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# Physical and thermal properties of injection molded HDPE based composites reinforced with waste tire powder and red pine wood wastes

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**Abstract:** The number of vehicles produced is increasing day by day with developing technology and population growth. Parallel to this, the numbers of tires are also increasing. The tires have ten years lifetime without using. Life expectancy of tires on use reduces less than 5 years. There will be great amount of waste tires in the future. In this study, waste tire powder was used as filler in the manufacturing of HDPE based wood-plastic composites. Waste tire micronized powder (WTP) was used as received from the plant. Retained on 200 mesh size sieve red pine wood wastes flour (RPWF) was also used as lignocellulosic filler. High-density polyethylene (HDPE) was pulverized in Pulverizator with cooling capabilities into the flour form. Maleic anhydrite grafted polyethylene (MAPE) and paraffin wax were utilized as coupling agents and a lubricant, respectively. The blends included HDPE, WTP, RPWF, MAPE and wax were compounded in a single-screw extruder at 40 rpm screw speed in the temperatures of 170-200 °C. After extruded blends were injection molded using an HDX-88 Injection Molding Machine (pressure: 100bar; injection speed: 80mm/sec; screw speed: 40rpm) to produce standard test samples. Water absorption, thickness swelling and thermal (TGA and DSC) properties of produced composites was investigated. With the addition of RPWF, water absorption and thickness swelling properties were increased. In addition, tensile properties, flexural properties, impact properties, harness properties, density and morphology of composites were determined in our previous study. Density of composites increased with addition of both fillers.
**Keywords**: HDPE, Waste tire powder, Red pine wood wastes, Thermal and physical properties, Injection molded

## 1. Introduction

About 318.4 million tires were produced in The United States in 2016 (Rubber Manufactures Association (RMA), 2017). At the end of December 2014, there are 18 million 828 thousand 721 vehicles on roads (Turkish Statistical Institute Report, 2015). The number of vehicles produced is increasing day by day with developing technology and population growth and as well as the number of tires are also increasing. The tires have ten years lifetime without using. With using that time reduces less than 5 years. It was reported that there was 10 million of waste tires all over the Brazil (Marques et all, 2008). Inaddition, approximately, 25.918 tons of the scrap tires are generated for a year in Algeria (Bekhiti et al., 2014). According to The Ministry of Environment and Urbanization of Turkey, 315.000 tons of waste tires were sold in renovation market in 2015 (LASDER, 2017). There will be occurred great resource for waste tires. However, most of the wastes are burned or abandoned to nature. These methods causes to some environmental problems such as air pollution. There are also some uses for waste tires such as into tire-derived fuel, used by the civil engineering applications, recycled by the ground rubber applications, land disposed and etc. (Lin et all, 2008). That great resource can be utilized in the production of lignocellulosic polymer composites as a filler material.

In previous studies, polystyrene (PS), polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), etc. as thermoplastic materials and wood flour, agricultural residue and industrial lignocellulosic waste were used in polymeric composites. In previous studies, 40-80 mesh size lignocellulosic materials were used by researchers (Karakuş, 2008; Mengeloglu and Kabakcı, 2008; Dönmez Cavdar, 2011; Avcı, 2012; Acar, 2014). Red pine wood wastes flour (RPWF) is also great resource for lignocellulosic material and it might be utilized in production of wood composite materials.

In this study, RPWF and WTP were used as filling material in pulverized high-density polyethylene-based thermoplastic composites. Thermal and physical properties of the produced composite were determined.

## 2. Materials and methods

### *2.1. Materials*

High-density polyethylene (HDPE) was pulverized in Pulverizator with cooling capabilities into the flour form. Pulverized high-density polyethylene (HDPE) was used as thermoplastic matrix and red pine wood wastes flour (RPWF) and waste tire powder (polybutadiene)(WTP) were used as fillers. Waste tire powder (WTP) was used as received from the plant. The plant was manufactured four different size of WTP (micronized powder, 0-1mm, 1-3 mm and 3-4 mm). Micronized waste tire powder was used for this study. Red pine wood wastes flours (RPWF) were screened and retained on 200 mesh size sieve were used. Maleic anhydrite grafted polyethylene (Licocene PEMA 4351 by Clarient) was utilized as coupling agents.

Paraffin wax (K.130.1000) was used as a lubricant. RPWF were collected from timber plant in the city of Kahramanmaraş, and also waste tire powder (WTP) was obtained from the ORBAY PLASTIK KAUÇUK GERİDÖNÜŞÜM SANAYI in the city of İzmir, TURKEY.

*2.2. Methods*

*2.2.1. Composite manufacturing*

The experimental design of the study was presented Table 1. Depending on the formulation given HDPE, RPWF, WTP, MAPE and paraffin wax were dry-mixed in a high-intensity mixer to produce a homogeneous blend. These blends were compounded in a single-screw extruder at 40 rpm screw speed in the temperatures (barrel to die) of 170-180-185-190-200 °C. Extruded samples were cooled in water pool and then granulated into pellets. The pellets were dried in oven at 103 °C (±2) for 24 hours. Dried pellets were injection molded using an HDX-88 Injection Molding Machine (pressure: 100bar; injection speed: 80mm/sec; screw speed: 40rpm) to produce standard test samples.

Table 1. Manufacture schedule

| ID | Pulverized HDPE (%) | RPWF (%) | WTP (%) | MAPE (%) | WAX (%) |
|---|---|---|---|---|---|
| TP 1 | 94.0 | 0 | 0.0 | 3.0 | 3.0 |
| TP 2 | 86.5 | 0 | 7.5 | 3.0 | 3.0 |
| TP 3 | 79.0 | 0 | 15 | 3.0 | 3.0 |
| TP 4 | 71.5 | 0 | 22.5 | 3.0 | 3.0 |
| TP 5 | 79.0 | 15 | 0.0 | 3.0 | 3.0 |
| TP 6 | 71.5 | 15 | 7.5 | 3.0 | 3.0 |
| TP 7 | 64.0 | 15 | 15 | 3.0 | 3.0 |
| TP 8 | 56.5 | 15 | 22.5 | 3.0 | 3.0 |
| TP 9 | 64.0 | 30 | 0.0 | 3.0 | 3.0 |
| TP 10 | 56.5 | 30 | 7.5 | 3.0 | 3.0 |
| TP 11 | 49.0 | 30 | 15 | 3.0 | 3.0 |
| TP 12 | 41.5 | 30 | 22.5 | 3.0 | 3.0 |

*2.2.2. Thermal property testing*

Thermal properties of the composites were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA of the samples was performed in a Shimadzu TGA-50 thermal analyzer at a heating rate of 10°C/min under nitrogen with 20 mL/min flow rate. 10 mg of powdered test samples were used for the analysis. The samples were heated from room temperature to 800°C. DSC analysis was performed by Shimadzu DSC-60. The samples were heated from room temperature to 500°C at a heating rate of 10°C/min under a dry nitrogen atmosphere with a 30mL/min flow rate. Degree of crystallinity ($X_c$ %) was determined from the second melting enthalpy values using the fallowing equation:

$$\mathrm{Xc}\ (\%) = \frac{\Delta \mathrm{Hm}}{(1-\alpha) * \Delta \mathrm{Hc}} * 100$$

ΔHm (J/g) : Melting enthalpy of the specimens
ΔHc (286.7 J/g) : The enthalpy value of melting of a 100% crystalline form of high-density polyethylene (HDPE)
(1-α) : The weight fraction of polymer into the composite material.

*2.2.3. Physical property testing*

Water absorption (WA) and thickness swelling (TS) of the thermoplastic composites were determined according to ASTM D 1037 (1996) and EN 317 (1993), respectively. Test samples were conditioned in an acclimatized room at 20°C and 65% relative air humidity before testing. The weight and thickness of samples were measured. The measured samples were dipped into water and their weight and thickness were measured periodically. Five samples were tested for each composite group.

**3. Results and discussion**

*3.1. Thermal properties*

Thermal properties of all groups were determined with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermographs of the TGA and DTGA analysis of the composites were given in Figure 1 and 2, respectively. Six different groups were given in the thermographs. When the manufacture schedule was examined, TP1 group did not include any filler, just has coupling agents and paraffin wax. To mention on that group, thermal degradation was observed single-stage and it was started at 425 °C and finished at 510 °C. Maximum thermal degradation was occurred at 492.8 °C with 93.2% amount of decomposition. Residue amount was 0.8% at 520 °C for TP1.

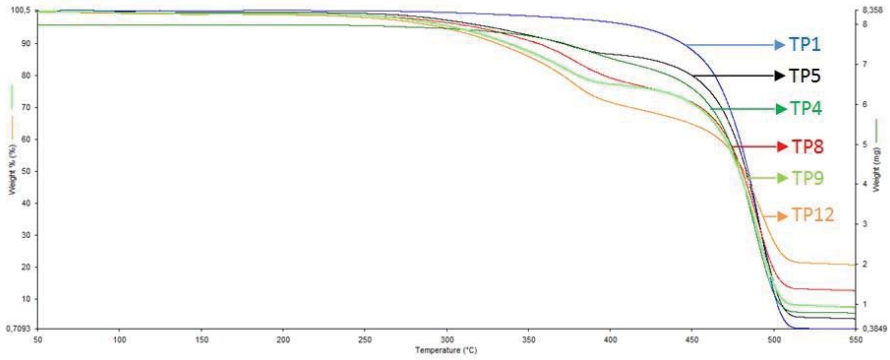


Figure 1. TGA Thermographs of Composites

Thermal degradation occurred in two stages for TP4 composite group produced with maximum waste tire powder rate (22.5%) (WTP) and without red pine wood wastes flours (RPWF). In the first stage, a small amount of thermal degradation occurred, while high amount in the second stage. The first decomposition temperature range was determined between 300 and 430 °C in first stage. Maximal degradation was observed at 351.4 °C with 13.6% rate. Second degradation began at 430 °C and finished 510 °C. Maximal degradation was observed at 487.9 °C with 75.2% rate. Residue amount was 10.04% at 520 °C for TP4. When TP1 and TP4 were compared, residue amount at 520 °C was increased with loading of the maximum WTP rate in HDPE matrix.

Thermal degradation occurred in two stages for TP3 and TP5 composites groups. They were produced with the same filler rate but TP3 included 15% WTP, while TP5 15% RPWF. Thermal degradation occurred in two stages for TP3 and TP5 composites groups. They were produced with the same filler rate but TP3 group included 15% WTP, while TP5 group 15% RPWF. The first decomposition temperature range was determined between 360-435 °C and 275-430 °C for TP3 and TP5 groups in first stage, respectively. In addition, maximal degradation was observed at 400.7 °C with 7.32% rate for TP3 group, while at 375.9 °C 14.4% for TP5 group in the first stage. To mention on the second stage of degradation, both composites were decomposed at closed temperature range. It was between 435-510 °C for TP3 group, while between 440-510 °C for TP5 group. Maximal degradations were observed at 490.7 °C with 79.6% rate and 492.6. °C with 78.6% rate for TP3 and TP5 groups, respectively. That second decomposition temperature peak for HDPE based composites was identical with the decomposition temperature of TP1 group which produced without filler (492.8°C). It was also reported that decomposition temperature of neat HDPE was 470 °C (Mengeloğlu and Karakuş, 2008). Moreover, first decompositions started with WTP and RPWF for TP3 and TP5 groups in the first stage, respectively. They degraded closed temperature range. However, WTP was more thermal stability than RPWF. Degradation started at 275 °C for RPWF, while at 360 °C for WTP. Residue amounts at 520 °C were 6.9% for TP3 group and 4.3% for TP5 group. When usage rates were same for WTP and RPWF, residue amount at 520 °C was higher while WTP used.

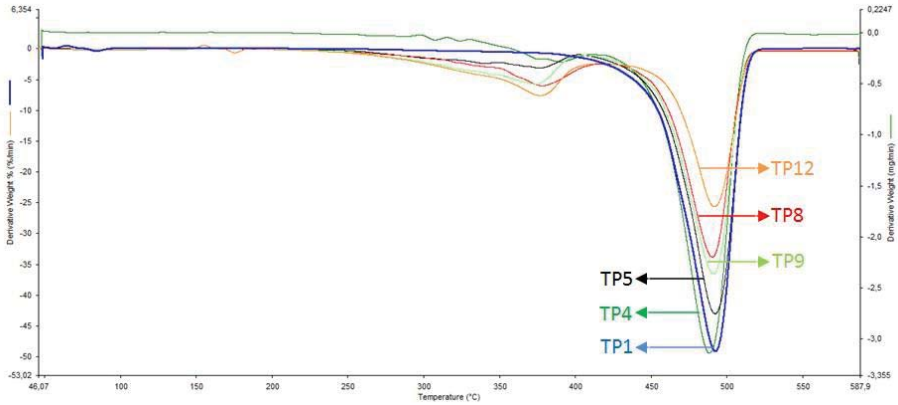


Figure 2. DTGA Thermographs of Composites

If the DTGA thermographs of composites were examined (Figure 2), It could be said that the thermal decomposition started earlier in the groups produced with maximum RPWF rate than produced with maximum WTP rate. Maximum residue amount at 520 °C was observed from TP12 group produced with maximum WTP rate (22.5%) and maximum RPWF rate (30%).

Results of Differential Scanning Calorimetry (DSC) analysis was presented in Table 2. When Table 2 was examined, melting temperature was same for all composites. However, the crystallinity ratio of polymer (Xc) which calculated by the help of energy for melting (ΔHm) shown variety. With the loading of the both fillers in HDPE matrix, melting temperature of composites and crystallinity ratio of polymer was slightly changed. DSC results of the composites were similar to control group. More precise results might be reached through XRD analyses.

Table 2. Results of Differential Scanning Calorimetry (DSC) analysis

| ID | Tm | ΔHm (J/g) | ΔHc (neat HDPE) (J/g) | Xc(%) |
|---|---|---|---|---|
| TP 1 | 132.7 | 151.6 | 286.7 | 52.88 |
| TP 2 | 132.7 | 142.8 | 286.7 | 53.85 |
| TP 3 | 132.8 | 126.9 | 286.7 | 52.07 |
| TP 4 | 132.6 | 118 | 286.7 | 53.11 |
| TP 5 | 132.7 | 124 | 286.7 | 50.88 |
| TP 6 | 132.7 | 119 | 286.7 | 53.56 |
| TP 7 | 132.4 | 105 | 286.7 | 52.32 |
| TP 8 | 132.5 | 91.8 | 286.7 | 51.23 |
| TP 9 | 132.4 | 103.9 | 286.7 | 51.77 |
| TP 10 | 132.4 | 94.3 | 286.7 | 52.63 |
| TP 11 | 132.4 | 72.3 | 286.7 | 45.85 |
| TP 12 | 132.3 | 69.9 | 286.7 | 51.33 |

### *3.2. Physical properties*

High-density polyethylene (HDPE) based red pine wood wastes flour (RPWF) and waste tire powder (WTP) filled composites were produced in the density range of 0,94-1.07 g/cm$^3$. Mean density values are presented in Table 3. Both WTP and RPWF filed composites had slightly higher densities than neat HDPE. Compared the WTP filling, RPWF filling increased the density twice as much. This increase was believed to be due to the higher cell wall density of lignocellulosic materials (Mengeloglu and Karakus 2008).

Table 3. Density of the manufactured composites

| ID | Density (g/cm$^3$) | ID | Density (g/cm$^3$) | ID | Density (g/cm$^3$) |
|---|---|---|---|---|---|
| TP 1 | 0.94 (0.008)* | TP 5 | 0.97 (0.003) | TP 9 | 1.04 (0.002) |
| TP 2 | 0.95 (0.006) | TP 6 | 0.99 (0.003) | TP 10 | 1.06 (0.001) |
| TP 3 | 0.96 (0.005) | TP 7 | 1.02 (0.002) | TP 11 | 1.07 (0.005) |
| TP 4 | 0.98 (0.003) | TP 8 | 1.03 (0.002) | TP 12 | 1.09 (0.002) |

* The numerical value in the parenthesis is standard deviation.

In this paper, water absorption and thickness swelling properties of all samples were determined for physical properties. The graphs of water absorption and thickness swelling properties are given in Figure 3-4. When Fig.3 and 4 examined, some of the composites did not reach the maximum water sorption and thickness in 113 days of testing. The results are ambiguous and it is hard to interpret with available data. However, the following conclusion can be reached with the available data;

- ✓ With the increasing of RPWF rate in the polymer matrix, water absorption properties were getting worse,
- ✓ Usage of WTP as filler in the composites provided better water absorption properties than usage of RPWF,
- ✓ It was hard to establish exact result for thickness swelling properties but it might be understood from Fig 4 thickness swelling properties of composites were shown parallel results with water absorption properties

Moreover, further study needs to be done to understand variety in behavior of produced samples.

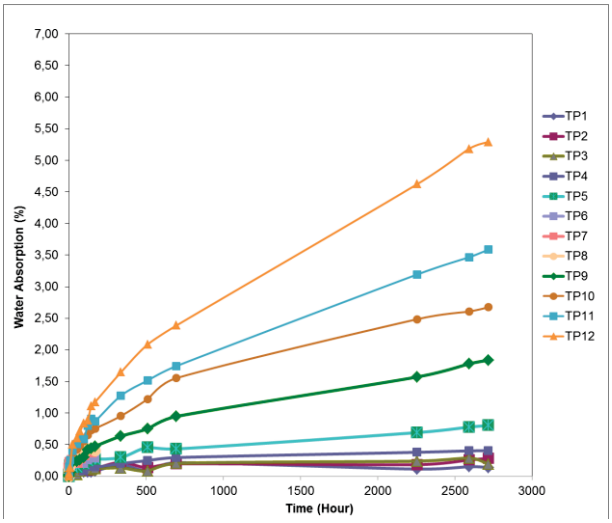


Figure 3. Water absorption properties

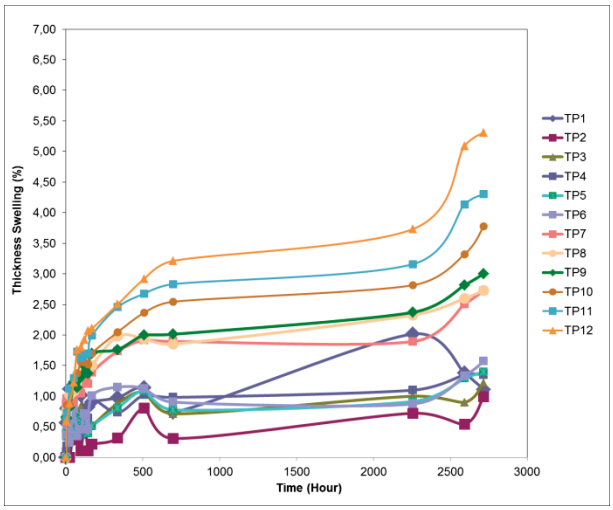


Figure 4. Thickness swelling properties

Morphology of the some of the produced samples was also studied. SEM images of neat HDPE samples (sample ID: TP1) and with highest WTP filler rate without RPWF (sample ID: TP4) was presented in Fig 5. SEM images of composite with 0% WTP and 15% RPWF content samples (sample ID: TP5) and with highest WTP and 15% RPWF rate (sample ID: TP8) was shown in Fig 6. SEM images of composite with 0% WTP and highest rate of RPWF content samples (sample ID: TP9) and with highest WTP and RPWF rate samples (sample ID: TP12) was shown in Fig. 7.

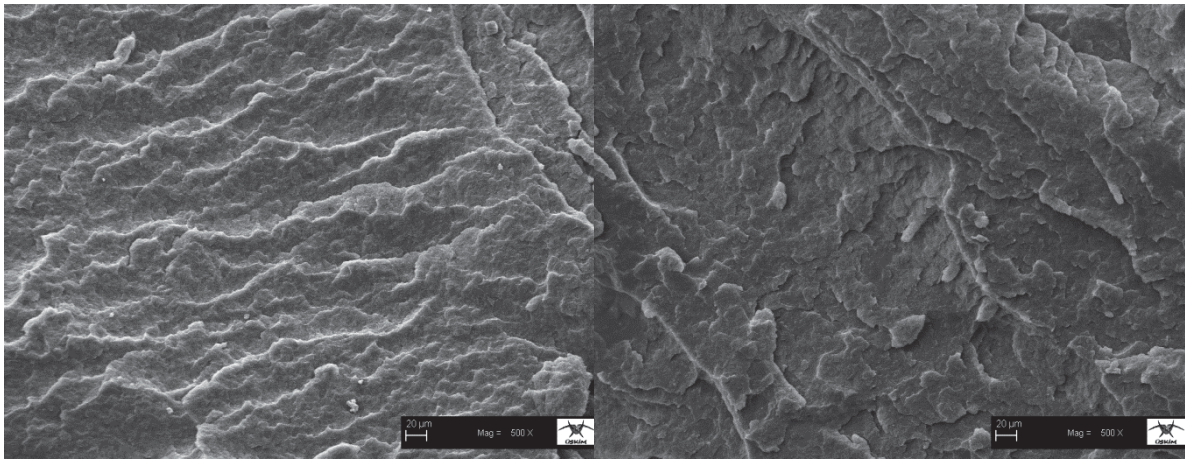

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Figure 5. SEM images of a- TP1; b- TP4

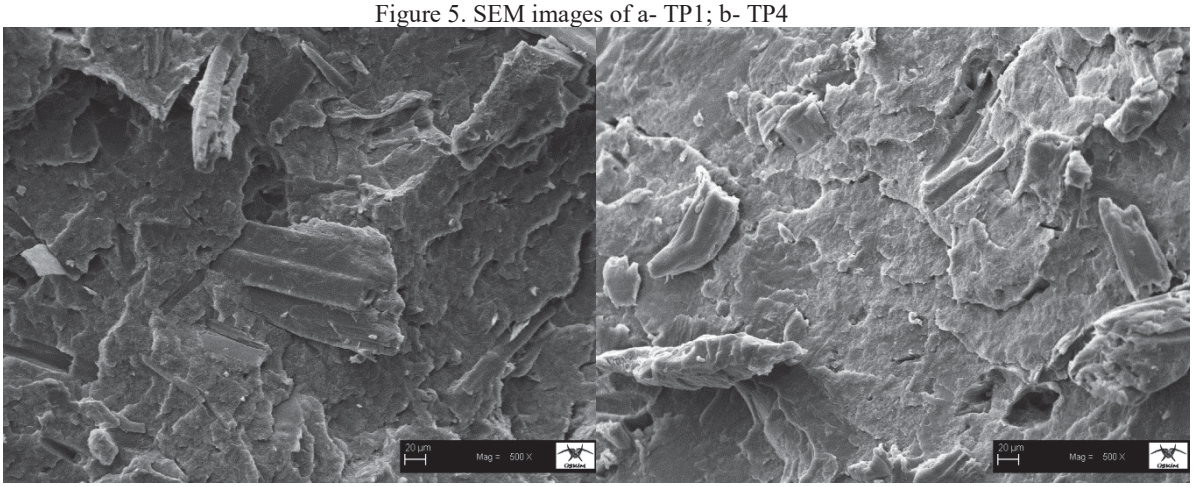

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Figure 6. SEM images of a- TP5; b- TP8

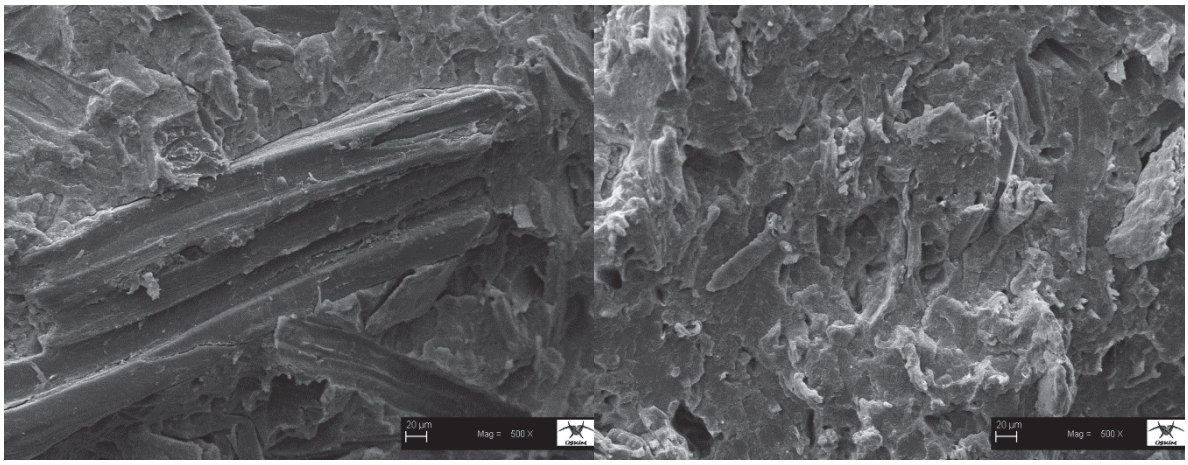


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Figure 7. SEM images of a- TP9; b- TP12

From these images, it is clear that polymer matrix, red pine wood waste flour (RPWF) and waste tire powder (WTP) were successfully mixed. In all composites, there are individual lignocellulosic fibers and tire powder pull out of the matrix indicating the lack of adhesion between the fillers and polymer matrix.

## 4. Conclusion

In this study, Red Pine Wood Wastes Flour (RPWF) and Waste Tire Powder (polybutadiene) (WTP) were successfully utilized in the manufacturing of HDPE based composites as filler. Thermal (TGA and DSC), water absorption and thickness swelling properties of produced composites were determined and the following conclusions were reached;

Loading of the both fillers was raised residue amount at 520 °C. However, with the same usage rate, residue amount at 520 °C was higher while WTP used. WTP was more thermal stability than RPWF. With the loading of the WTP and RPWF fillers in HDPE matrix, crystallinity ratio of polymer was slightly changed. However, XRD analyses might be used for more precise results. Loading of the RPWF was more effective than loading of the WTP on the physical properties.

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## Reference

Acar, H. 2014. “MDF Tozu ve Pirinç Sapı Atıklarının Termoplastik Kompozitlerin Üretiminde Değerlendirilmesi” Yüksek Lisans Tezi. KSÜ Fen Bilimleri Enstitüsü. s74.

Avcı, E. 2012. “Ahşap Plastik Kompozitlerin Kullanım Performansları Üzerine Araştırmalar” Doktora Tezi. İstanbul Üniversitesi Fen Bilimleri Enstitüsü. s267.

Bekhiti, M., Trouzine, H., Asroun, A., 2014. Properties of Waste Rubber Powder. Engineering, Technology & Applied Science Research, 4(4): 669-672.

Dönmez Çavdar, A. 2011. “Farklı Lignoselülozik ve Termoplastik Maddelerle Üretilen Odun-Plastik Kompozitlerin Özelliklerinin İncelenmesi” Doktora Tezi. KTÜ Fen Bilimleri Enstitüsü. s268.

Karakuş, K. 2008. “Üniversitemizdeki Polietilen ve Polipropilen Atıkların Polimer Kompozit Üretiminde Değerlindirilmesi” Yüksek Lisans Tezi. KSÜ Fen Bilimleri Enstitüsü. s75.

LASDER, 2017. Waste Tire in Turkey, http://www.lasder.org.tr/turkiyede-otl/, Accessed: 06.08.2017.

Lin, C., Huang, C.L. & Shern, C.C. 2008. “Recycling Waste Tire Powder for the Recovery of Oil Spills” Resources, Conservation and Recycling, (52), 1162–1166. doi:10.1016/j.resconrec.2008.06.003

Marques, A.C., Akasaki, J.L., Trigo, A.P.M., Marques, M.L., 2008. Influence of the surface treatment of tire rubber residues added in mortars. Ibracon Structures and Materials Journal, 1(2): 113-120.

Rubber Manufactures Association (RMA). Scrap tire markets in the United States. 2017 ed.Washington, DC: RMA; 2017, https://www.ustires.org/, 11 May 2017.

Mengeloglu, F., Kabakci, A. 2008. Determination of Thermal Properties and Morphology of Eucalyptus Wood Residue Filled High Density Polyethylene Composites. Int. J. Mol. Sci., 9: 107–119.

Mengeloglu, F., Karakus, K. (2008). Thermal degradation, mechanical properties and morphology of wheat straw flour filled recycled thermoplastic, Sensors ISSN 1424-8220 8. pp. 497-516.

Turkish Statistical Institute Report, 2015. Issue 18762, 11 Feb 2015.