MANAS Journal of Engineering
ISSN 1694-7398 | e-ISSN 1694-7398

Volume 13, Issue 1, (2025) Pages 23-29
https://doi.org/10.51354/mjen.1543960

Experimental characterization of thermal, mechanical, physical and morphological performance of thermoplastic polyurethane composites containing acidic pumice

Ahmet Bulut[1], Ümit Tayfun[2], Mehmet Yurderi[3,*]

[1] Bartın University, Faculty of Science, Bartın, Türkiye, abulut@bartin.edu.tr, ORCID: 0000-0002-1697-8623
[2] Bartın University, Faculty of Engineering, Architecture and Design, Bartın, Türkiye, utayfun@bartin.edu.tr, ORCID: 0000-0001-5978-5162
[3] Bartın University, Bartın Vocational School, Bartın, Türkiye, myurderi@bartin.edu.tr, ORCID: 0000-0002-0233-8940

ABSTRACT

Pumice powder, with its porous structure and low density, is a metal support material in water purification, catalysis manufacturing, and light construction materials. Acidic pumice has a significant proportion of silica. In this study, it was aimed to increase the mechanical and physical performances, as well as the reduction in the specific gravity and cost values, with the addition of acidic pumice to the thermoplastic polyurethane (TPU) polymer, which is used in various sectors such as textile, logistics, construction, and medical applications. Acidic pumice powder was blended with TPU at 2.5, 5.0, 7.5, and 10.0 weight percentages via the melt blending technique for this aim. In addition to mechanical testing such as tensile and hardness, thermal gravimetric analysis, melt flow rate, and electron microscopy (SEM) characterization methods were used on injection-molded composite samples. The structure of the pumice powder was studied using SEM/energy diffraction X-rays. Results revealed that the inclusion of pumice reduces the tensile strength and percent elongation values of TPU, but the composite sample with 2.5% pumice produced virtually equal values to the reference polymer. The hardness of the pumice increased with the loading rate. The low percentage of pumice reinforcement improved TPU's thermal stability. The melt flow rate produced varying results at different pumice ratios. As the morphological qualities were studied using electron microscopy, it was determined that the pumice particles were homogeneously disseminated in the TPU phase when reinforced at 2.5% and 5.0%. Based on these findings, TPU-based composites with the lowest addition quantity of 2.5% pumice produced the best outcomes. The use of pumice-filled TPU composites in automotive and construction applications can be established effectively thanks to performance improvement in the properties of examined samples.

ARTICLE INFO

Research article

Received: 05/09/2024
Accepted: 13/02/2025

Keywords:
acidic pumice, polymer composites, melt blending, thermoplastic polyurethane

*Corresponding author

1. Introduction

Porous and amorphous, pumice is a volcanic rock containing SiO_2 in its structure. The precipitation of dissolved gases forms its porous structure during the cooling of lava as it moves rapidly in the air [1,2]. Türkiye has approximately 3 billion m^3 reserves and has important acidic pumice deposits around Nevşehir, Van, and Kayseri regions [3,4]. Pumice powder is used to produce soap, toothpaste, insulation plaster, detergent, and as a cheap filling material in the plastic industry [5-7]. Pumice containing building materials such as concrete, mortar, fiber-board, phase-change, and catalysis-support materials were developed [8-12]. In these cases, weight reduction is the main strategy thanks to the characteristic microporous morphology of the pumice structure.

Pumice was compounded with various polymers for performance improvement of composite materials corresponding to the literature survey. Polymer matrices involving acidic pumice particles are epoxy resin [13-15], polypropylene [16-18], polyethylene [19-21], polyethylene terephthalate (PET) [22,23], poly (vinyl alcohol) [24,25], polyethylene glycol (PEG) [26,27], poly (lactic acid) [28], hydroxyapatite [29], poly (phenylene sulfide) [30-33], poly (hydroxyethyl methacrylate) [34], polyaniline [35,36], ethylene propylene diene rubber (EPDM) [37], poly (vinyl pyrrolidone) [38], nitrile rubber [39], poly (β-hydroxybutyrate) [40], and acrylonitrile-styrene-butadiene copolymer (ABS) [41], based on the literature. In most of these studies, the mechanical performances of resulted polymeric materials were investigated. Additionally, phase-change behavior, weight-reduction, thermal stability, fire and wear resistance properties were enhanced in related research works.

Thermoplastic polyurethane (TPU) is preferred in industrial applications due to its recyclability, ease of processing, and high wear resistance. TPU has been used in several sectors, such as film and packaging, textiles, pharmaceuticals, sports equipment, transportation, electronics, and cables.

According to the literature, pumice additions improved thermoset polyurethane's acoustic and thermal insulation properties published by Soyaslan [42]. This study aimed to increase mechanical and physical performances and decline specific gravity and production costs via acidic pumice inclusion to TPU polymer, which is used in various application fields such as textile, logistics, construction, and medical equipment. Performance enhancement in mechanical and thermal behaviors of TPU via the pumice inclusion contributes to achieving requirements in related applications. In addition to mechanical tests, such as tensile and hardness, force measurement, thermal gravimetric analysis (TGA), melt flow rate, and scanning electron microscope (SEM) characterization methods were applied to the composite samples shaped by injection molding.

2. Materials and method

2.1.Materials

Ester-based TPU with the trade name Ravathane® R130A85 was supplied by Ravago Petrochemical, İzmir, Türkiye. Acidic pumice was supplied in ground powder form in 25-micron grain size from Yoltaş Pomza Ürünleri A.Ş., Nevşehir, Türkiye.

Figure 1. *Melt-compounding, injection molding, and characterization steps of composites*

2.2.Composite fabrication

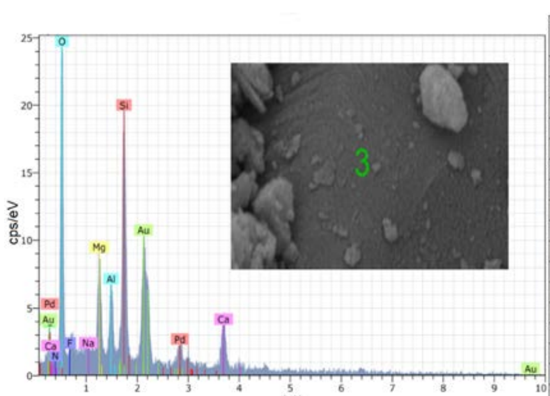
TPU-based composites were produced using MC15HT (Xplore Instruments) extruder. Mixing temperature, mixing speed, and time were set as 200 ˚C, 100 rpm, and 5 min, respectively. During the preparation of the composites, acidic pumice powder was blended with TPU at 2.5, 5.0, 7.5, and 10.0 weight percent ratios using the melt blending technique. The preparation and shaping steps of the study are visualized in Fig. 1.

2.3.Characterization techniques

The particle size of basic pumice powder was analyzed with the Malvern Mastersizer 3000 particle size measuring device. Tensile test was performed to determine the stress-deformation behavior of the material. In this study, according to the ASTM D-638 standard and with the Lloyd LR 30 K tensile test device, using dog bone-shaped composites with a 5 kN load chamber and a speed of 5 cm/min. Shore hardness measurements were carried out by the Tronic brand Shore hardness device according to the ISO 7619-1 standard. The fracture surfaces of the composite samples obtained from the tensile strength test were subjected to TESCAN MAIA3 analytical scanning electron microscope, and SEM images were taken with x1000, x2500, and x5000 magnifications. X-ray fluorescence (XRF) and energy diffraction X-ray (EDS) analyses of pumice powders were also performed using the same device. Hitachi STA 7300 brand thermogravimetric analyzer was utilized to evaluate thermogravimetric analysis (TGA) of composites in the range of 25-600 °C and at a speed of 10 °C/min. MFI (melt flow index) values are indicative parameters for thermoplastics in the case of processability. MFI values of the produced samples were determined via the Coesfeld Melt-Flixer device in accordance with a standard load of 2.16 kg. Xplore Instruments software was used to measure the force values during the extrusion process. The screw force values in the melt were determined using the software of the micro-mixer as a function of the mixing time.

3. Results and Discussion

The elemental content of the supplied pumice powder was obtained by EDS analysis and displayed in Fig. 2.
According to Fig. 2, it was observed that acidic pumice was rich in silica (SiO_2) with 63.9% composition. Other parts of AP contained metal oxides, mainly Al_2O_3, Fe_2O_3, SO_3, PbO, ZnO, K_2O, and MnO.



Compound	Composition (%)
SiO_2	63,90
Al_2O_3	8,59
Fe_2O_3	6,73
SO_3	4,76
PbO	3,55
ZnO	2,30
K_2O	1,75
MnO	1,42
CuO	0,97
MgO	0,53
Sb_2O_3	0,28
BaO	0,27
P_2O_5	0,24
TiO_2	0,2
As_2O_3	0,13
CaO	0,12
Na_2O	-

Figure 2. *EDS data of AP*

Force measurement provides experimental data for planning the production of the resulting composite materials before the large-scale production stages. As seen from the extrusion force of different mixing ratios of TPU and AP against time in Fig. 3, it was found to be AP additions cause an increase in the mixing force values due to the addition of powder, which improves the wear force because of the increased melt viscosity during the extrusion process. Similarly, a high amount of mineral filler loadings resulted in a remarkable increase in mixing force values in accordance with the studies in the literature dealt with the polymers involving minerals [43,44].

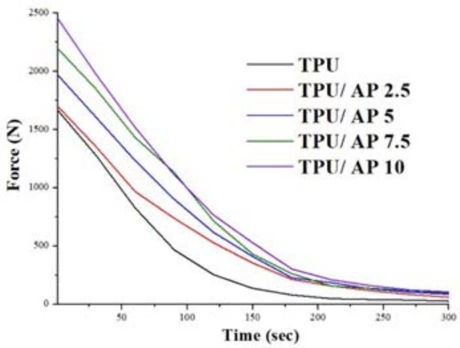


Figure 3. *Force-time graphs of TPU and composites*

The following experimental study is the tensile strength test, which is given as the graphs of tensile strength versus elongation with different mixing ratios of TPU and AP in Fig. 4. Although the tensile strength and percent elongation values of TPU are slightly reduced with the addition of acidic pumice, the composite containing 2.5% pumice presents similar values to the reference polymer. As the AP loading amount increases, the tensile strength and percent elongation values at break declined. Further additions of AP beyond the loading level of 2.5% caused pumice powder to deteriorate the composite structure by forming agglomeration. The highest tensile strength values were obtained for composite samples filled with the lowest amount of pumice powder based on the similar studies in the literature.[16,19,28].

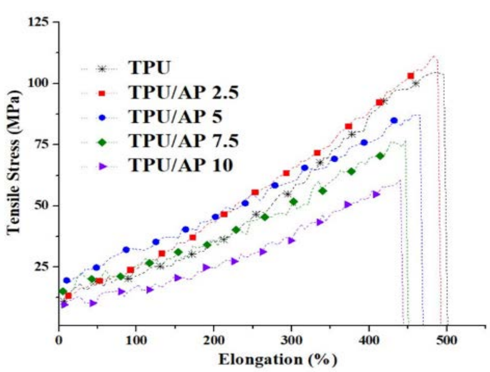
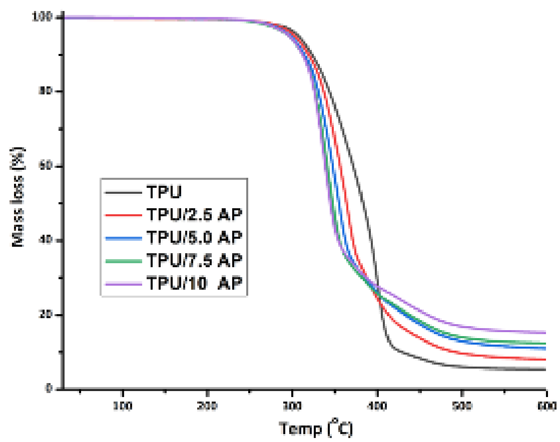
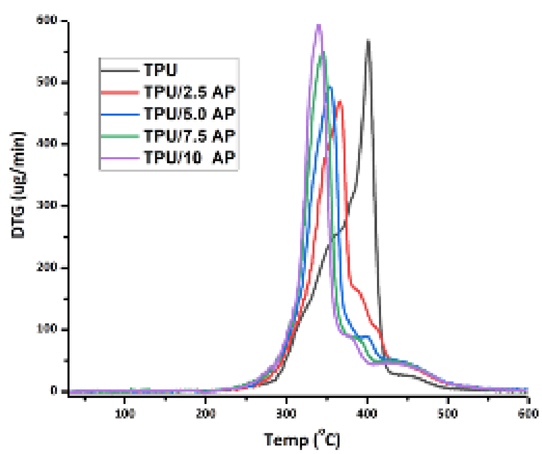


Figure 4. *Tensile test curves of TPU and composites*

The chain structure of TPU elastomer involves repeating soft and hard segments. The hard segment consists of diamine reacted with low molecular weight glycols or diisocyanate and strengthened by crosslinking. The soft segment consists of polyester or polyether units. TPU revealed a two-step degradation curve owing to isocyanate and polyol segments, respectively [45,46]. As the TGA and DTG curves of the composites are examined in Fig. 5, it was determined that especially low-ratio pumice reinforcement positively affected the thermal stability of TPU. Composites containing AP started to decompose at lower temperatures, and as the AP ratio increased, the decomposition temperature tended to decrease. According to the research works performed with pumice additive, several polymers such as polypropylene (PP) [16], polylactide (PLA) [28], and acrylonitrile-butadiene-styrene terpolymer (ABS) [41] exhibited lowering in thermal degradation after AP inclusions.



(a) TGA curves



(b) DTG curves

Figure 5. *Thermo-gravimetric curves of composites*

Fig. 6 represents MFI graphs against mixing ratios of AP.

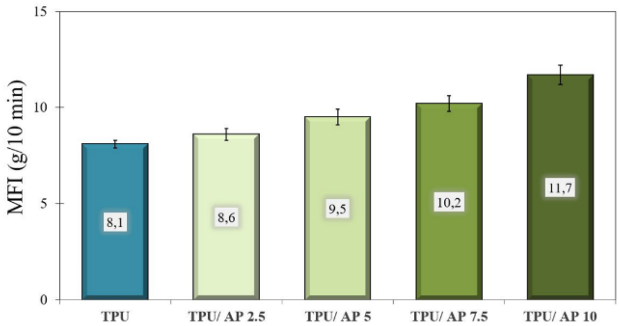


Figure 6. *MFI results of TPU and composites*

According to Fig. 6, MFI values gave variable results at different pumice ratios. The addition of AP caused an increase in the MFI value of TPU due to high specific gravity of the pumice. At low AP addition percentages, closer MFI values were obtained to unfilled TPU. This finding implies that the processing stages of TPU/AP composites can take place with no serious problems since technical difficulties in injection molding can be caused by the high level of melt-flow rates such as warpage or flow-lines as well as short-shot or delamination with high MFI values.

Table 1. The *Shore A hardness values of TPU and relevant composites*

Sample	Hardness (Shore A)
TPU	85.0±0.1
TPU/ AP 2.5	85.4±0.1
TPU/ AP 5	85.7±0.2
TPU/ AP 7.5	86.1±0.1
TPU/ AP 10	86.5±0.1

Shore hardness parameters of TPU and TPU/AP composites with varied filling amounts are listed in Table 1. Shore A hardness value of unfilled TPU showed an increasing trend with the increase in pumice loading ratio. Similar results were obtained from the literature, which found that incorporating pumice enhanced the shore hardness of polymeric composites [41,47]. Improvement in shore hardness values refers to the donation of scratch resistance of composite material related to the indentation volume of the polymer surface [48].

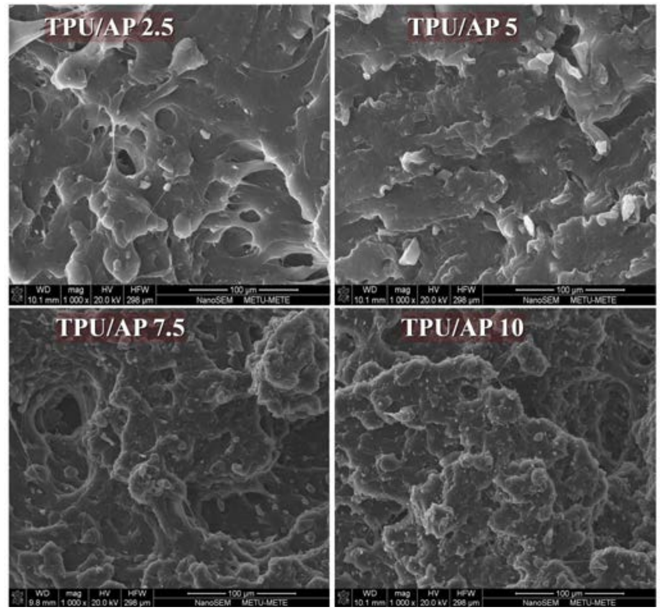


Figure 7. *SEM photographs of composites*

As the scanning electron microscope micro-photographs given in Fig. 7 are examined, it was determined that the pumice particles are homogeneously distributed within the TPU phase when their morphological structures were reinforced at 2.5% and 5.0%. The homogeneous distribution in the composite structure disappears at high AP loading rates. As visualized in Fig. 7, the agglomerated morphology of AP at high-loading amounts is the reason for obtaining a reduction in the mechanical performance of TPU/ AP 7.5 and TPU/ AP 10 composite samples. The decline in dispersion homogeneity was obtained for the morphology of mineral-filled polymeric composites according to the literature [15,20,23].

4. Conclusion

In addition to mechanical tests such as tensile and hardness, force measurement, thermal gravimetric analysis, melt flow rate, and electron microscope (SEM) characterization methods were applied to composite samples prepared by mixing acidic pumice powder with TPU using the melt blending technique at 2.5, 5.0, 7.5 and 10.0 wt% ratios. According to the results obtained, it was observed that the tensile strength and percentage elongation values of TPU increased with the addition of 2.5% AP, and these values decreased slightly with higher AP reinforcements. The shore hardness value increases with the pumice loading rate. TPU's melt-flow index increases directly proportional to the AP rate. According to TGA analysis, composites containing AP start to decompose at low temperatures compared to TPU. AP addition percentage negatively affects the thermal stability of composites. As a result of SEM characterization, pumice particles tend to exhibit homogeneous distribution in the TPU phase at low AP concentrations. Based on the findings, TPU-based composites containing the lowest addition rate of pumice exhibited optimum results. Acidic pumice can potentially reduce costs while maintaining the performance of TPU-based composites in the case of low filling ratios. Results revealed that pumice can be used as an effective additive for TPU-based composite materials since mechanical and thermal performance increased.

Statement of conflicts of interest

There is no conflict of interest between the authors.

Author contributions

All authors contributed equally to the study.

References

[1]. Ersoy B., Sariisik A., Dikmen S., Sariisik G., “Characterization of acidic pumice and determination of its electrokinetic properties in water”, Powder Technology, 197, (2010), 129–135.

[2]. Lura P., Bentz D.P., Lange D.A., Kovler K., Bentor A., “Pumice aggregates for internal water curing”, International RILEM Symposium, 22–24, (2004), 137–151.

[3]. Yazıcıoğlu S., Arıcı E., Gönen T., “Pomza taşının kullanım alanları ve ekonomiye etkisi”, F.Ü. DAUM Dergisi, 1, (2003), 118-123

[4]. Elmastas N., “A mine becoming increasingly important for economy of Turkey: Pumice”. International Journal of Social Research, 5, (2012), 197-206

[5]. Bodude M.A., Akano T.T., Owa A. F., ‘’Mechanical and microstructural characterization of rubber particle reinforced thermoplastic for automobile bumper application’’, MANAS Journal of Engineering, 7(2), (2019), 89-93.

[6]. Çoban O., Yilmaz T., “Volcanic particle materials in polymer composites: A review”, Journal of Materials Science, 57(36), (2022), 16989-17020.

[7]. Whitham A.G., Sparks R.S.J., “Pumice”, Bulletin of Volcanology, 48, (1986), 209-223.

[8]. Dayan O., Kilicer A., Bulut A., Ceylan E., Tayfun U., Uzun O., Zahmakiran M., Yurderi M., “Pumice-supported ruthenium nanoparticles as highly effective and recyclable catalyst in the hydrolysis of methylamine borane”, International Journal of Hydrogen Energy, 52, (2024), 1-10.

[9]. Acet Ö., “Investigation of BSA adsorption performances of metal ıon attached mineral particles embedded cryogel discs”, MANAS Journal of Engineering, 9, (2021), 65-71.

[10]. Hossain K.M., “Potential use of volcanic pumice as a construction material”, Journal of Materials in Civil Engineering, 16(6), (2004), 573-577.

[11]. Kurt M., Gul M.S., Gul R., Aydin A.C., Kotan T., “The effect of pumice powder on the self compactability of pumice aggregate lightweight concrete”, Construction and Building Materials, 103, (2016), 36-46.

[12]. Sari D., Pasamehmetoglu A.G., “The effects of gradation and admixture on the pumice lightweight aggregate concrete”, Cement and Concrete Research, 35, (2005), 936–942.

[13]. Koyuncu M., “The influence of pumice dust on tensile, stiffness properties and flame retardant of epoxy/wood flour composites”, Journal of Tropical Forest Science, 30, (2018), 89-94.

[14]. Shahapurkar K., Zelalem Y.M., Chenrayan V., Soudagar M.E., Fouad Y., Kalam M.A., Kiran M.C., “Investigation on the mechanical and fracture properties of lightweight pumice epoxy composites”, Polymer Engineering & Science, 64(3), (2024), 1071-1082.

[15]. Fleischer C.A. , Zupan M., “Mechanical performance of pumice-reinforced epoxy composites”, Journal of Composite Materials, 44, (2010), 2679-2696.

[16]. Kanbur Y., Tayfun U., "Mechanical, physical and morphological properties of acidic and basic pumice containing polypropylene composites", Sakarya University Journal of Science, 22, (2018), 333-339.

[17]. Almiron J., Roudet F., Duquesne S., "Influence of volcanic ash, rice husk ash, and solid residue of catalytic pyrolysis on the flame-retardant properties of polypropylene composites", Journal of Fire Science, 37(4–6), (2019), 434–451.

[18]. Sever K., Atagür M., Tunçalp M., Altay L., Seki Y., Sarıkanat M., "The effect of pumice powder on mechanical and thermal properties of polypropylene", Journal of Thermoplastic Composite Materials, 32, (2019), 1092-1106.

[19]. Wang C., Ajji A., ‘Ethylene scavenging film based on low-density polyethylene incorporating pumice and potassium permanganate and its application to preserve avocados’’, LWT, 172, (2022), 114200.

[20]. Han B., Sun Z., Chen Y., Tian F., Wang X., Lei Q., "Space charge distribution in low-density polyethylene (LDPE)/pumice composite", Proceedings of 9th International Conference on Properties and Applications of Dielectric Materials, China, (2009), 19-23.

[21]. Han B., Sun Z., Chen Y., Tian F., Wang X., Lei Q., ‘’Space charge distribution in Low-density Polyethylene (LDPE)/Pumice composite’’, IEEE 9th International Conference on the Properties and Applications of Dielectric Materials, (2009), 969-972.

[22]. Kurtulmus E., Karaboyacı M., Yigitarslan S., ‘’Production and characterization of a composite insulation material from waste polyethylene teraphtalates’’, AIP Conference Proceedings, 1569, (2013), 487-491.

[23]. Sari N.H., Setyawan P.D., Thiagamani S.M.K., Suteja Tamimi R., Rangappa S.M., Siengchin S., ‘’Evaluation of mechanical, thermal and morphological properties of corn husk modified pumice powder reinforced polyester composites’’, Polymer Composites, 43(3), (2022), 1763-1771.

[24]. Jayakrishnan P., Ramesan M.T., "Synthesis, characterization and properties of poly (vinyl alcohol)/chemically modified and unmodified pumice composites", Journal of Chemical and Pharmaceutical Sciences, 1, (2016) 97-104.

[25]. Ramesan M.T., Jose C., Jayakrishnan P., Anilkumar T., "Multifunctional ternary composites of poly (vinyl alcohol)/cashew tree gum/pumice particles", Polymer Composites, 39, (2018), 38-45.

[26]. Sarı A., Hekimoğlu G., Tyagi V.V., Sharma R.K., ‘’Evaluation of pumice for development of low-cost and energy-efficient composite phase change materials and lab-scale thermoregulation performances of its cementitious plasters’’, Energy, 207, (2020), 118242.

[27]. Sarı A., ‘’Composites of polyethylene glycol (PEG600) with gypsum and natural clay as new kinds of building PCMs for low temperature-thermal energy storage’’, Energy and Buildings, 69, (2014), 184-192.

[28]. Dike A.S., ‘’Türk Pomza mineralinin modifikasyonu ve poli (laktik asit) bazli biyo-kompozit malzemelerinde eklenti olarak kullanimi’’, Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi, 20(1), (2020), 111-117.

[29]. Koc S., ‘’Pumice and perlite co-substituted hydroxyapatite: Fabrication and characterization’’, MANAS Journal of Engineering, 8(2), (2020), 132-137.

[30]. Sahin A., Karsli N.G., Sinmazcelik T., "Comparison of the mechanical, thermomechanical, thermal, and morphological properties of pumice and calcium carbonate-filled poly (phenylene sulfide) composites", Polymer Composites, 37, (2016), 3160-3166.

[31]. Bora M.Ö., Çoban O., Kutluk T., Fidan S., Sinmazçelik T., "The influence of heat treatment process on mechanical properties of surface treated volcanic ash particles/polyphenylene sulfide composites", Polymer Composites, 39, (2018), 1604–1611.

[32]. Sahin A., Yildiran Y., Avcu E., Fidan S., Sinmazcelik T., "Mechanical and thermal properties of pumice powder filled PPS composites", Acta Physica Polonica A, 2, (2014), 518-520.

[33]. Avcu E., Coban O., Bora M.O., Fidan S., Sinmazcelik T., Ersoy O., "Possible use of volcanic ash as a filler in Polyphenylene Sulfide composites: thermal, mechanical, and erosive wear properties", Polymer Composites, 35, (2014), 1826–1833.

[34]. Akkaya R., "Uranium and thorium adsorption from aqueous solution using a novel polyhydroxyethylmethacrylate-pumice composite", Journal of Environmental Radioactivity, 120, (2013), 58-63.

[35]. Yılmaz K., Akgoz A., Cabuk M., Karaagac H., Karabulut O., Yavuz M., "Electrical transport, optical and thermal properties of polyaniline–pumice composites", Material Chemistry and Physics, 130, (2011), 956-961.

[36]. Gok A., Gode F., Turkaslan B.E., "Synthesis and characterization of polyaniline/pumice composite", Material Science and Engineering B, 133, (2006), 20-25.

[37]. Rahmaniar S.T., Prasetya H.A., Marlina P., Purbaya M., Chalid M., Hasan A., ‘’The effect of pumice and clay composition in natural rubber-ethylene propylene diene monomer blends towards its curing characteristics and physic-mechanical properties’’, Material Science and Engineering, 980, (2020), 012003.

[38]. Ramesan M.T., George A., Jayakrishnan P., Kalaprasad G., "Role of pumice particles in the thermal, electrical and mechanical properties of poly(vinyl alcohol)/poly(vinyl pyrrolidone) composites", Journal of Thermal Analysis and Calorimetry, 126, (2016), 511-519.

[39]. El-Nemr K.F., Radi H., Helal R.H., ‘’Partial replacement of silica by naturally occurring pumice powder for enhancing mechanical and thermal properties of nitrile rubber cured by electron beam irradiation’’, Pigment & Resin Technology, 53(4), (2022), 442-449.

[40]. Alvarado S., Morales K., Srubar W., Billington S., "Effects of natural porous additives on the tensile mechanical performance and moisture absorption behavior of PHBV-based composites for construction", Stanford Undergrad Research Journal, 10, (2011), 30-35.

[41]. Tayfun Ü., Tirkeş S., Doğan M., Tirkeş S., Zahmakıran M., ‘’Comparative performance study of acidic pumice and basic pumice inclusions for acrylonitrile–butadiene–styrene-based composite filaments’’, 3D Printing and Additive Manufacturing, 11(1), (2024), 276-286.

[42]. Soyaslan I.I., "Thermal and sound insulation properties of pumice/polyurethane composite material", Emerging Materials Research, 9(3), (2020), 859-867.

[43]. Akar A.Ö., Yıldız Ü.H., Tayfun Ü., "Halloysite nanotube loaded polyamide nanocomposites: Structural, morphological, mechanical, thermal and processing behaviors.", AIP Conference Proceedings. 2607(1), (2023), 070005.

[44]. Aksoy E., Tirkeş S., Tayfun Ü., Tirkeş S., ‘’Expanded perlite mineral as a natural additive used in polylactide-based biodegradable composites’’, Turkish Journal of Science and Technology, 19(1), (2023), 113-122.

[45]. Herrera M., Matuschek G., Kettrup A., ‘’Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI’’, Polymer Degradation and Stability, 78(2), (2002), 323-331.

[46]. Wei Z., Chen X., Jiao C., ‘’Thermal degradation and flame retardancy of fumaric acid in thermoplastic polyurethane elastomer’’, Polymers for Advanced Technologies, 30(2), (2019), 475-482.

[47]. Yurderi M., Tayfun Ü., Bulut A., ‘’Development of polyurethane elastomer-based bio-composites reinforced with basaltic pumice’’, Journal of the Institute of Science and Technology, 14(4), (2024), 1622-1631.

[48]. Chu J., Xiang C., Sue H.J., Hollis, R.D., ‘’Scratch resistance of mineral-filled polypropylene materials’’, Polymer Engineering & Science, 40(4), (2000), 944-955.