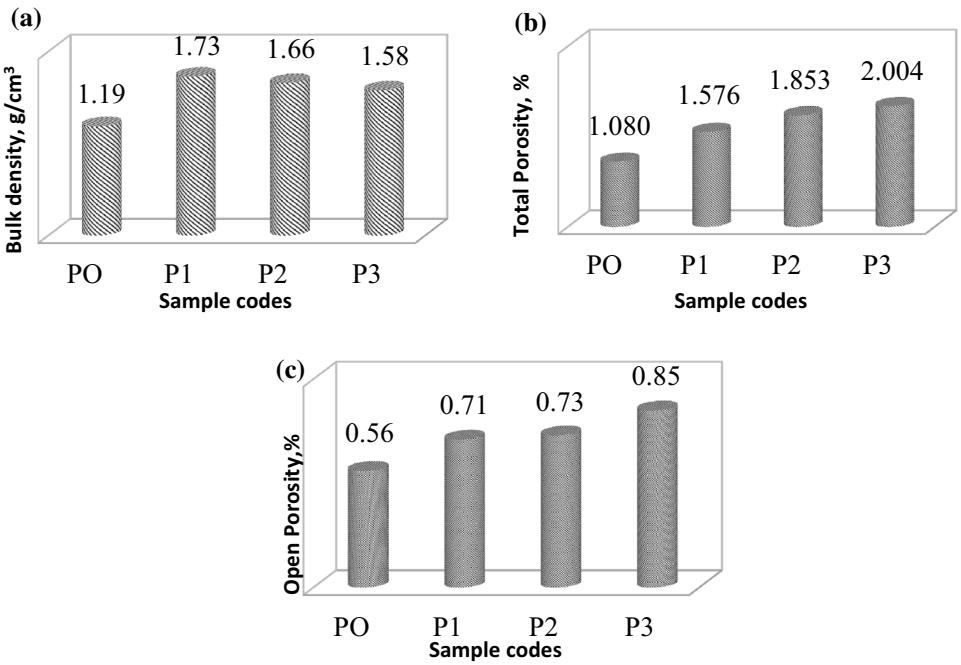

Fig. 4 **a** Bulk density, **b** Total porosity percentage and **c** open porosity percentage of composite samples

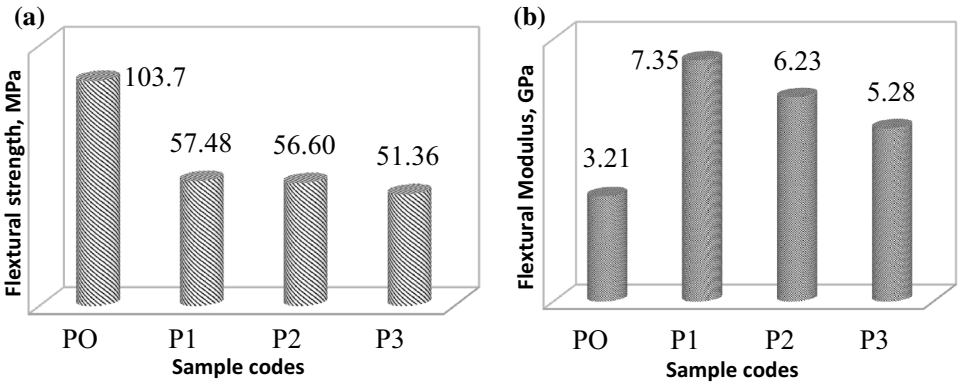

Fig. 5 **a** Flexural strength, **b** Flexural modulus of composite samples

volume. The increasing viscosity in structure caused the increase of void formation during the casting. The increasing viscosity also adversely affected the interface interaction because the polyester phase wetted the filler. When the images belonging to P1, P2 and P3 prescriptions in Fig. 3 were reviewed, it was seen that the interface interaction was adversely affected along with the increasing pinecone amount. It was thought that this resulted from the fiber–matrix interaction, distribution and tacticity of fibers, fiber agglomeration and air voids remaining on the structure [1]. When Fig. 3 was reviewed, it was seen that the voids were more distinctive as a good wetting did not occur between the pinecone grains in composite structures. The polyester material had the lowest total porosity value due to the lowest viscosity. But when the porosity values were reviewed, it was seen that they showed a similar behavior with the total porosity.

Flexural Strength and Flexural Modulus

In Fig. 5a, b, the flexural strength and flexural modulus values belonging to the composite and pure polyester samples are given. The flexural strength value of composite samples was determined between 51.36 and 57.48 MPa. These values were lower than the value of the pure polyester sample, which was 103.7 MPa. The bending strength decreased along with the pinecone amount in the increasing organic fibrous structure. In the studies concerning fiber materials, in general the flexural strength value increased along with the increasing fibrous structure amount and it was thought that the reason for the decrease in this study resulted from the poor interaction between the organic and inorganic filling phase as seen from the microstructure images (Fig. 3) and porosity values (Fig. 4) [6, 19]. The fibrous structure caused big grain size, agglomeration formation during the mixture and increase of % porosity amount in the composite structure and this caused the decrease of flexural strength. It was seen in the microstructure images (see Fig. 3) that the inorganic filler materials distributed homogenously and the pinecone did not distribute homogenously due to its fibrous structure and coarser size.

It was seen that the flexural modulus value increased as the inorganic filler amount increased. Basturk et al. determined in their study that the flexural modulus value of composite obtained with the reinforcement of pinecone was 1.3 GPa [20]. In this paper, the flexural modulus value varied between 5.28 and 7.35 GPa. These values were higher than the value of pure polyester and the flexural modulus values of composites obtained in other studies. The increase of decreasing porosity amount positively affected as well as the fact that the hard ceramic phase was effective on the increase of flexural modulus. The flexural modulus value increased at the ratio of ~40% along with the increase of ceramic phase (Marble + ATH) amount by vol. 11% and the decrease of polyester + pinecone amount by 11%.

Hardness

In Fig. 6 the Shore-D hardness value belonging to the composite and pure polyester samples is given. The hardness value was similar to the value of composite samples and varied between 90.2 and 90.6 and these values were higher than the value of the pure polyester sample, which was 82.5. Although there was a ceramic reinforcement phase between ~27 and 38% by volume in all composite

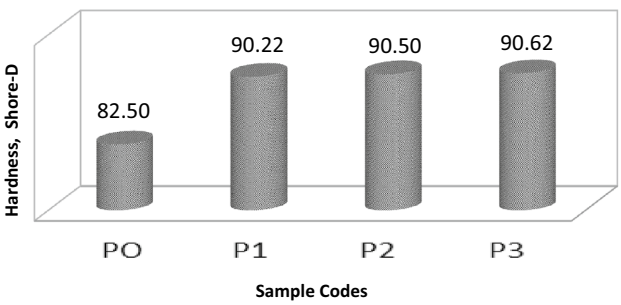

Fig. 6 Shore D hardness of composite samples and polyester

compounds, a distinctive change was not observed on the hardness value of composite samples with the hard ceramic phase.

Conclusions

Researchers focus on improving the properties of materials used in many applications and manufactured from renewable resources because of the requirement for environmentally sustainable products.

This study includes a general overview of the mechanical and physical properties of polyester matrix composites reinforced with pine cone powder, waste marble dust and ATH.

Both organic and inorganic fillers were used together to manufacture the polyester composite, but experimental results of mechanical and physical analysis showed that selected filler materials did not promote the expected properties. Authors mentioned that flexural strength and hardness value of the composite materials decreased with the increasing ratio of pine cone: marble + ATH because of the low interfacial properties between pinecone fiber and polymer matrix that reduce their potential as reinforcing agents up to fiber hydrophilic nature. Chemical treatments are usually advised for lignocellulosic fibers that are used as a filler material in order to better interfacial adhesion between polymer matrices and the fiber. Besides chemical modification, the use of coupling agent is another way of improving the compatibility between organic and inorganic fillers in polymeric blends.

Also, physical treatments change the structural and surface properties of the fiber and thus influence the mechanical bonding with the polymer matrix.

Applied properly, physical processing and/or chemical treatments depending on the raw material have key roles in preventing adverse effects on the weak filler/matrix interface and in bringing increased positive efficiency into further manufacturing process.

References

1. Gopinath, A., Kumar, S., Elayaperumal, A.: Experimental investigations on mechanical properties of jute fiber reinforced composites with polyester and epoxy resin matrices. Procedia Eng. **97**, 2052–2063 (2014)
2. Arrakhiz, F.Z., Achaby, M.E., Benmoussa, K., Bouhfid, R., Essassi, E.M., Qaiss, A.: Evaluation of mechanical and thermal properties of Pine cone fibers reinforced compatibilized polypropylene. Mater. Design. **40**, 528–535 (2012)
3. Cheung, H., Ho, M., Lau, K., Cardona, F., Hui, D.: Natural fibre-reinforced composites for bioengineering and environmental engineering applications. Compos. Part B. **40**, 655–663 (2009)
4. Akil, H.M., Omar, M.F., Mazuki, A.A.M., Safiee, S., Ishak, Z.A.M., Bakar, A.A.: Kenaf fiber reinforced composites: A review. Mater. Design. **32**, 4107–4121 (2011)
5. Wambua, P., Ivens, J., Verpoest, I.: Natural fibres: can they replace glass in fibre reinforced plastics? Compos. Sci. Technol. **63**, 1259–1264 (2003)
6. Dong, C., Davies, I.J.: Flexural Properties of Macadamia Nutshell Particle Reinforced Polyester Composites. Compos. Part B. **43**, 2751–2756 (2012)
7. Gürü, M., Tekeli, S., Akın, E.: Manufacturing of Polymer Matrix Composite Material Using Marble Dust and Fly Ash. Key Eng. Mat. **336/338**, 1353–1356 (2007)
8. Arrakhiz, F.Z., Benmoussa, K., Bouhfid, R., Qaiss, A.: Pine cone fiber/clay hybrid composite: mechanical and thermal properties. Mater. Design. **50**, 376–381 (2013)
9. Wei, W., Gu, H: Characterisation and utilization of natural coconut fibres composites. Mater. Design. **30**, 2741–2744 (2009)
10. Prasad, A.V.R., Rao, K.M.: Mechanical properties of natural fibre reinforced polyester composites: Jowar, sisal and bamboo. Mater. Design. **32**, 4658–4663 (2011)
11. Sathishkumar, T.P., Navaneethakrishnan, P., Shankar, S.: Tensile and flexural properties of snake grass natural fiber reinforced isophthallic polyester composites. Compos. Sci. Technol. **72**, 1183–1190 (2012)
12. Ramesh, M., Palanikumar, K., Hemachandra Reddy, K.: Mechanical property evaluation of sisal–jute–glass fiber reinforced polyester composites. Compos. Part B. **48**, 1–9 (2013)
13. Moussoruis, Y., Regato, P.: An overview of non timber forest products in the Mediterranean region. FAO Online Publications, http://www.fao.org/docrep/x5593e/x5593e00.htm (2017). Accessed 26 January 2017
14. Buyuksari, U., Avci, E., Ayrilmis, N., Akkilic, H.: Effect of pine cone ratio on the wettability and surface roughness of particleboard. Bioresources. **5**, 1824–1833 (2010)
15. Ayrilmis, N., Buyuksari, U., Avci, E., Koc, E.: Utilization of pine (Pinus pinea L.) cone in manufacture of wood based composite. Forest Ecol. Manag. **1**, 65–70 (2009)
16. Demirel, B.: The effect of the using waste marble dust as fine sand on the mechanical properties of the concrete. Int. J. Phys. Sci. **5**, 1372–1380 (2010)
17. Aruniit, A., Kers, J., Tall, K.: Influence of filler proportion on mechanical and physical properties of particulate composite. Biosyst. Eng. **1**, 23–29 (2011)
18. Naheed, S., Paridah, M.T., Mohammad, J.: A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. Polymer. **6**, 2247–2273 (2014)
19. Santos, A.S., Farina, M. Z., Pezzin, P. T., Silva, D. A. K.: The application of peach palm fibers as an alternative to fiber reinforced polyester composites. J Reinf. Plast. Comp. **27**, 1805–1816 (2008)
20. Baştürk, S.B., Kanbur, K., Polatoğlu, İ., Yürekli, Y.: Mechanical properties of acorn and pine cone filled polymer composites. Am. Sci. Res. J. Eng. Technol. Sci. (ASRJETS). **14**, 144–153 (2015)