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Research Article

Production and Characterization of Polylactic acid/Rock wool Biocomposites

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Abstract

Rock wool is a man-made fiber produced by melting inorganic stones such as basalt, diabase, dolomite obtained from volcanic rocks, and it is an environment friendly resource and generally used for building insulation. Rock wool has good thermal resistance and insulation properties. In this study, PLA/Rock wool biocomposites with 20-30-40% rock wool support were produced with twin-screw extruder and then press molded. Tensile and flexural tests were applied to reveal mechanical properties of composites. FT-IR spectroscopy was used for investigation of chemical changes. TGA /DTG analysis were carried out to determine thermogravimetric properties of biocomposites, where thermal conductivity was measured to investigate heat transfer characteristics. The results showed that flexural strength of composites decreased 5-40% with increasing ratio of rock wool (20-40%), while tensile strength decreased 40-60% with increasing amount of rock wool (20-40%). Besides that, rock wool accelerated thermal degradation of PLA, but the composites have 25% better heat insulation property than neat PLA.

Keywords: PLA, Rock wool, Biocomposite, Characterization, Mechanical properties

1. Introduction

The growing attention to sustainable natural resources and fibers increased their importance for the last decade [1]. The mechanical properties of some natural fibers have comparable properties to synthetic fibers, thus such materials can be alternative to glass fibers for polymeric biocomposites [2]. On the other hand, natural inorganic resources can be used to make fibrous structures (i.e. rock wool/stone wool and basalt fibers), which are used for heat and sound insulation and cheaper than glass fibers [3]. Polylactic acid (PLA) as a polymer matrix in the composite has great potential for indoor uses such as automobile interior parts [4]. PLA is made from renewable materials (i.e. corn), which are fermented to lactic acid. PLA is biodegradable, brittle and a stiff material, which can be transformed into several forms such as cups, plates, packaging or polymer films [5]. PLA degradation consists of hydrolysis to lactic acid. The biodegradation occurs in 2 weeks and after 3-4 weeks, material can completely disappear [6].

The PLA is a semi-crystalline polymer with a glass transition temperature (T_g) in the range of 60-70°C and a melting temperature (T_m) around 160-180°C. PLA is a polymer with elastic modulus and tensile strength and good mechanical properties in the range of 3.2-3.7 GPa and 55-60 MPa, respectively [7].

Rock wool/slag wool are named as mineral wool and they are produced from different raw materials [8]. The inorganic fibers of rock wool can be obtained from basalt, dolomite, dolerite rocks and are produced by blowing or centrifugation at high temperatures [9]. Mineral fibers have great sound absorption and thermal insulation properties. They have good thermal resistance because they are not deformed under high temperature [10]. Rock wool is an environmental material and has large application area like insulation pipes, industrial buildings and vessels [11]. On the other hand, mineral fibers can be recycled and their wastes can be used in composite materials. Rock wool can be an alternative to glass fibers, which are generally exported from abroad. However, rock wool can be produced in Turkey and are sold at very reasonable prices.

Cheng et al. investigated the addition of rock wool wastes to cement-based composites and the results showed that the compressive strength, splitting tensile strength, abrasion resistance, and absorption of cement-based composites was improved [12].

There are a few studies on rock wool utilization in plastic composites. Öztürk investigated jute and rock wool fiber with phenol-formaldehyde matrix composites. It was observed that tensile strength of composites was improved with increasing fiber content until 42% vol. of rock wool. The best values of flexural strength were observed at 42% vol. for jute/PF composites and 34% vol. for rock wool/PF composites [13].

Zihlif and Ragosta studied on properties of rock wool/polystyrene composite. They found that compressive yield stress increased slightly at low fiber content and decreased rapidly at higher fiber content, and the impact strength of the samples increased with the fiber content, and decreases with the glass transition temperature [14].

In this study, we investigated rock wool reinforced PLA biocomposites. As a natural resourced fiber, rock wool and a biodegradable polymer PLA were used to produce environmentally friendly alternative to petrol-based materials. Novel biocomposites were investigated by chemical, mechanical and thermal characterization methods.

2. Experimental

2.1. Materials

Commercial PLA from NatureWorks Ingeo 4043D Natural was used in this work. Rock wool fibers (RF) were supplied from İzocam A.Ş. (Turkey).

2.2. Fabrication of Composites

PLA and rock wool fibers were milled to 0.5 mm (Fritsch pulverisette 19, Germany). The composition of composites is shown in Table 1. After that, polymer and RFs were mixed at 600 rpm for 5 minutes. The PLA/rock wool mixtures were dried at 100°C for 18h before compounding. Dried mixtures were compounded with 40 L/D twin-screw extruder (Table 2) (Gülnar Machine, Konya-Turkey). After extrusion, composites were dried at 100°C for 18h and molded with hot press (Carver, USA) at 190°C and 0.24 MPa. Produced composite sheets were cut by a laser cutting machine (Kaya Grup KG-960, Turkey) to obtain standard specimens.

Table 1. Composition of biocomposites

Composites	Weight ratio of composites (%)
PLA/Rock wool fiber	100:0
PLA/Rock wool fiber (PR2)	80:20
PLA/Rock wool fiber (PR3)	70:30
PLA/Rock wool fiber (PR4)	60:40

Table 2. Temperatures of extruder

Die	7	6	5	4	3	2	1	Feed
170°C	175°C	180°C	180°C	180°C	180°C	175°C	165°C	25°C

Five thermal conductivity specimens, which have 10x10x1 cm sizes, were prepared accordingly ASTM C-518. Specimens were molded at 190 °C for 10 min. Before thermal conductivity measurement, 10x10x1 cm specimens were placed in the middle of a 30x30 cm polystyrene (EPS) foam. Thermal conductivity measurement was carried out by FOX 314 Laser Comp device. The lower and upper plates of equipment were settled at 10°C and 30°C, respectively.

2.3. Mechanical Properties of Composites

The tensile and flexural properties were measured on a Shimadzu universal test machine. Before mechanical tests, specimens were conditioned at %50 RH and 23°C for 48h. Tensile test were applied at 3 mm/min according to ASTM D-638. Flexural test were applied at 10 mm/min according to ASTM D-790.

2.4. FT-IR Analysis

To obtain chemical structure of composites, FT-IR spectroscopy were recorded with Bruker FT-IR machine, which have ATR accessory. The measurements were applied between 4000-400 cm^{-1} wavelength with 4 cm^{-1} resolution.

2.5. TGA Analysis

TGA tests were carried out with Simultaneous Thermogravimetric Analyzer (Hitachi Hi-Tech STA7200, Tokyo, Japan) analyzer with 75 ml/min nitrogen flow and 10 °C/min of heating rate from 30°C to 800°C.

3. Results and Discussion

3.1. Density of Composites

The density of composites are shown in Table 3. As it is known, the density of the stone fibers is about 2.7 g/cm^3 [15]. Interestingly, the density of all composites are lower than neat PLA except PR4. PR2 and PR3 composites have the lowest values with about 1.12 g/cm^3, where the density is increased with increasing fiber ratio for PR4 composite (PR4 significantly different than PR2 and PR3 ($p<0.05$)). It was expected that the mineral fibers might increase the density more; however, there is no sharp changes even with 40% increase of RFs. This might be due to the high porosity of the biocomposites.

Table 3. Density of composites

Sample	Density (g/cm3)
PLA	[a]1.21±0.01
PR2	[b]1.12±0.02
PR3	[b]1.14±0.02
PR4	[a]1.20±0.01

*(a)PLA and PR4, (b) PR2 and PR3 samples are not significantly different (p=0.05), but group ‘a’ and ‘b’ are significantly different (p<0.05)

3.2. FT-IR Analysis

Figure 1 shows the FTIR spectra of neat PLA, and PR2, PR3, PR4 composites. On the spectra, PLA shows very sharp carbonyl (C=O) stretching peak at 1747 cm^{-1}. There are also several vibrations on the composite spectra at 2993 cm^{-1} (-CH3 asymmetric), 2947 cm^{-1} (-CH3 symmetric), 1180 cm^{-1} (C-O-C), which belong to PLA [16]. FTIR of basalt fibers shows some intensive bands around 1000–1700 cm^{-1}. According to literature, these signals can be attributed to the stretching vibrations of the Al-O-Si network and in the 1400–1700 cm^{-1} range a group of bands that can be attributed to the stretching vibrations of the metal-OH bonds [17]. However, those peaks of mineral fiber cannot be observed due to overlapping with the PLA peaks. The only observable change in the spectra of composites after addition of mineral fibers is around 1080 cm^{-1} peak that the intensity of the peak decreased considerably. This peak belongs to the carbonyl stretching of the PLA, and the intensity decrease can be interpreted as a weak interaction intermolecular interaction between mineral fibers and π electrons of the carbonyls.

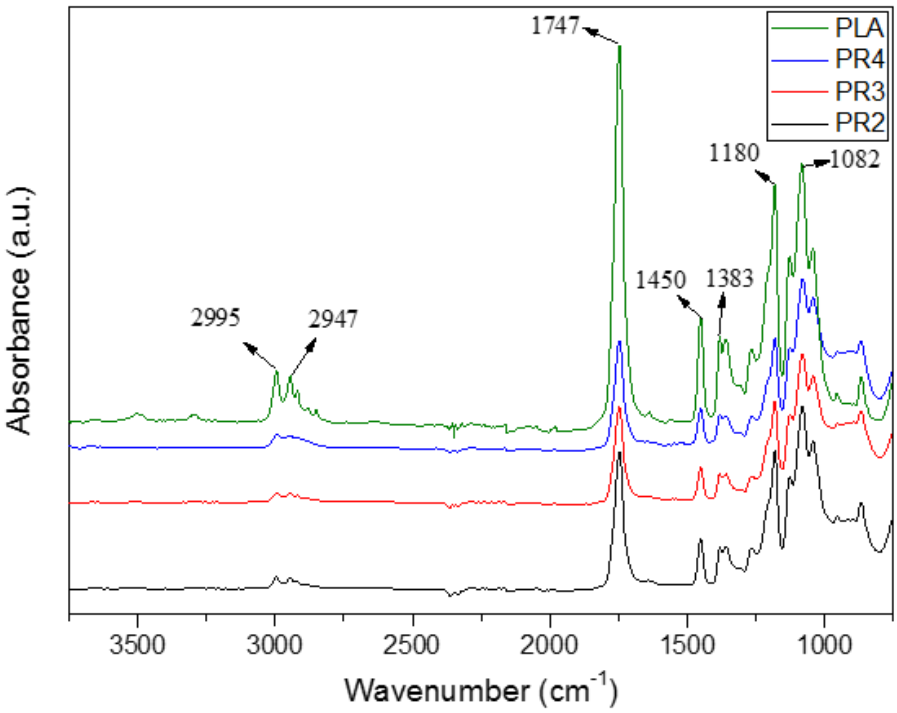

Figure 1. FT-IR spectra of composites

3.3. TGA Analysis

As shown in the TGA spectra (Figure 2), 10% of PLA degraded at 342°C, 50% degradation was occurred at 364°C and at 420°C PLA was completely decomposed (Table 3). The thermal degradation of PLA composites started at lower temperatures than neat PLA and the amount of thermal residue increased with increasing fiber ratio because of the inorganic materials that come from rock wool fibers [18]. Such situation can be explained by the presence of any metal ion on the surface of the mineral fibers, which could catalyze the thermal degradation of the PLA [19].

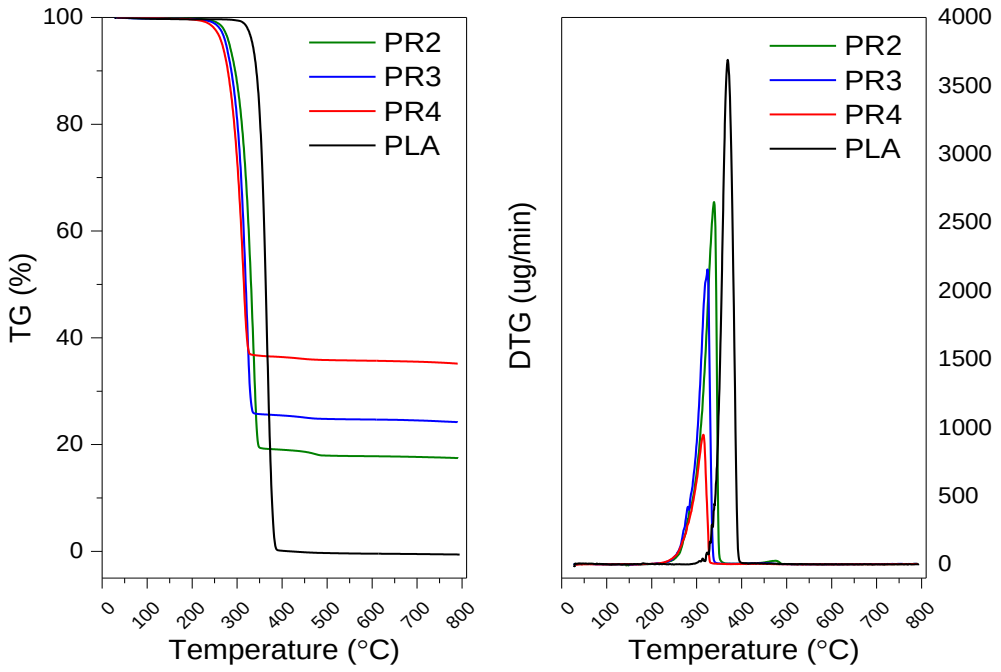

Figure 2. TGA thermogram and DTG of composites

Table 4. Simultaneous TGA data obtained for the neat PLA and biocomposites.

Sample	T5% (°C)	T10% (°C)	T50% (°C)	R (%)
PLA	334	342	364	0
PR2	282	295	330	17.46
PR3	275	285	319	24.20
PR4	266	278	314	35.15

*T5% : Temperature at %5 mass loss, T10% : Temperature at %10 mass loss, T50% : Temperature at %50 mass loss, R: residue amount at 800 °C.

3.4. Mechanical Properties of Composites

In Figure 3, flexural strength and modulus of neat PLA and biocomposites are shown. Flexural strength of neat PLA was measured as 62 MPa. With addition of 20% rock wool, flexural strength of biocomposites decreased slightly. Addition of more rock wool end up with reduced flexural strength. The flexural strength of PR2, PR3, PR4 were obtained 56, 48, 34 MPa, respectively. On the other hand, flexural modulus increased with increasing fiber ratio because rock wool fibers improved resistance to plastic deformation.

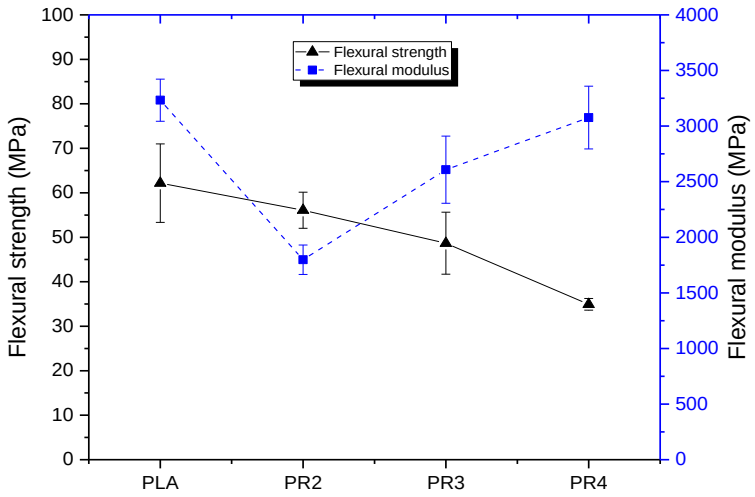

Figure 3. Flexural properties of composites

Figure 4 shows the tensile strength of neat PLA which was measured as 41 MPa. The tensile strength of PLA/Rock wool composites decreased considerably (up to 60%) but tensile modulus of composites increased as the material become stiffer. The highest value of tensile modulus was obtained at PR2 composite with 2487 MPa. The modulus increase is expected for such reinforcing fiber composites. This effect can be due to the lack intermolecular bonding of the rock fibers and matrix or different crystallization units of polymer at manufacturing process. The properties can be improved by using a coupling-agents, such as silanes or anhydrides [14].

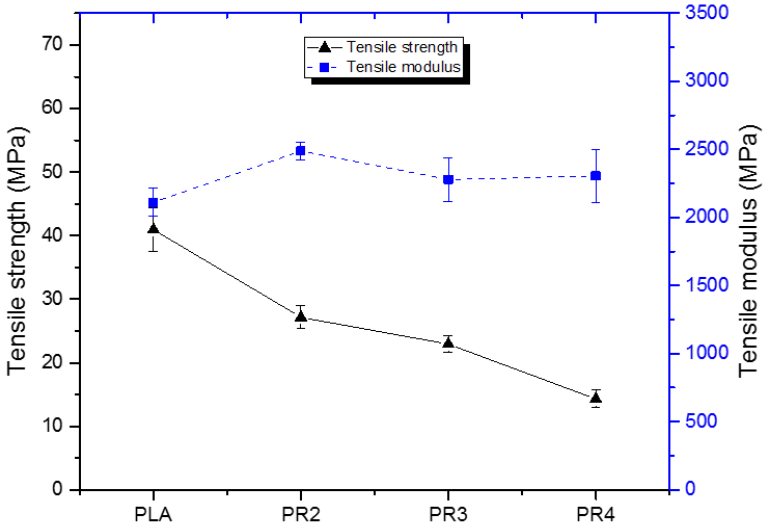

Figure 4. Tensile properties of composites

Figure 5 shows that the strain of neat PLA is higher than composites. It was observed that the elasticity was decreased with increasing fiber ratio [20]. Elongation at break 1.8% for PLA, elongation at break of PR2, PR3 and PR4 composites were obtained 1.5%, %1.0, %0.6, respectively. Figure 5 clearly shows that modulus of PLA was increased with increasing mineral fiber content, while the strain at break was decreased [21].

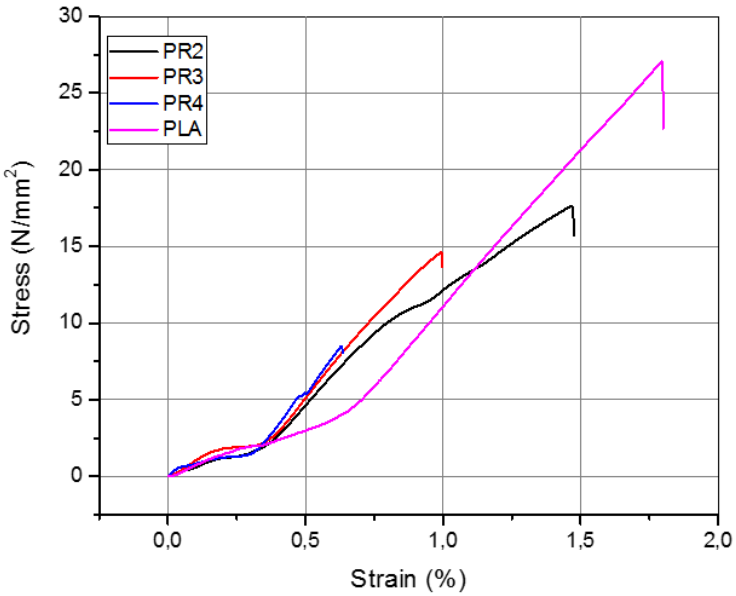

Figure 5. Stress-strain graph

3.5. Thermal Conductivity of Biocomposites

Thermal conductivity of rock wool is 0.035 W/m.K as reported [22]. Thermal conductivity of neat PLA was determined 0.12 W/m.K which is compatible with the literature [23, 24]. It was observed that thermal conductivity of composites decreased with increasing fiber ratio. Thermal conductivity values of PR2, PR3 and PR4 are 0.10, 0.09, 0.09 W/m.K, respectively. Thermal conductivity of PLA/Rock wool composites decreased about 25%, which can be interpreted as better insulation property than neat PLA.

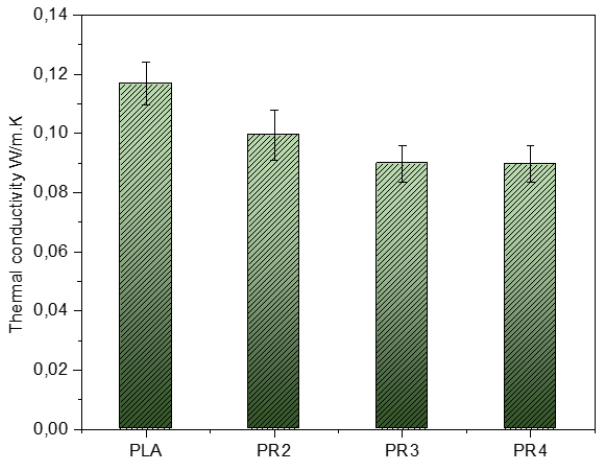

Figure 6. Thermal conductivity values of neat PLA and biocomposites

4. Conclusions

In this study, mechanical, thermal properties and thermal insulation of PLA/rock wool biocomposites (without any coupling agents) have been successfully evaluated. The tensile and flexural strength of PLA/Rock wool composites decreased but the tensile modulus and flexural modulus increased. In view of thermogravimetric analysis, biocomposites

were thermally degraded at lower temperature than neat PLA which can be associated with depolymerization of PLA with increasing catalysis activity of metal ions in rock wool. Thermal insulation properties of biocomposites were enhanced compared to neat PLA. Consequently, the usage of 20% rock wool can provide improved thermal insulation with reasonable reduction in flexural strength (5%). Here, we did not use coupling-agents to improve adhesion of biocomposites. It is thought that the usage of coupling-agents like silanes or anhydrides can improve adhesion between rock wool and PLA polymer, so several features of the biocomposites including mechanical properties can be improved. On the other hand, considering price of the PLA polymer, addition of rock wool can decrease the price of composites and provide partially biodegradable and a sustainable material.

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References

[1] Di Ruocco, G. (2016). Basalt fibers: the green material of the XXI-century, for a sustainable restoration of historical buildings. Vitruvio - International Journal of Architectural Technology and Sustainability, 1:2:25-39.

[2] Yallew, T.B., Kumar, P., Singh, I. (2016). Mechanical Behavior of Nettle/Wool Fabric Reinforced Polyethylene Composites. Journal of Natural Fibers, 13(5):610–618.

[3] Latif, E., Lawrence, R.M.H., Shea, A.D., Walker, P. (2018). An experimental investigation into the comparative hygrothermal performance of wall panels incorporating wood fibre, mineral wool and hemp-lime. Energy Build, 165:76–91

[4] Sin, L.T., Rahmat, R.R., Rahman, W.A.W.A. (2012). Polylactic Acid: PLA Biopolymer Technology and Applications, Elsevier.

[5] Oksman, K., Skrifvars, M., Selin, J.F. (2003). Natural fibres as reinforcement in polylactic acid (PLA) composites. Composites Science and Technology, 63(9):1317-1324.

[6] Meinander, K., Niemi, M., Hakola, J.S., Selin, J-F. (1997). Polylactides - degradable polymers for fibres and films. Macromolecular Symposia, 123(1):147–153

[7] Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K.,Wintermantel, E. (2003). Thermal and mechanical properties of plasticized poly(L-lactic acid). Journal of Applied Polymer Science, 90(7):1731–1738.

[8] Väntsi, O., Kärki, T. (2014). Mineral wool waste in Europe: a review of mineral wool waste quantity, quality, and current recycling methods. Journal of Materials Cycles and Waste Management, 16(1):62–72.

[9] Jamshaid, H., Mishra, R. (2016). A green material from rock: basalt fiber – a review. The Journal of The Textile Institute, 107(7):923–937.

[10] Yang, S.J., Zhang, L.W. (2012). Research on Properties of Rock-Mineral Wool as Thermal Insulation Material for Construction. Advanced Materials Research, 450–451:618–622.

[11] Guo, J.L., Du, Q., Lu, L. (2013). Application of Rock-Wool in Outer-Wall External Thermal Insulation System. Advanced Materials Research, 753–755:512–515.

[12] Cheng, A., Lin, W-T., Huang, R. (2011). Application of rock wool waste in cement-based composites. Materials & Design, 32(2):636–642.

[13] Öztürk, B. (2010). Hybrid effect in the mechanical properties of jute/rockwool hybrid fibres reinforced phenol formaldehyde composites. Fibers and Polymers, 11:464–473.

[14] Zihlif, A.M., Ragosta, G. (2003). A Study on the Physical Properties of Rock Wool Fiber—Polystyrene Composite. Journal of Thermoplastic Composite Materials, 16(3):273–283.

[15] VIVERA CORPORATION (2017) Mineral Wool from THERMOSELECT Processes, http://www.viveracorp.com/index_htm_files/20170228-%20THERMOSELECT%20 Mineral%20Wool.pdf.

[16] Chieng, B.W., Ibrahim, N.A., Yunus, W.M.Z.W., Hussein, M.Z. (2014). Poly(lactic acid)/Poly(ethylene glycol) Polymer Nanocomposites: Effects of Graphene Nanoplatelets. Polymers (Basel), 6(1):93–104.

[17] Rybin, V.A., Utkin, A.V., Baklanova, N.I. (2013). Alkali resistance, microstructural and mechanical performance of zirconia-coated basalt fibers. Cement and Concrete Research, 53:1–8.

[18] Yu, T., Li, Y., Ren, J. (2009). Preparation and properties of short natural fiber reinforced poly(lactic acid) composites. Transactions of Nonferrous Metals Society of China, 19: 651–655.

[19] Quispe-Dominguez, R., Naseem, S., Leuteritz, A., Kuehnert, I. (2019). Synthesis and characterization of MgAl-DBS LDH/PLA composite by sonication-assisted masterbatch (SAM) melt mixing method. RSC Advances, 9:658–667.

[20] Kasuga, T., Ota, Y., Nogami, M., Abe, Y. (2000). Preparation and mechanical properties of polylactic acid composites containing hydroxyapatite fibers. Biomaterials, 22(1):19–23.

[21] Suryanegara, L., Nakagaito, A.N., Yano, H. (2009). The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. Composite Science and Technology, 69(7-8):1187–1192.

[22] İzocam Tic. ve San. Isı Yalıtım Malzemeleri. https://www.izocam.com.tr/isi-yalitim-malzemeleri/

[23] Haleem, A., Kumar, V., Kumar, L. (2017). Mathematical Modelling & Pressure Drop Analysis of Fused Deposition Modelling Feed Wire. International Journal of Engineering Technolgy, 9(4):2885–2894.

[24] Angın, N., Çaylak, S., Ertaş, M. (2019). Studies on Thermal and Morphological Properties of Polyurethane Foam Filled Polypropylene/Poly(lactic acid) Blends. Journal of Innovative Science and Engineering, 3(2):47–56.