Preparation and Characterization of Calcite Loaded Poly (Lactic Acid) Composite Materials

Ali Sinan DİKE

*Corresponding Author: asdike@atu.edu.tr

Abstract

In this work, calcite (KS) mineral was compounded with poly (lactic acid) (PLA) at the concentrations of 5, 10, 15 and 20 wt% using extrusion process. Test samples of PLA and composites were prepared by injection molding. Characterization of composites were done based on mechanical tests including tensile, hardness and impact tests, flow behavior by melt flow rate test (MFR) and morphological studies by scanning electron microscopy (SEM) method. Mechanical test results showed that the highest improvements in tensile strength and tensile modulus values were obtained for 10 wt% of KS filled composite. Further addition of KS caused remarkable decrease in tensile strength. Impact strength of PLA reduced by KS additions. The highest impact energy value was found in PLA-15 KS sample among composites. Hardness of neat PLA increased after KS inclusions. KS loaded PLA gave slightly higher MFR values compared to neat PLA. SEM micro-images of composites implied that KS particles dispersed homogeneously in PLA matrix at their lower loading ratio. Large agglomerates and poor dispersion were obtained for higher concentrations of KS since they favor particle-particle interactions. According to these results, concentrations of 10wt% and 15wt% were determined as suitable for calcite containing PLA composites.

Keywords: poly (lactic acid), calcite, composite material, extrusion

Kalsit Takviyeli Poli (Laktik Asit) Kompozit Malzemelerinin Hazırlanması ve Karakterizasyonu

Öz

Bu çalışmada, kalsit (KS) minerali ağırlıkça %5, 10, 15 ve 20 konsantrasyonlarında poli (laktik asit) (PLA) ile ekstrüzyon işlemi kullanarak karıştırılmıştır. PLA ve kompozitlerin test numuneleri enjeksiyon kalıplama ile hazırlanmıştır. Kompozitlerin karakterizasyonları, çekme, sertlik ve darbe testlerini içeren mekanik testler, erime ağız hızı testi (MFR) ile ağız davranışları ve taramalı elektron mikroskopi (SEM) yöntemleri ile morfolojik çalışmalar baz alınarak yapılmıştır. Mekanik test sonuçları, çekme dayanımı ve modülde en yüksek artısa %10 KS eklenmiş kompozitte saptandığı göstermiştir. Daha fazla KS eklenmesi çekme dayanımında belirgin düşüşe neden olmuştur. PLA’nın darbe dayanımı KS eklemesi ile artmıştır. Kompozitler arasında en yüksek darbe enerjisi PLA-15 KS numunesinde bulunmaktadır. Eklentisiz PLA’nın sertliği KS ekmelermelerinden sonra artmıştır. Eklentisiz PLA’ya kıyasla, kalsit takviyeli PLA biraz yüksek MFR değerleri vermiştir. Kompozitlerin SEM mikro-resimlerini göstermiştir ki; KS parçacıkları düsük ekleme oranlarında PLA matrisi içinde homojen şekilde dağılmıştır. KS yüksek konsantrasyonlarda parçacık-parçacık etkileşimlerini tercih ettiğinden büyük aglomeratlar ve zayıf dağılım gözlenmiştir. Bu sonuçlara göre, %10 ve %15 konsantrasyonları kalsit içeren PLA kompozitleri için uygun olarak belirlenmiştir.

Anahtar Kelimeler: poli (laktik asit), kalsit, kompozit malzeme, ekstrüzyon
1. Introduction

Environmentally friendly composite materials gain scientific attention because of recent progress in pollutant problems. Development and widely usage of bio-degradable polymers seem to be one of the favorite solution in the case of these environmental problems. Environmentally friendly composites provide several advantages including weight reduction, practical production and bio-compatibility. These promising materials have found effective usage mostly in packaging, textile, and transportation applications in recent years (Weber, 2002; Bismarck et al., 2006; Tayfun, 2015; Mann et al., 2018; Yıldızhan et al., 2018).

Poly (lactic acid) (PLA) is one of the commercially available bio-degradable polymers. PLA has various advantages such as recyclability, bio-degradability, environmentally friendly, bio-compatibility and practical processing characteristics (Hottle et al., 2013; Doppalapudi et al., 2014). It has a potential of reduction for disposal problem related with packaging applications. Compounding of PLA with several fillers open way to perform its efficient applications by enhancement of related properties of PLA based composites (Lezak et al., 2008; Rasal et al., 2010; Ren, 2011; Bajpai et al., 2012; Murariu and Dubois, 2016; Piekarska et al., 2016; Tayfun and Dogan, 2016; Eselini et al., 2019). As a biomaterial, PLA and its composites are used in numerous applications including bio-resorbable stents, drug delivery systems, orthopedic devices and tissue engineering (Farah et al., 2016; Piorkowska, 2019).

Environmentally friendly composites are developed by adding natural fillers to bio-degradable polymers. Naturally occurring minerals are widely used as natural additives for plastics since they have low cost. There are several characteristic factors which effect the final performance of mineral containing polymer composites such as their particle size, adding amount and shape (Theberge, 1982; Liang, 2003; Rathon, 2003; Metin et al., 2004; Xanthos, 2005; Dike et al., 2017; Kanbur and Tayfun, 2018).

Calcite (KS) is the most abundant crystalline form of calcium carbonate mineral. It is obtained from the marine deposits areas. KS has been widely used as an additive to polymers for the main purpose of obtaining cheap plastic materials (Wake, 1971; Jerzy, 1993). However, addition of calcite yields increase on varied behaviors of polymers besides reduction of cost. The effects of calcite additions on the basic properties including mechanical, rheological, thermal, breathability, flame resistance and waterproofness of polymeric materials were studied (Demjen et al., 1998; Tayfun, 2006; Yang et al., 2006; Tian and Tagaya, 2007; Gorna et al., 2008; Dogan and Bayramli, 2009; Fuad et al., 2010; Isitman et al., 2011; Betingytė et al., 2012; Zhitong et al., 2014; Ozen and Simsek, 2016; Mat et al., 2017; Ayaz et al., 2018). Research works related with PLA composites containing KS mostly performed in biomaterial field according to literature (Cho et al., 1997; Maeda et al., 2002a).
Preparation and Characterization of Calcite Loaded Poly (Lactic Acid) Composite Materials

In these studies, apatite-forming abilities of KS containing PLA composites were postulated in order to examine the recovery of the part of bone defects.

The main aim of this study is to postulate the effect of calcite concentration on the mechanical, melt-flow and morphological properties of KS loaded PLA bio-composites. Composite materials were prepared using lab-scale extrusion and test samples were shaped by injection molding process. Tensile test, hardness measurements, impact test, melt-flow rate test and scanning electron microscopy (SEM) analysis were conducted in order to characterize the properties of PLA based composites. Conventionally used fabrication and characterization techniques were preferred to provide detailed information for the industrial application of PLA/KS composite system.

2. Material and Methods

2.1. Materials

The commercial PLA was supplied from Natureworks LLC, USA with the trade name of Ingeo biopolymer 6100D. This extrusion grade PLA is available in pellet form. It has a number average molecular weight (Mn) and density of nearly 190,000 and 1.24 g/cm³, respectively. Calcite powder (OMYACARB 3 EXTRA- GZ) was obtained from Omya Mining Inc, Istanbul, Turkey. It has an average particle size of 5 microns.

2.2. Production of composites

Composite materials were produced using DSM Xplore twin screw extruder with processing temperature, mixing rate and mixing time of 210°C, 100 rpm and 5 minutes, respectively. The unfilled PLA was mixed under the same processing conditions and named as PLA. Loading ratio of KS was varied with 5, 10, 15 and 20 wt%. Test samples of prepared composites were shaped by micro-injection molding, Daca Instruments at a barrel and mold temperatures of 210°C and 60°C, respectively.

2.3. Characterization methods

Tensile tests were done using Lloyd LR 30 K universal tensile testing device with 5 kN load cell and crosshead speed of 5 cm/min. Tensile strength, percentage elongation and tensile modulus parameters were recorded as minimum of three samples with the standard deviations. Hardness tests were carried out by Zwick digital hardness tester device and shore D type hardness values of samples were determined. Impact test was performed by Coesfeld material impact tester. Melt flow rates (MFR) of samples were measured using Coesfeld meltfixer LT with the standard load of 5 kg at temperature of 210°C. The fractured surfaces of composites obtained from impact test were used for the morphological characterization using FEI Quanta 400F scanning electron microscope (SEM).

3. Research Findings

3.1. Tensile test

Tensile test data of PLA and composites are listed in Table 1. It can be seen from Table 1 that tensile strength of PLA slightly increased with the addition of KS at lower concentrations. 20% loading of KS showed remarkable decrease in tensile strength values. The tensile strength values of PLA-10 KS and PLA-15 KS were found to be higher relative to other composite samples. These results may be due to the agglomeration formations of KS particles into PLA phase after 15% concentration. Composites gave remarkably lower percent elongation values compared to
unfilled PLA. It is well-known tensile behavior of plastics that increase in tensile strength yields reduction in elongation values (Vishu, 1998; Brown, 1999; Piekarska et al., 2017; Alghadi et al., 2020; Hatipoglu and Dike, 2020) Tensile modulus of PLA and composites were found nearly identical according to Table 1.

Table 1. Tensile test results

| Samples        | Tensile Strength (MPa) | Tensile Modulus (GPa) | Elongation (%) |
|----------------|------------------------|-----------------------|----------------|
| PLA            | 58.1±0.7               | 1.0±0.1               | 11.8±0.5       |
| PLA-5 KS       | 59.4±0.8               | 1.0±0.1               | 9.5±0.5        |
| PLA-10 KS      | 60.6±1.0               | 1.1±0.1               | 8.8±0.3        |
| PLA-15 KS      | 59.9±0.7               | 1.1±0.1               | 9.1±0.5        |
| PLA-20 KS      | 56.8±0.9               | 1.0±0.1               | 9.7±0.4        |

3.2. Impact test

Impact strength values of PLA and composites are shown in Figure 1. Additions of KS caused improvement in impact energy of PLA regardless of loading ratios. This finding indicates that PLA gained resistance to suddenly applied load by incorporation of KS. Impact strength of composites increased with the amount of KS up to concentration of 15%. Further addition of KS gave lower impact energy as can be seen from Figure 1. The highest impact strength value was obtained for PLA-15 KS sample. Similar results were reported in the literature that calcite additions had positive effect for impact resistance of polymer composites (Thio et al., 2002; Zuiderduin et al., 2003; Jiang et al., 2007; Gahleitner et al., 2012).

3.3. Hardness test

Shore hardness values of PLA and composites are listed in Table 2. Hardness of neat PLA increased with the addition of KS. Shore hardness of composites improved as the concentration of KS increase in PLA matrix. In other words, KS inclusion caused increase in rigidity of PLA.

Table 2. Hardness test results

| Samples        | Shore (Type D) |
|----------------|----------------|
| PLA            | 50.5           |
| PLA-5 KS       | 51.6           |
| PLA-10 KS      | 53.2           |
| PLA-15 KS      | 54.3           |
3.4. MFR measurements

According to MFR values shown in Figure 2, inclusion of KS caused remarkable increase for MFR value of PLA. MFR values displayed increasing trend with filling ratio of KS. This result revealed that processing applications of KS containing composites can be easily performed due to melt-flow property of PLA not much affected by KS additions. The related studies in the literature support that calcite and similar particle inclusions showed no dramatic changes for melt viscosity of polymers (Ge et al., 2009; Jikan et al., 2009; Kiehl et al., 2012; Tayfun et al., 2017; Kanbur and Tayfun, 2017; Dike and Yilmazer, 2019).

3.5. SEM studies

SEM micro-images of composites are represented in Figure 3. Calcite particles were well-dispersed into PLA matrix at lower filling ratios. Formations of agglomerates were observed for higher concentrations of KS. These findings may cause from the increasing particle-particle interactions with respect to particle-matrix interactions as the amount of KS increases. Relatively more homogeneous dispersion of KS into PLA matrix was found at lower concentrations due to the increase in particle-matrix interactions between PLA and KS phases. Improvement of mechanical properties were related with these observations.

4. Conclusion

In this research study, the effect of calcite addition on the mechanical, melt flow and morphological properties of PLA based composites were investigated. Mechanical test results implied that KS containing composites gave higher tensile strength and impact strength values compared to neat PLA. Additions of KS resulted in slight decrease for elongation of PLA. Tensile modulus of PLA stayed nearly the same after KS inclusions. Hardness of PLA also increased with the increased amount of KS. The optimum concentration of KS was estimated as 15 %wt in the case of mechanical characterization. MFR value of PLA showed slight improvement with the additions of KS. The observation of nearly identical MFR parameters for PLA and KC confirmed that KC additions caused no significant change for processing conditions of PLA based composites. According to SEM analysis, more homogeneous dispersion was observed for composites contain lower amount of KS with
respect to the higher content of KS. Relatively better interactions were reached between calcite and PLA phases at lower filling ratios of KC. Morphological characterizations supported the findings which provided improvement in mechanical properties of composites at 10\%wt and 15\%wt concentrations of KC.

5. References

Alghadi, A.M., Tirkes, S. and Tayfun, U. 2020. “Mechanical, thermo-mechanical and morphological characterization of ABS based composites loaded with perlite mineral”, Material Research Express, 7(1), 015301. DOI: 10.1088/2053-1591/ab551b

Ayaz, M., Ghasemi, F.A., Rahimloo, V.P. and Menbari, S. 2018. “Multi-response optimization of the mechanical properties of PP/talc/CaCO\textsubscript{3} ternary nanocomposites by the response surface methodology combined with desirability function approach”, Journal of Elastomers & Plastics, DOI: 10.1177/0095244318819184

Bajpai, P.K., Singh, I. and Madaan, J. 2012. “Development and characterization of PLA-based green composites: A review”, Journal of Thermoplastic Composite Materials, 27, 52-81. DOI: 10.1177/0892705712439571

Betingytė, V., Žukienė, K., Jankauskaitė, V., Milašienė, D., Mickus, K.V. and Gulbinienė, A., 2012. “Influence of calcium carbonate fillers on the properties of recycled poly (e-caprolactone) based thermoplastic polyurethane”, Materials Science, 18(3), 243-249. DOI: 10.5755/j01.ms.18.3.2433

Bismarck, A., Baltazar, A., Jimenez, Y. and Sarikakis, K. 2006. “Green composites as panacea? Socio-economic aspects of green materials”, Environment, Development and Sustainability, 8(3), 445-463. DOI: 10.1007/s10668-005-8506-5

Brown, T. (1999) “Handbook of Polymer Testing-Physical Methods”, Rapra Technology, Shawbury.

Cacciotti, L., Mori, S., Cherubini, V. and Nanni, F. 2018. “Eco-sustainable systems based on poly(lactic acid), diatomite and coffee grounds extract for food packaging”, International Journal of Biological Macromolecules, 112, 567-575. DOI: 10.1016/j.ijbiomac.2018.02.018

Cho, S.B., Kikuchi, M., Suetsugu, Y. and Tanaka, J. 1997. “Novel calcium phosphate/polylactide composites-its in vitro evaluation”, Key Engineering Materials, 132-136, 802-805. DOI: 10.4028/www.scientific.net/KEM.132-136.802

Demjen, Z., Pukanszky, B. and Nagy, J. 1998. “Evaluation of interfacial interaction in polypropylene surface treated CaCO\textsubscript{3} composites”, Composites Part A: Applied Science and Manufacturing, 29, 323–329. DOI: 10.1016/S1359-835X(97)00032-8

Dike, A.S., Tayfun, U. and Dogan, M. 2017. “Influence of zinc borate on flame retardant and thermal properties of polyurethane elastomer composites containing huntite&hydromagnesite mineral”, Fire and Materials, 41(7), 890-897. DOI: 10.1002/fam.2428

Dike, A.S. and Yilmazer U. 2019. “Improvement of organoclay dispersion into polystyrenebased nanocomposites by incorporation of SBS and maleic anhydride-grafted SBS”, Journal of Thermoplastic Composite Materials, DOI: 10.1177/0892705719882998

Dogan, M. and Bayramli, E. 2009. “Effect of polymer additives and process temperature on the physical properties of bitumen-based composites”, Journal of Applied Polymer Science, 113(4), 2331-2338. DOI: 10.1002/app.30280
Doppalapudi, S., Jain, A., Khan, W. and Domb, A.J., 2014. “Biodegradable polymers-an overview”, *Polymers for Advanced Technologies*, 25(5), 427-435. DOI: 10.1002/pat.3305

Eselini, N., Tirkes, S., Akar, A.O. and Tayfun, U. 2019. “Production and characterization of poly (lactic acid)-based biocomposites filled with basalt fiber and flax fiber hybrid”, *Journal of Elastomers & Plastics*, DOI: 10.1177/00952443198884716

Farah, S., Anderson, D.G. and Langer, R., 2016. “Physical and mechanical properties of PLA, and their functions in widespread applications-A comprehensive review”, *Advanced Drug Delivery Reviews*, 107, 367-392. DOI: 10.1016/j.addr.2016.06.012

Fuad, M.Y.A., Hanim, H., Zarina, R., Ishak, Z.H.M. and Hassan, A. 2010. “Polypropylene/calcium carbonate nanocomposites effects of processing techniques and maleated polypropylene compatibiliser”, *Express Polymer Letters*, 4, 611–620. DOI: 10.3144/expresspolymlett.2010.76

Gahleitner, M., Grein, C. and Bernreitner, K. 2012. “Synergistic mechanical effects of calcite micro- and nanoparticles and β-nucleation in polypropylene copolymers”, *European Polymer Journal*, 48(1), 49-59. DOI: 10.1016/j.europolyjm.2011.10.013

Ge, C., Ding, P., Shi, L. and Fu, J. 2009. “Isothermal crystallization kinetics and melting behavior of poly (ethylene terephthalate)/barite nanocomposites”, *Journal of Polymer Science B Polymer Physics*, 47, 655-668. DOI: 10.1002/polb.21669

Gorna, K., Hund, M., Vucak, M., Grohn, F. and Wegner, G. 2008. “Amorphous calcium carbonate in form of spherical nanosized particles and its application as fillers for polymers”, *Materials Science and Engineering: A*, 477, 217-225. DOI: 10.1016/j.msea.2007.05.045

Hatipoglu, A. and Dike, A.S. 2020. “Effects of concentration and surface silanization of barite on the mechanical and physical properties of poly (lactic acid)/barite composites”, *Polymers and Polymer Composites*, 28(2), 140-148. DOI: 10.1177/0967391119883083

Hottle, T.A., Bilec, M.M. and Landis, A.E., 2013. “Sustainability assessments of bio-based polymers”, *Polymer Degradation and Stability*, 98(9), 1898-1907. DOI: 10.1016/j.polymdegradstab.2013.06.016

Isitman, N.A., Dogan, M., Bayramli, E. and Kaynak, C. 2011. “Fire retardant properties of intumescent polypropylene composites filled with calcium carbonate”, *Polymer Engineering and Science*, 51(5), 875-883. DOI: 10.1002/pen.21901

Jerzy, W. (1993) “Fillers”, *Chem Tech Publishing*, Toronto.

Jiang, L., Zhang, J. and Wolcott, M.P. 2007. “Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: reinforcing effects and toughening mechanisms”, *Polymer*, 48, 7632-7644. DOI: 10.1016/j.polymer.2007.11.001

Jikan, S.S., Samsudin, M.S.F., Ariff, Z.M., Ishak, Z.A.M. and Ariffin, A. 2009. “Relationship of rheological study with morphological characteristics of multicomponent (talc and calcium carbonate) filled polypropylene hybrid composites”, *Journal of Reinforced Plastics and Composites*, 28(21), 2577-2587. DOI: 10.1177/0731684408092440

Kanbur, Y. and Tayfun, U. 2017. “Mechanical, physical and morphological properties of polypropylene/huntite composites”, *Sakarya University Journal of Science*, 21(5), 1045-1050. DOI: 10.16984/saufenbilder.281035
Preparation and Characterization of Calcite Loaded Poly (Lactic Acid) Composite Materials

Kanbur, Y. and Tayfun, U. 2018. “Mechanical, physical and morphological properties of acidic and basic pumice containing polypropylene composites”, Sakarya University Journal of Science, 22(2), 333-339. DOI: 10.16984/saufenbilder.287861

Kasuga, T., Maeda, H., Kato, K., Nogami, M., Hata, K.I. and Ueda, M. 2003. “Preparation of poly (lactic acid) composites containing calcium carbonate (vaterite)”, Biomaterials, 24(19), 3247-3253. DOI: 10.1016/S0142-9612(03)00190-X

Kiehl, J., Huser, J., Bistac, S., & Delaite, C. (2012). “Influence of fillers content on the viscosity of unsaturated polyester resin/calcium carbonate blends”, Journal of Composite Materials, 46(16), 1937-1942. DOI: 10.1177/0021998311427780

Lezak, E., Kulinski, Z. Masirek, R. Piorkowska, E. Pracella, M. and Gadzinowska, K. 2008. “Mechanical and thermal properties of green polylactide composites with natural fillers”, Macromolecular Bioscience, 8, 1190-1200. DOI: 10.1002/mabi.200800040

Liang J.Z. 2013. “Reinforcement and quantitative description of inorganic particulate-filled polymer composites”, Composites Part B: Engineering, 51, 224-232. DOI: 10.1016/j.compositesb.2013.03.019

Maeda, H. Kasuga, T., Nogami, M., Hibino, Y., Hata, K., Ueda, M. and Ota, Y. 2002. “Biomimetic apatite formation on poly (lactic acid) composites containing calcium carbonates”, Journal of Materials Research, 17, 727-730. DOI: 10.1557/JMR.2002.0104

Maeda, H. Kasuga, T. Nogami, M. Hibino, Y. Hata, K. Ueda, M. and Ota Y. 2002. “Preparation of bioactive polylactic acid composites containing calcium carbonates”, Key Engineering Materials, 240-242, 163-166. DOI: 10.4028/www.scientific.net/KEM.240-242.163

Mann, G.S., Singh, L.P., Kumar, P. and Singh, S. 2018. “Green composites: A review of processing technologies and recent applications”, Journal of Thermoplastic Composite Materials, DOI: 10.1177/0892705718816354

Mat, N.S.C., Ismail, H. and Othman, N. 2017. “Curing characteristics and mechanical and aging properties of ethylene propylene diene monomer/calcium carbonate/bentonite hybrid composites”, Journal of Elastomers & Plastics, 49(5), 397–407. DOI: 10.1177/0095244316663812

Metin, D., Tihminhoglu, F., Balkose, D. and Ulku, S. 2004. “The effect of interfacial interactions on the mechanical properties of polypropylene/natural zeolite composites”, Composites Part A: Applied Science and Manufacturing, 35(1), 23-32. DOI: 10.1016/j.compositesa.2003.09.021

Murariu, M. and Dubois, P. 2016. “PLA composites: From production to properties”, Advanced Drug Delivery Reviews, 107, 17-46. DOI: 10.1016/j.addr.2016.04.003

Ozen, I. and Simsek, S. 2016. “Effect of stretching temperature on breathability and waterproofness properties of polyethylene films containing different calcium carbonates”, Journal of Plastic Film & Sheeting, 32(4), 380–401. DOI: 10.1177/8756087915597025

Piekarska, K., Sowinski, P., Piorkowska, E., Haque, M.M.U. and Pracella, M. 2016. “Structure and properties of hybrid PLA nanocomposites with inorganic nanofillers and cellulose fibers”, Composites Part A: Applied Science and Manufacturing, 82, 34-41. DOI: 10.1016/j.compositesa.2015.11.019

Piekarska, K., Piorkowska, E. and Bojda, J., 2017. “The influence of matrix crystallinity, filler grain size and modification on properties of PLA/calcium carbonate composites”, 169
Preparation and Characterization of Calcite Loaded Poly (Lactic Acid) Composite Materials

Polymer Testing, 62, 203-209. DOI: 10.1016/j.polymertesting.2017.06.025

Piorkowska, E. (2019). “Overview of Biobased Polymers”, In: “Advances in Polymer Science”, Springer, Berlin, Heidelberg. DOI: 10.1007/12_2019_52

Rasal, R.M., Janorkar, A.V. and Hirt, D.E. 2010. “Poly (lactic acid) modifications”, Progress in Polymer Science, 35, 338-356. DOI: 10.1016/j.progpolymsci.2009.12.003

Ren, J. (2011). “Biodegradable poly (lactic acid): Synthesis, modification, processing and applications”, Springer, Verlag.

Rothon, R.N. (2003). “Particulate-filled polymer composites”, 2nd Edition, Rapra Technology Limited, UK.

Tayfun, U. 2006 “Effects of fillers on morphological, mechanical, flow and thermal properties of bituminous composites”, MSc Thesis, Middle East Technical University Graduate School of Natural and Applied Sciences, Ankara, 54.

Tayfun, U. and Dogan, M. 2016. “Improvement the dyeability of poly (lactic acid) fiber using organoclay during melt spinning”, Polymer Bulletin, 73(6), 1581-1593. DOI: 10.1007/s00289-015-1564-4

Tayfun, U., Dogan, M. and Bayramli, E. 2017. “Polyurethane elastomer as a matrix material for short carbon fiber reinforced thermoplastics”, Anatolu University Journal of Science and Technology A - Applied Sciences and Engineering, 18(3), 682-694. DOI: 10.18038/aubtda.271011

Theberge, J.E. 1982. “Mineral reinforced thermoplastic composites”, Journal of Elastomers & Plastics, 14(2), 100-108. DOI: 10.1177/009524438201400202

Thio, Y.S., Argon, A.S. and Cohen, R.E. 2002. “Toughening of isotactic polypropylene with CaCO3 particles”, Polymer, 43: 3661-3674. DOI: 10.1016/S0032-3861(02)00193-3

Tian, H.Y. and Tagaya, H. 2007. “Preparation, characterization and mechanical properties of the polylactide/perlite and the polylactide/montmorillonite composites”, Journal of Material Science, 42, 3244-3250. DOI: 10.1007/s10853-006-0230-5

Vishu, S. (1998) “Handbook of Plastic Testing Technology”, Second Edition, Wiley-Interscience Publication, Germany.

Wake, W.C. (1971) “Fillers for Plastics”, Iliffe for the Plastics Institute, London.

Weber, C.J., Hauaggaard, V., Festersen, R. and Bertelsen, G. 2002. “Production and applications of biobased packaging materials for the food industry”, Food Additives & Contaminants, 19, 172-177. DOI: 10.1080/02652030110087483

Xanthos, M. (2005). “Functional fillers for plastics”, Wiley VCH, Weinheim.

Yang, K., Yang, Q., Li, G., Sun, Y. and Feng, D., 2006. “Morphology and mechanical properties of polypropylene/calcium carbonate nanocomposites”, Materials Letters, 60(6), 805-809. DOI: 10.1002/app.10789

Yıldızhan, Ş., Çalık, A., Özcanlı, M. and Serin, H. 2018. “Bio-composite materials: a short review of recent trends, mechanical and chemical properties, and applications”, European Mechanical Science, 2(3), 83-91. DOI: 10.26701/ems.369005

Zhitong, Y., Meisheng, X., Liugin, G., Tao, C., Haiyan, L. and Ying, Y. 2014. “Mechanical and thermal properties of polypropylene (PP) composites filled with CaCO3 and shell-waste derived bio-fillers”, Fibers and Polymers, 15, 1278-1287. DOI: 10.1007/s12221-014-1278-5

Zuiderduin, W.C.J., Westzaan, C., Huetink J. and Gaymans, R.J. 2003. “Toughening of
polypropylene with calcium carbonate particles”, *Polymer*, 44, 261–275. DOI: 10.1016/S0032-3861(02)00769-3