# EFFECT OF THE MARBLE POWDER AND WOOD POWDER CONTENT ON THE TECHNOLOGICAL PROPERTIES OF THERMOPLASTIC COMPOSITES

Prof.Dr. Dundar T., Prof.Dr. Ayrilmis N., Ph.D. Student Akkus M., Ph.D. Ulay G.

Department of Wood Mechanics and Technology, Forestry Faculty, Istanbul University, Bahcekoy, Sariyer, 34473, Istanbul, Turkey

dundar@istanbul.edu.tr, nadiray@istanbul.edu.tr, memis.akkus@istanbul.edu.tr,

***Abstract:*** The waste powder produced during the manufacture of marble, which is presently mostly discarded in landfills, has the potential for higher-valued usage. Recycling marble waste powder will contribute to the protection of nature as well as economic gain. The goal of this study is to investigate the potential use of marble waste powder as filler in the thermoplastic composites with wood. Thermoplastic composites were manufactured by adding marble factory waste powder and wood powder in different ratios to polypropylene (PP). Maleic anhydride grafted polypropylene (MAPP) were used as coupling agent to improve interfacial adhesion between hydrophilic wood–fibers and hydrophobic polypropylene. The waste marble powder and wood powder were mixed by weight of with polypropylene in the percentage of 0%, 10%, 20%, 30%, 40%, and 50%. Physical and mechanical tests were performed on the specimens prepared from the thermoplastic composites. Although mechanical properties of the composites decreased with increasing content of the marble powder, the water absorption of the composites significantly decreased with increasing content of the marble powder.

***KEYWORDS:*** THERMOPLASTIC COMPOSITES, TECHNOLOGICAL PROPERTIES, WOOD POWDER, MARBLE POWDER,

## 1. Introduction

Studies of polymer composites mixing with organic or inorganic fillers have steadily increased due to the advantages of the fillers in economic and environmental aspects. Organic wood fibers have characteristics of low density, biodegradability, and sustainable productivity [1, 2], and inorganic fillers have attracted great attention because of their cost efficiency, abundance [3]. The fillers (organic or inorganic materials) generally increase stiffness, strength, and hardness of polymer composites by hybridization [4, 5, 6]. Inorganic and organic fillers have long been considered as a future candidate to replace glass fiber or carbon fiber in thermoplastic composites, and thus, it can help resolving environmental issues and taking economic advantage over those artificial fibers [7].

Marble, used frequently in construction applications, is utilized by an industry that produces a significant amount of solid waste during the cutting process. Recycling the marble powder produced during cutting is an important issue because of the current development of environmental awareness and costs for filler [8]. It is estimated that approximately 2.2 million tons of marble blocks are processed in Turkey annually, of which 660,000 tons of marble powder is thrown out without being recycled. If that potential material is evaluated in industry, it is provided significant gains to the economy [9]. The unused marble powders have significant effects, not only economically, but environmentally as well. The large number of marble processing facilities in the world is the cause of the intensification of marble waste areas, which negatively affect the environment and natural beauty, especially in the regions where these facilities are located [10].

When studies on the economic use of marble wastes were examined, it was observed that they reported on the construction sector in general, such as using marble powder wastes in filler processes, the manufacture of light construction blocks, improving floors with marble powder, and as an additive substance in the manufacture of cement [9, 11, 12, 13, 14, 15, 16, 17]. Excluding the use of wastes from marble processing facilities as construction materials, it was observed that they are used as powder wastes reduced to different dimensions as a raw material decoration in architecture, a filler material, and as an additive substance for agricultural purposes [18, 19].

The use of organic wastes of wood industry and agricultural industry as an additive substance in the manufacture of thermoplastic composites has drawn a lot of attention in recent years. In previous studies, in addition to waste wood fibers, some other natural fibers such as kenaf [20], jute [21], sisal [22], flax [23], hemp [24], coir [25], pine cones [26], walnut shell [27], and sunflower stalk [28] have been investigated, and positive results have been obtained. Altough some inorganic fillers such as talc [29], kaolin [7], clay [30], boron-nitride [31], and zinc-borate [32] have widely been adopted in thermoplastic composites with wood fiber, to our knowledge, there are no reports on the utilization of marble waste powders as a filler in thermoplastic composites.

The objective of this study was the manufacture of thermoplastic composites by adding marble powder and wood powder in different ratios to polypropylene and studying their physical and mechanical properties. We aimed to investigate the effect of marble powder content on the density, water resistance and mechanical properties of the thermoplastic composites.

## 2. Materials and methods

### 2.1. Materials

The waste marble powder were obtained from the collected liquid precipitation ponds at a factory manufacturing travertine marble powders in Denizli, Turkey. The technical compositions of the travertine marble are given in Table 1. The marble powders were passed through a mesh screen and retained on a 0.25-mm mesh screen (Fig.1). The marble powders were then oven-dried to a moisture content of 0 to 1% using a laboratory oven at 100 °C for 48 h, and then stored in a sealed container.

Wood particles were obtained from beech ((*Pinus nigra* Arnold var. *pallasiana*, oven-dry$q$ = 0.490 g/cm$^3$) lumbers by using laboratory type disc chipper with three knives. The moisture content of the wood particles, as determined by oven-dry weight, was found to be 40–50% prior to the treatment. The wood particles were ground in a laboratory *Wiley*grinder. The wood powder passing through a US 35-mesh screen was retained by a US 80-mesh size. The wood powder was dried in a laboratory oven at 102 °C for 24-h to a moisture content of 0–1% based on the oven-dry weight of wood ant then stored in a polyethylene bag.

Polypropylene (PP) (melting temperature = 160°C, density = 0.9 g/cm$^3$, melt flow index at 230°C and 2.16 kg = 6.5 g/10 min) produced by Petkim Petrochemical Co. (Izmir, Turkey) was used as the polymeric material. MAH-grafted PP [MAPP-OPTIM-415 with the reactive modifier MAH (MAH content = 1 wt %)] was supplied by Pluss Polymers Pvt., Ltd. (New Delhi, India).

***Table 1.*** *Technical Properties of the Marble (Test report of Demirkayalar Marble Company, Denizli, Turkey, 2009).*

| Property | Unit | Travertine Marble |
|---|---|---|
| Hardness | Mohs | 3 to 3.5 |
| Unit Weight | g/cm$^3$ | 2.44 |
| Density | g/cm$^3$ | 2.66 |
| Particle Size | µm | <250 |
| Water Absorption in Atmospheric Pressure | By weight (%) | 1.62 |
| Water Absorption Under Pressure | By weight (%) | 3.94 |
| Porosity | % | 3.94 |
| Compressive Strength | N/mm$^2$ | 54.4 |
| Compressive Strength After Freezing | N/mm$^2$ | 50.8 |
| Degree of Pores | % | 3.94 |
| $SiO_2$ | % | 1.91 |
| $F_2O_3$ | % | 79.10 |
| MgO | % | 1.15 |
| CaO | % | 2.43 |

***Fig. 1.*** *Waste marble powder*

### *2.2. Composite Manufacturing*

The marble powder, wood powder, PP, and MAPP granulates were pre-blended in a mixer and then processed in a 30- mm conical, co-rotating, twin-screw extruder (Aysa Instrument Com., Istanbul, Turkey) with a length to diameter ratio of 30 : 1. The raw materials were fed into the main feed throat with a gravimetric feed system. The barrel temperatures of the extruder were controlled at 170, 180, 190, and 190°C for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200°C. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were stored in a sealed container and then dried for about 3–4 h before they were injection-molded. The temperature used for the injection-molded samples was 170–190°C from the feed zone to the die zone. The WPC samples were injected at an injection pressure between 45 and 50 kg/m² with a cooling time of about 30 s. Finally, the samples were conditioned at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5% according to ASTM D 618-08.12. The formulations of the composites are given in Table 2.

### *2.3. Mechanical properties*

The flexural properties, modulus of rupture (MOR), and modulus of elasticity (MOE) were measured in three-point bending tests with a standard material testing system at a crosshead speed of 1.3 mm/min in accordance with ASTM D 790-03. The MOR and MOE values of the samples with dimensions of 127 × 12.7 × 3.2 (thickness) mm$^3$ were determined at ambient conditions of 23 ± 2°C and 50 ± 5% relative humidity according to ASTM D 618-08. The tensile tests were conducted according to the ASTM D 638. Tensile specimens [dogbone shape (Type III)] were tested with a crosshead speed of 5 mm/min in accordance with ASTM D 638. Seven specimens were tested for the tensile and flexural properties of each composite formulation.

***Table 2:*** *The raw material formulations of the WPCs.*

| WPC code | Wood powder (%wt) | Marbel powder (%wt) | Polypropylene (PP) (wt%) | MAPP ( wt%) |
|---|---|---|---|---|
| A | 50 | 0 | 47 | 3 |
| B | 40 | 10 | 47 | 3 |
| C | 30 | 20 | 47 | 3 |
| D | 20 | 30 | 47 | 3 |
| E | 10 | 40 | 47 | 3 |
| F | 0 | 50 | 47 | 3 |

### *2.4. Water resistance*

Thickness swelling (TS) and water absorption (WA) tests were carried out according to ASTM D 570-05 specifications. The test samples were in the form of disks 50.8 mm in diameter and 3.2 mm in thickness. Ten replicate samples were tested for each WPC formulation. The conditioned samples were placed in a container of distilled water maintained at a temperature of 23 ±1°C. The weights and thicknesses of the samples were measured at different time intervals during the long period of immersion. At the end of 24, 168 (7 days), and 672 (28 days) h of submersion, the samples were removed from the water one at a time, all surface water was wiped off with a dry cloth, and the samples were weighed to the nearest 0.001 g and measured to the nearest 0.001 mm immediately. The value of WA as a percentage was calculated as follows:

$$WA\ (t) = \frac{W(t) - W_0}{W_0} \times 100$$

The value of the TS as a percentage was calculated as follows:

$$TS\ (t) = \frac{T(t) - T_0}{T_0} \times 100$$

where TS(t) is the thickness swelling at time t (%), $T_0$ is the initial thickness of the sample, and T(t) is the thickness at time t. The density of the sample was measured on the TS sample.

## *3. Result and discussion*

### *3.1. Mechanical properties*

The mechanical properties of the WPCs are presented in Table 3. The MOR of the WPCs decreased with increasing content of the marble powder. In particulare, the MOR more decreased as the amount of marble powder was above 30 wt% (Figure 2). The addition of 10 wt% marble powder improved the MOE considerably. Further incerement in the marble content up to 50 wt% decreased the MOE of the composites but still it was higher than that of the control group without marble powder (Table 3, Figure 3).

***Table 3:*** *The results of the mechanical properties of the composites.*

| WPC code | MOR (N/mm²) | MOE (N/mm²) | Tensile Strength (N/mm²) | Tensile Modulus (N/mm²) |
|---|---|---|---|---|
| A | 55,3 | 3616,0 | 31,0 | 3842,3 |
| | (3,49)* | (648,16) | (3,39) | (159,08) |
| B | 55,0 | 4843,2 | 29,4 | 3800,3 |
| | (0,93) | (514,06) | (1,34) | (87,38) |
| C | 54,0 | 4763,3 | 28,9 | 3622,8 |

| | | | | |
|---|---|---|---|---|
| | (2,36) | (645,10) | (0,95) | (241,24) |
| D | 52,0 | 4549,1 | 22,8 | 3218,0 |
| | (0,76) | (743,09) | (2,26) | (193,52) |
| E | 45,2 | 3965,1 | 21,2 | 2863,9 |
| | (2,44) | (610,99) | (1,52) | (247,95) |
| F | 44,8 | 3813,5 | 20,0 | 2755,0 |
| | (1,18) | (743,82) | (1,81) | (220,00) |

* Standard deviations

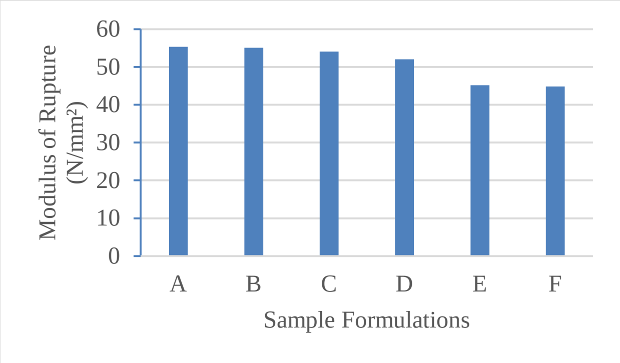


***Fig. 2:*** *The MOR of the composites*

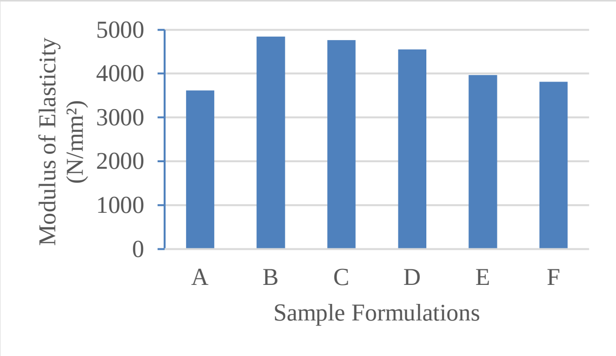


***Fig. 3:*** *The MOE of the composites*

The tensile strength and tensile modulus of the composites are shown in Figures 4 and 5, respectively. As increased the marble content of composites, both the tensile strength and the tensile modulus decreased. Specifically, as the amount of marble content was above 20 wt%, the tensile strength and modulus decreased remarkable when compared to the composites having 20 wt% and below. The decreament ratio in the tensile strength was more pronounced than the decreament ratio in the tensile modulus.

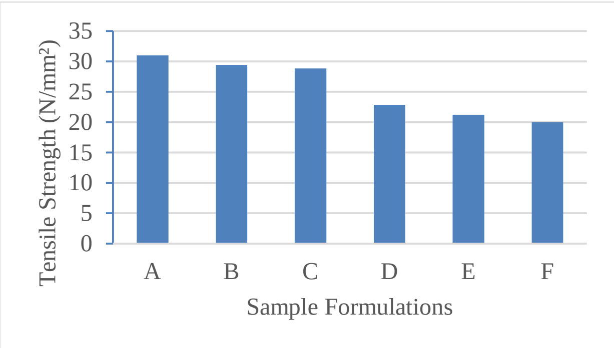


***Fig. 4:*** *The tensile strength of the composites*

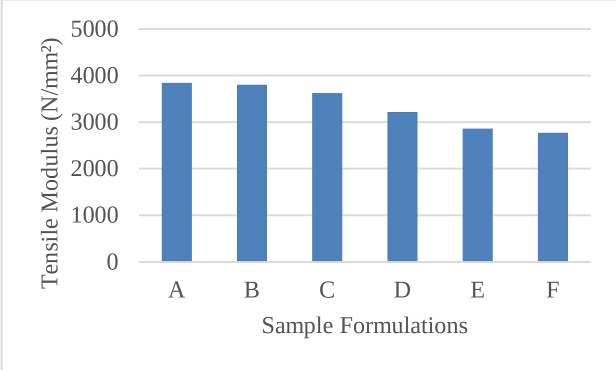


***Fig. 5:*** *The tensile modulus of the composites*

### *3.2. Water resistance*

The results of water resistance are presented in Table 4. In general, the water absorption and thickness swelling decreased with increasing amount of the marbel powder and decreasing amount of wood powder (Table 4, Figures 6 and 7). The water absorption and thickness swelling of composites sharply decreased when the amount of marble content reached to 30 wt%. The highest water absorption and thickness swelling values were found in the specimens produced with 50 wt% wood powder while the lowest values were found in the specimens produced with 50 wt% marble powder as seen Figures 6 and 7.

***Table 4:*** *The results of water reistance of the composites.*

| WPC code | Water Absorption (%) | | | Thickness Swelling (%) | | |
|---|---|---|---|---|---|---|
| | One day | One week | Four week | One day | One week | Four week |
| A | 0,21 | 0,56 | 1,30 | 0,40 | 0,85 | 1,53 |
| | (0,08)* | (0,08) | (0,15) | (0,18) | (0,25) | (0,35) |
| B | 0,19 | 0,47 | 1,24 | 0,30 | 0,66 | 1,45 |
| | (0,03) | (0,08) | (0,16) | (0,12) | (0,17) | (0,23) |
| C | 0,17 | 0,47 | 1,10 | 0,26 | 0,63 | 1,43 |
| | (0,07) | (0,08) | (0,14) | (0,08) | (0,14) | (0,18) |
| D | 0,12 | 0,32 | 0,65 | 0,24 | 0,58 | 0,93 |
| | (0,05) | (0,14) | (0,16) | (0,10) | (0,14) | (0,22) |
| E | 0,11 | 0,18 | 0,25 | 0,19 | 0,35 | 0,64 |
| | (0,09) | (0,06) | (0,08) | (0,06) | (0,13) | (0,23) |
| F | 0,09 | 0,09 | 0,14 | 0,13 | 0,22 | 0,42 |
| | (0,06) | (0,05) | (0,05) | (0,07) | (0,13) | (0,22) |

* Standard deviations

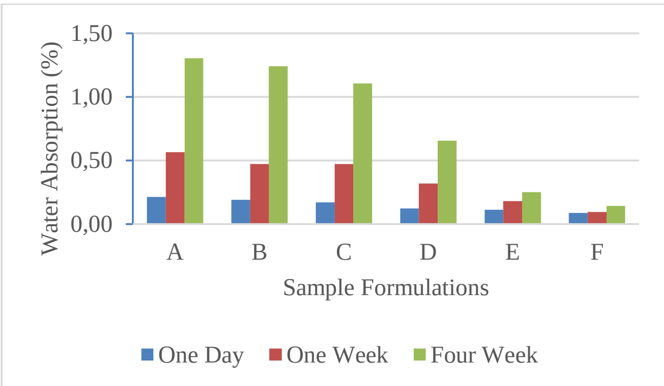


***Fig. 6:*** *The water absorption ratios of the composites*

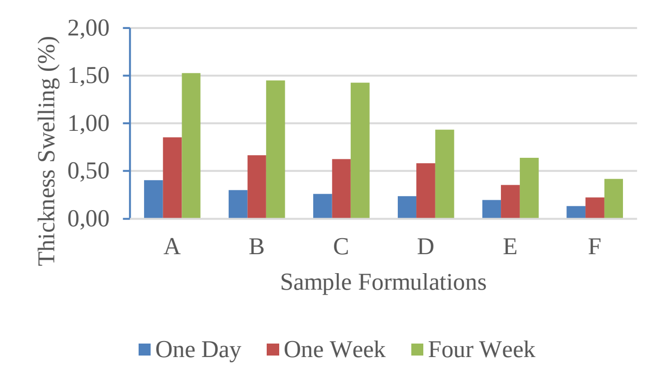


***Fig. 7:*** *The thickness swelling ratios of the composites*

## 4. Conclusions

The results of the research revealed that the increase in the amount of the marble powder in the composites had a negative effect on the mechanical properties of the composites while the increase in the amount of the wood powder had a positve effect. One exception of this was observed in the MOE values where the MOE of composites improved considerably with the addition of 10 wt% marble powder and then decreased again with the further incerement in the marble content up to 50 wt%. The decrease in the mechanical properties of composites was more remarkable when the marble content in the composites was over than 20 wt%. The water absorption and thickness swelling decreased with increasing amount of the marbel powder and decreasing amount of wood powder.

## 5. Acknowledgement

This work was supported by Research Fund of the Istanbul University. Project number: BEK-20082. The authors wish to acknowledge Research Fund of the Istanbul University for financial support.

## 6. References

[1] Pickering KL, Abdalla A, Ji C, McDonald AG and Franich RA. 2003. The effect of silane coupling agents on radiata pine fibre for use in thermoplastic matrix composites. Composites Part A: Applied Science and Manufacturing 34: 915–926.
[2] Valadez-Gonzaleza A, Cervantes-Uc JM, Olayo R and Herrera-Franco PJ. 1999. Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. Composites Part B: Engineering 30: 309–320.
[3] Lubomir Lapcik J, Jindrova P, Lapcikova B, Tamblyn R, Greenwood R and Rowson N. 2008. Effect of the talc filler content on the mechanical properties of polypropylene composites. Journal of Applied Polymer Science 110: 2742–2747.
[4] Gwon JG, Lee SY, Chun SJ, Doh GH and Kim JH. 2010. Effect of chemical treatments of wood fibers on the physical strength of polypropylene based composites. Korean Journal of Chemical Engineering 27(2): 651–657.
[5] Bakar MBA, Leong YW, Ariffin A and Ishak ZAM 2008. Effect of chemical treatments on the mechanical, flow, and morphological properties of talc- and kaolin-filled polypropylene hybrid composites. Journal of Applied Polymer Science 110: 2770–2779.
[6] Faruk O, Bledzki AK and Matuana LM, 2007. Microcellular foamed wood–plastic composites by different processes: a review. Macromolecular Materials Engineering 292: 113–127.
[7] Gwon JG, Lee SY, Chun SJ, Doh GH and Jung Kim H, 2011. Physical and mechanical properties of wood–plastic composites hybridized with inorganic fillers. Journal of Composite Materials 0(0) 1–7.
[8] Bilensoy, M, 2010. *Utilization of the Marble Factory Powder Wastes*, M.S. thesis, Institute of Sciences, Eskişehir Osmangazi University, Eskişehir (in Turkish).
[9] Bilgin, N, 2010. *The Use of Marble Powder Wastes in the Manufacture of Construction Materials*, M.S. thesis, Institute of Sciences, Yildiz Technical University, Istanbul (in Turkish).
[10] Şentürk A, Gündüz L, Tosun Yİ, and Sarıışık A, 1996. *Marble Technology*, Tuğra Yayıncılık, Isparta (in Turkish).
[11] Khristova Y, and Aniskevich K, 1994. Prediction of creep of the epoxy resin filled with marble flour. Mechanics Composite Materials 30(5): 426-432.
[12] Ali M M, Agarwal SK, Solankey AK, and Handoo SK, 2000. High-performance, marble-like plaster coatings. Cement and Concrete Research 30(6): 977-980.
[13] Garcia J, Mallol C, Bou E, Silva G, Fernandez J, Molina A, and Romera J, 2003. Recycling marble working wastes in manufacturing ceramic products. CFI Ceramic Forum International 80(E): 84-90.
[14] Zorluer I, and Usta M, 2003. Improvement of floors with marble powder. *Proceedings of* the *Fourth National Marble Symposium* (*MERSEM '2003)*, Afyonkarahisar, pp. 305-311 (in Turkish).
[15] Agarwal SK, and Gulati D, 2006. Utilization of industrial wastes and unprocessed micro-fillers for making cost effective mortars. Construction and Building Materials 20(10): 999-1004.
[16] Tanyıldızı H, and Coşkun A, 2011. Investigation of compressive strength and ultrasonic pulse velocity properties of lightweight concrete containing rosso levanto marble in Elazığ. Erciyes University Journal of the Institute of Science and Technology 27(2): 150-154 (in Turkish).
[17] Erdem R T, and Öztürk AU, 2012. Effect of marble powder additive on freezing-thawing properties of cement mortar. Bulent Ecevit University Journal of Science 1(2): 85-91 (in Turkish).
[18] Gündüz L, and Şentürk A, 1996. Utilizability of marble wastes aimed at stabilization in mining enterprises. *Proceedings of I. National Aggregate Symposium*, Chamber of Mining Engineers of Turkey, Istanbul, pp. 125-138 (in Turkish).
[19] Demirel B, and Yazıcıoğlu S, 2010. The impact on mechanical properties of concrete of the waste marble powder used as a fine material. *International Sustainable Buildings Symposium*, Ankara, 26-28 May, pp. 173-176 (in Turkish).
[20] Chow P, Lambert RJ, Bowers CT, McKenzie N, Youngquist JA, Muehl JH, and Kryzsik AM, 2000. Proceedings of the 2000 International Kenaf Symposium, p.139, 2000.
[21] Rahman R, Hasan M, Huque M, and Islam N, 2010. Physico-Mechanical Properties of Jute Fiber Reinforced Polypropylene Composites. J. Reinfor. Plast. Compos. 29, 445.
[22] Joseph P V, Mathew G, Joseph K, Thomas S, and Pradeep P, 2003. Mechanical properties of short sisal fiber-reinforced polypropylene composites: Comparison of experimental data with theoretical predictions. J. Appl. Polym. Sci., 88, 602.
[23] Arbelaiz A, Cantero BG, Llano-Ponte R, Valea A, and Mondragon I, 2005. Compos. Part A-Appl. S., 36, 1637.
[24] A. Schirp and J. Stender, 2010. Eur. J. Wood Prod., 68, 219.
[25] Ayrilmis N, Jarusombuti S, Fueangvivat V, Bauchongkol P, and White RH, 2011. Coir fiber reinforced polypropylene composite panel for automotive interior applications. Fibers and Polymers 12 (7): 919-926.
[26] Ayrilmis N, Buyuksari U, and Dundar T, 2010. Waste pine cones as a source of reinforcing fillers for thermoplastic composites. Journal of Applied Polymer Science 117 (4): 2324-2330.
[27] Ayrilmiş N, Kaymakci A, Ozdemir F, 2013. Physical, mechanical, and thermal properties of polypropylene composites filled with walnut shell flour. Journal of Industrial and Engineering Chemistry 19(3):908–914.
[28] Kaymakci A, Ayrilmis N, and Gulec T, 2013. Surface Properties and Hardness of Polypropylene Composites Filled With Sunflower Stalk Flour. BioResources 8 (1): 592-602.
[29] Lee SY, Kang IA, Yoon HG, Park BD, and Wu Q, 2008. Thermal and Mechanical Properties of Wood Flour/Talc-filled Polylactic Acid Composites: Effect of Filler Content and Coupling Treatment. Journal of Thermoplastic Composite Materials 21 (3): 209-223.
[30] Yeh SK, Mulla AA, and Gupta RK, 2005. ANTEC, Society of Plastic Engineers, Brookfield, CT.
[31] Ayrilmis N, Dundar T, Kaymakci A, Ozdemir F, and Kwon JH, 2014. Mechanical and Thermal Properties of Wood-Plastic Composites Reinforced With Hexagonal Boron Nitride. Polymer Composites 35 (1).
[32] Tascioglu C, Yoshimura T, Tsunoda K, 2013. Biological performance of wood–plastic composites containing zinc borate: Laboratory and 3-year field test results. Composites: Part B 51: 185–190.