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Araştırma Makalesi / Research Article

Modification of Pumice Mineral and Its Use as Additive for Poly (Lactic Acid) Based Bio-Composite Materials

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Abstract

In this study, pumice (P) mineral was treated with silane in order to increase the compatibility for poly(lactic acid) (PLA) which is a fully biodegradable polymer widely used in packaging and outdoor applications. Neat and treated P powders were compounded with PLA at the concentrations of 5, 10, 15 and 20 wt% by melt mixing process. Surface characteristics of P samples were examined using infrared spectroscopy. Mechanical, water uptake, melt-flow and morphological properties of prepared composites were investigated by tensile and impact tests, water absorption test, melt flow rate test (MFR) and scanning electron microscopy (SEM) technique, respectively. Mechanical test results revealed that the highest increase in tensile strength and modulus values was obtained for 15 wt% of silanized P containing composite which are found as 4.5% and 40% increase, respectively. Addition of silane-treated P into PLA resulted in an increase in impact strength of about 33% compared to samples containing that were not treated with silane with the same proportion of P. Impact strengths of composites increased with increasing P concentration. Silanized P filled composite gave slightly higher MFR values with respect to pristine P. Water absorption values of composites were found as about two-fold higher than that of unfilled PLA. Composites containing silanized P exhibited lower water uptake values compared to untreated P samples because of the hydrophobic character of silicon containing surfaces. SEM micro-images of composites displayed that more homogeneous dispersion in PLA matrix was taken place for silane treated P particles than that of neat P stem from the increase of adhesion between P and PLA surfaces after silanization process.

Keywords

Pumice; Poly (lactic acid); Bio-composites; Extrusion; Polymer composites

Pomza Mineralinin Modifikasyonu ve Poli (Laktik Asit) Bazlı Biyo-Kompozit Malzemelerinde Eklenti Olarak Kullanımı

Öz

Bu çalışmada, pomza (P) minerali, ambalaj ve dış ortam uygulamalarında sıkça kullanılan tamamen biyobozunur bir polimer olan poli (laktik asit) (PLA) ile uyumunu artırmak amacıyla silan ile muamele edilmiştir. Muamele edilen ve edilmeyen P tozları PLA ile eriyik karıştırma yöntemi ile ağırlıkça yüzde 5, 10, 15 ve 20 konsantrasyonlarında eklenmiştir. P numunelerinin yüzey özellikleri infrared spektrofotometre kullanılarak incelenmiştir. Hazırlanan kompozitlerin mekanik, su alma, erime-akış ve morfolojik özellikleri sırasıyla çekme ve darbe testleri, su emme testi, erime akış hızı testi (MFR) ve taramalı elektron mikroskopi (SEM) teknikleri ile araştırılmıştır. Mekanik test sonuçlarına göre, çekme dayanımı ve modülde en yüksek artışa %15 silanlanmış P içeren kompozitte sırasıyla %4,5 ve %40 artış ile rastlanmıştır. PLA içine silan ile muamele edilmiş P eklenmesi, silan ile muamele edilmemiş ve aynı oranda P içeren numuneler ile kıyasla darbe dayanımında %33 civarında artışa neden olmuştur. Kompozitlerin darbe dayanımları artan P konsantrasyonu ile artmıştır. Silanlanmış P eklenmiş kompozit, silanlanmamış P eklenmiş kompozite göre bir miktar yüksek MFR değeri vermiştir. Kompozitlerin su emme değerleri eklentisiz PLA'dan yaklaşık iki kat fazla olarak bulunmuştur. Silikon içeren yüzeylerin su sevmeyen özelliğinden dolayı silanlanmış P içeren kompozitler, modifiyesiz P ile kıyaslandığında daha düşük su emme değerleri sergilemiştir. Kompozitlerin SEM mikro-resimleri göstermektedir ki; silanlama işleminden sonra P ile PLA arasında yapışma arttığı için silan ile muamele edilmiş P parçacıklarında edilmeyenlere göre daha homojen dağılım gerçekleşmiştir.

Anahtar kelimeler

Pomza; Poli (laktik asit); Biyo-kompozitler; Ekstrüzyon; Polimer kompozitler

1. Introduction

The scientific and industrial attentions for production of environmentally friendly materials has become trend topic due to the recent ecological restrictions. Bio-composites are developed for the main purpose of the replacement of conventional petroleum based composite materials. Bio-composites are chosen over conventional composites because of having advantages of weight reductions, easy fabrication, recyclable and biodegradable character. They have recently used in industrial areas including packaging, textile, automotive and outdoor applications thanks to described advantageous properties (Bismarck *et al.* 2006, Mohanty *et al.* 2002, Tayfun 2017a).

Poly (lactic acid) (PLA) is the most popular candidate among renewable polymers. This commercialized bio-polymer has ability to decrease of the disposal problem encountered in packaging applications (Bajpai *et al.* 2012, Weber *et al.* 2002). Investigations of additives for PLA is a trending topic because of bio-polymers having limitations including insufficient mechanical strength, low thermal stability and narrow processing window(Murariu and Dubois 2016, Rasal *et al.* 2010, Ren 2011).

Natural minerals are used as fillers for polymeric materials due to their low cost and easy to handle. Influence of mineral additives for plastics is related with some factors such as size, loading ratio, shape and interfacial compatibility with polymer matrix (Theberge 1982, Xanthos 2005). Enhancement of adhesion of mineral filler to polymer is important for fabrication of composite materials having required properties (Kanbur and Tayfun 2017, Metin *et al.*2004, Oktem and Tincer 1994, Rothon 2003).

Pumice mineral is obtained from volcanic eruption areas. Turkey has a large portion of pumice reserves among other countries such as Italia, Spain, Mexico, Chile, USA, Iceland, Greece and Indonesia. Nevsehir, Kars, Ankara, Afyon, Izmir and Kayseri are the main areas where Turkish pumice deposits are found (Bolen 2008, Elmastas 2012, Kul *et al.* 2017, Yazicioglu *et al.* 2003). Because of pumice has a very porous structure, it is mainly used as light weight building materials. According to the literature, pumice was used as additive for polyethylene (Han *et al.* 2009), polypropylene (Kanbur and Tayfun 2018), polyvinyl alcohol (Jayakrishnan and Ramesan 2016), polyacrylonitrile (Yavuz *et al.* 2008), polyvinyl pyrolidone (Ramesan *et al.* 2016), polyaniline (Gok *et al.* 2006), polyphenylene sulphide (Sahin *et al.* 2013), and polyhydroxyethylmethacrylate (Akkaya 2013) matrices.

The aim of this study is development of biodegradable polymer composites by using pumice mineral as natural additive material. Mechanical, physical and morphological properties of pumice filled PLA bio-composites were investigated in order to demonstration of their possible use in industrial applications. Silanization process was applied to pumice powder for improvement of its compatibility to PLA matrix. Silane treated and pristine powder surfaces were characterized by infrared spectroscopy. Composites were produced using lab-scale extrusion and test samples were prepared by injection molding process. Tensile test, impact test, water absorption study, Melt flow rate measurement and scanning electron microscopy were performed in order to characterize the properties of composites.

2. Materials and methods

2.1. Materials

The commercial grade PLA was purchased from Natureworks LLC, USA with the trade name of Ingeo biopolymer 6100D. It has a density of 1.24 kg/m^3 according to supplier. Pumice powder was obtained from Miner Mining Inc, Nevsehir, Nigde, Turkey. The avarage particle size of P used in this study was 200 microns. Silane coupling agent, 3-Aminopropyltriethoxysilane and reagent grade ethanol were obtained from Merck AG, Germany.

2.2. Surface silanization of pumice

During silanization process, pumice powder was mixed in 2 wt% of 3-Aminopropyltriethoxysilane /ethanol solution for 100 minutes at room

temperature. After several washings sample was dried at 80˚C for 6 hours. Pristine and silane treated pumice samples were named as P and P (S), respectively.

2.3. Production of composites

Composite materials were fabricated using DSM Xplore micro-compounder at 210˚C for 5 minutes. The mixing speed was preferred as 100 rpm. Unfilled PLA was mixed under the same processing conditions and named as PLA. Filling ratios of P and P (S) were 5, 10, 15 and 20 wt%. Test samples of were prepared using Daca Instruments micro-injection molding machine at a barrel and mold temperatures of 210˚C and 60˚C, respectively.

2.4. Characterization methods

Infrared spectroscopy (IR) technique in ATR mode (Bruker Optics, 66/S series) was performed to investigate the surface characteristics of pristine and silane treated P powders. Tensile tests were carried out according to ASTM D638M-91a standard by Lloyd LR 30 K universal tensile testing device with 5 kN load cell and crosshead speed of 5 cm/min. The tensile strength, tensile modulus and percentage strain values were recorded by testing at least five samples for each composition and taking the averages values. Impact test was done by Coesfeld material impact tester with the 4J pendulum using ASTM D256 standard procedure . At least five samples were used for each composition set, the average and standard deviation values were calculated during impact test. Melt flow rates (MFR) measurements were performed by Coesfeld meltfixer LT with the standard load of 5 kg at 210˚C in accordance with ASTM D1238-79 standard. Test samples were conditioned and immersed in water bath at room temperature in 10 days during water absorption test using test route indicated in ASTMD570 standard. In order to perform scanning electron microscopy (SEM) analysis, the fractured surfaces of composites ontained from impact test were examined by FEI Quanta 400F FESEM scanning electron microscope for morphological characterization.

3. Results and discussion

3.1 IR analysis

IR spectrum of P and P (S) samples are shown in Figure 1. The peak centered at 1000 cm^{-1} is attributed to oxygen functionality (Dogan *et al.* 2016, Silverstein and Webster 2006) P (S) sample gave broader band for that oxygen related peak. The peaks seen at range of 600 cm^{-1} and 1000 cm^{-1} wavenumbers assign the Si–O vibrations (Kilinc *et al.* 2019, Shokoohi *et al.* 2008, Yang *et al.* 2003). The spectra of P (S) displayed higher intensity for these peaks due to forming silanol bonds at powder surface. These findings confirm that neat pumice surfaces were covered by silane coupling agent.

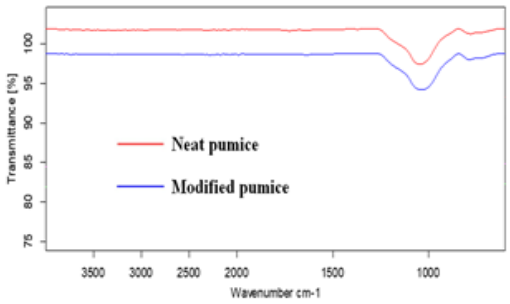

Figure 1. IR spectra of pumice samples

3.2 Mechanical tests

Mechanical test data of PLA and composites are listed in Table 1 and the tensile test curves are represented in Figure 2.

Impact strength results of unfilled PLA and composites can be seen from the last column of Table 1. Impact strength of PLA displayed reduction with P inclusions. Impact strength values of composites increased with the concentrations of P and P (S). P (S) containing composites gave nearly 2.5 points higher impact strength values compared to P at the same concentrations. The highest impact strength was found for PLA-P (S) 20 sample among composites. These results may due to the improvement of adhesion between PLA and P phases by the formation of silane layer on the P surface after treatment (Eselini *et al.* 2019, Hatipoglu *et al.* 2019).

It can be seen from Table 1 that tensile strength decreases with the addition of pumice at lower concentrations.

Table 1. Mechanical test results

Samples	Tensile Strength (N/m^2)	Tensile Modulus (GPa)	Elongation at Break (%)	Impact Strength (kJ/m^2)
PLA	58.4±1.6	1.0±0.1	11.6±0.7	11.6±0.4
PLA-P 5	53.6±1.2	1.1±0.1	8.5±0.4	6.8±0.2
PLA-P 10	54.1±1.3	1.1±0.1	9.0±0.6	7.5±0.3
PLA-P 15	56.0±1.7	1.3±0.2	8.7±0.5	8.4±0.2
PLA-P 20	53.3±1.5	1.2±0.2	8.8±0.7	9.0±0.3
PLA-P (S) 5	58.0±1.6	1.2±0.1	9.3±0.6	9.3±0.3
PLA-P (S) 10	60.4±1.4	1.3±0.2	9.6±0.5	10.1±0.4
PLA-P (S) 15	61.0±1.8	1.4±0.1	9.2±0.5	11.2±0.3
PLA-P (S) 20	57.2±1.3	1.3±0.1	9.4±0.4	11.9±0.3

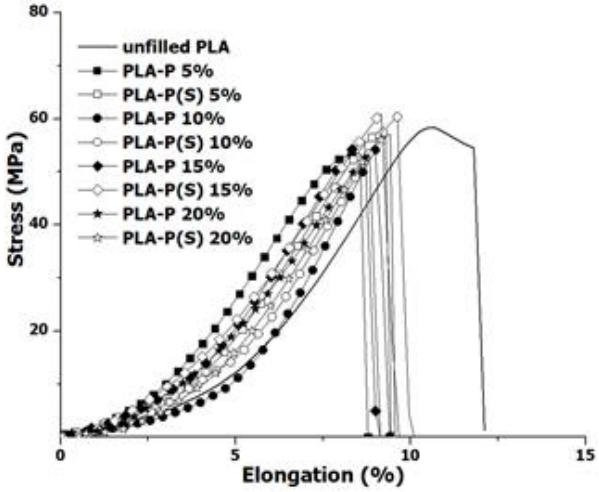

Figure 2. Tensile curves of PLA and composites

Further additions caused increase in strength values. The highest result was obtained at the filling ratio of 15 wt% for both of P and P (S). P (S) containing composites gave remarkably higher tensile strength values as compared with the same concentrations of P. Improvement of adhesion between P (S) and PLA matrix may be the reason of this finding (Alghadi *et al.* 2020, Tayfun and Dogan 2016). Tensile modulus increases with the concentration. In contrast, elongation values showed decreasing trend by the addition of P and P (S). According to Figure 2, the highest elongation was obtained for unfilled PLA.

3.3. Melt-flow rate

According to MFR values shown in Figure 3, all of the MFR values are seen in a narrow range. This result indicates that processing of these composites can be performed practically in industrial scale production applications. Additions of P and P (S) led to increase for MFR value of unfilled PLA. MFR values displayed improvement with increase in concentration. Silane treated P containing composites showed slightly higher MFR values as compared with pristine P due to increase of compatibility between P (S) with polymer matrix (Ge *et al.* 2009, Tayfun *et al.* 2017b, Tian and Tagaya 2007).

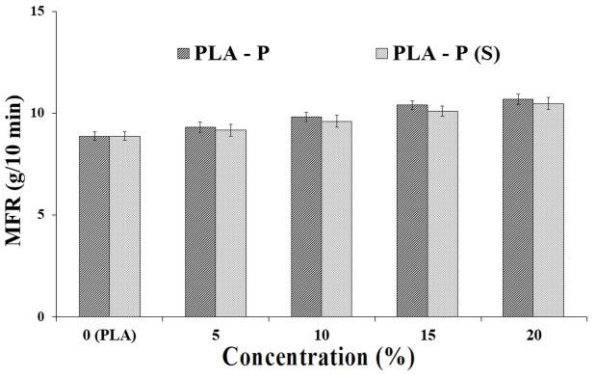

Figure 3. MFR results of PLA and composites

3.4. Water absorption

Water absorption test data of unfilled PLA and its composites for the time period of 15 days are listed in Table 2. The unfilled PLA sample reached to absorption value of about 1%. Water uptake values of composites shifted to higher amounts with the increase of P concentration. P (S) filled composites exhibited relatively lower water absorption values than untreated P containing composites at their identical concentrations. This result caused from the hydrophobicity silane containing surface of treated P sample (Arbelaiz *et al.* 2005, Tayfun *et al.* 2016).

Table 2. Water absorption test results

Samples	Water Absorption (%)
PLA	0.9±0.1
PLA-P 5	1.7±0.1
PLA-P 10	2.0±0.2
PLA-P 15	2.5±0.1
PLA-P 20	2.9±0.1
PLA-P (S) 5	1.2±0.2
PLA-P (S) 10	1.6±0.1
PLA-P (S) 15	2.1±0.2
PLA-P (S) 20	2.4±0.1

3.5. Morphological characterization

SEM micro-images of composites having their lowest (5%) and the highest (20%) concentrations are represented in Figure 4. Poor adhesion of pumice particles inside to PLA matrix can be easily seen from the SEM image of PLA-P 5 composite. On the other hand, the surface of P (S) particles can be seen as surrounded by PLA matrix. Formations of agglomerates for pristine P particles into PLA was observed for higher concentrations. In contrast,

P (S) particles showed homogeneous dispersion into PLA the matrix according to SEM image of PLA-P (S) 20 composite. These results prove that well-dispersion of pumice particles were obtained for silanized P samples thanks to the enhancement of adhesion between two phases.

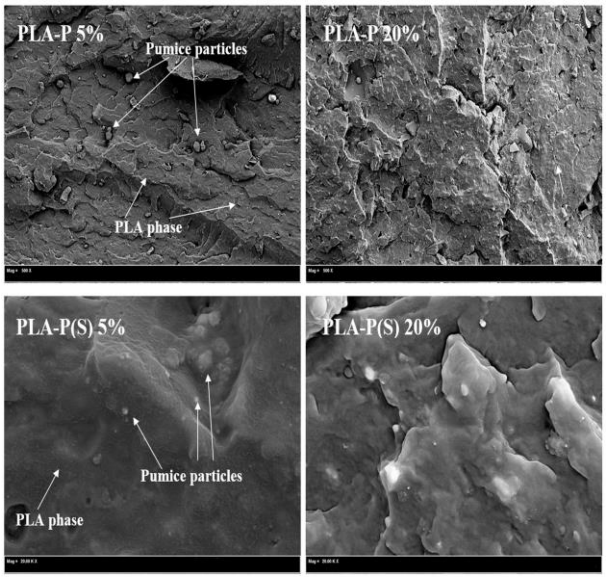

Figure 4. SEM micro-images of composites

4. Conclusion

In this study, influence of surface silanization and filling ratio of pumice mineral on the mechanical, melt flow, water uptake and morphological properties of PLA based composites are postulated. IR analysis confirmed that surface of P is covered by silane coupling agent after silane treatment. Mechanical test results reveal that silanized P containing PLA composites showed higher tensile strength and impact strength compared to untreated P samples. The optimum concentration of P was obtained as 15 wt% in the case of tensile strength. Additions of P powders resulted with slight decrease for elongation of PLA. MFR value of PLA increased with the additions of P and P (S). According to water absorption test, silane treated P containing composites gave lower water uptake compared to untreated P because of hydrophobic character of silane containing surface. SEM analysis implied that more homogeneous dispersion was observed for P (S) samples than P into PLA matrix. This finding is the evidence of increasing of adhesion between two phases that resulted with improvement for mechanical and physical properties of PLA based composites.

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