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Investigation thermal and mechanical properties of PP/beech flour composite

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Composite materials are put into use while their properties are improved by the researchers each passing day due to the advantages they provide and their variety in the application fields. One such renewable material is wood flour which is one of the most common forms of reinforcement in thermoplastics. Wood plastic composites (WPCs) are preferred in our study due to their advantages such as good resistance, low costs, availability and low wear on the processing equipment.

In this study beech tree flour and polypropylene (PP) composites were produced and this composites mechanical properties were investigated. It has been observed that 5 composites which were produced by increasing the beech flour by 5wt% , have increased in Elasticity Module and hardness based on the ratio of the beech flour but on the other hand, its elongation and tensile strength has decreased. PP-20% beech flour mixture is seen to have the highest Elasticity Module and hardness. 61% decrease has been observed in tensile strength with the increasing flour ratio. Characterization of PP and PP-Wood beech composites has been carried out via thermal analysis and SEM methods.

Keywords: Polypropylene, thermo plastic, wood plastic composites (WPCs), thermal and mechanical properties.

INTRODUCTION

Forestry products companies and plastic factories show a great deal of interest in Wood Polymer Composites (WPCs) which are one of the most dynamic units in Plastics sector. As a result of this interest, the properties of the wood polymer composites are constantly being improved and renewed.

Wood polymer composites add advanced properties to wood panels such as water absorption, resistance against biodegradation. However, correct compatibilizers are required to bridge over between wood and polymer in order to achieve this.

There are a lot of studies with regard to the mechanical properties of the composites reinforced with wood flour in different properties and thermoplastic PP [1-4].

Although particle filling/reinforcement materials are generally used on polymeric materials in order to decrease the cost, mechanical, thermal, electrical and chemical properties of the composite materials which are produced with the use of particles with advanced properties are improved.

Wu et al. studied the effect of carrying out preliminary processes on the wooden filling surface to the interfacial tension by Polypropylene (PP) composites with wood flour.

As a result of their study they proved that the bond structure between the surfaces of the filling matrix effect the interfacial tension and the mechanical properties of the composite [5].

Adhesive properties of the interface between the polymer matrix and wooden filling can be improved by using coupling agents. Surface bonding materials used improve the mechanical and chemical bonding properties by establishing a bond between wood flour (reinforcement) and thermoplastic (matrix).

Dalvag et al. have shown that in case the maleated polypropylene (MAPP) is used as a bonding agent in Polypropylene (PP)/wood flour composite there are improvements in tensile strength, rupture, elongation and Charpy impact properties [6-7].

Wood flour is an industrial product used in the production of natural composite. There are different studies with regard to the effect of process parameters on polymer-wood composite processing [8-12].

Le and Gauther have studied the effects of different parameters such as the rate of maleic anhydride (MA) in PP-graft-MA, sisal fiber fractions, chemical treatment of the fibers in the composites during the reactive extrusion. They have shown that the grafting of the fibers by PP-graft-MA enhanced both the impact strength and breaking stress [13].

Stamhuis has used Styrene Butadiene Styrene (SBS), SEBS, Nitrile Butadiene Rubber (NBR), Ethyl Vinyl Acetate (EVA) and Ethylene propylene monomer (EPDM) as impact modifier within PP with filling, composite. He reported that with the addition of such materials there is an improvement in the impact properties but the best result is achieved with covering the filling surface with the reinforcement. He has also shown that MA

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contents within PP-g-MA have caused an increase in impact tension and the tension in the rupture [14].

Bledzki et al. have studied the effect of MAPP contents on physico-mechanical properties of PP which has been reinforced with hard and soft wood flour [15].

L.Soccalingame et al. evaluated the bonding effect of PP-g-MA on flour particle size and degradation of the spruce flour dust – PP composite after injection molding. In order to evaluate the level of degradation we need to consider process parameters, flour and bonding agents. Additionally, strong effect of PP-g-MA bonding agent on tensile properties was observed while no effect was observed on the impact [16].

Property of water absorption of composites is important to determine various application potentials such as floor covering in outdoor use [17-18].

Composite prepared with fibers which are not covered with MAPP has a lower tensile and higher humidification properties when compared to composite prepared with fibers which are covered with MAPP. It correlates with low interface bonding among these components [16].

Bhaskar et al. have prepared a wood polymer composite (WPCs) by using recycled polypropylene (rPP) together with pine tree flour (Pine radiate). Researchers have compared the water absorption property of polymer processed with (rPP), virginPP (vPP) and maleated polypropylene (MAPP) which is a bonding agent. In accordance with the test results, water absorption has increased in accordance with the increased flour ratio. On the other hand bonding agent MAPP has greatly decreased the water absorption property [19].

The aim of this study is to evaluate the effects of MA and flour ratio on composite material after the sieving and injection molding cycle. In the study wood reinforced polymer composite materials were produced in the ratios of 5%, 10%, 15%, and 20% by increasing the wood flour ratio by 5wt%. For determining the strength, ductility and elongation parameters of the composite materials produced they have been subjected to single axis tensile test and Shore D hardness test for determining their hardness values. Wood flour is used to increase the resistance and hardness of the polypropylene composite material and to decrease the costs.

2.MATERIALS AND METHODS

2.1.Materials

In this study beech tree flour (WB) which grows in Karabük-Yenice (Turkey) is used. The flour which has been sieved using laboratory test sieves with the pores in 200 microns and dried for 24 hours.

Wood flour consists of the composition of cellulose, hemicellulose, lignin and foreign materials. Chemical properties of the beech flour dust are shown in Table 1.

Table 1. Chemical properties of the beech wood (WB)

Chemical Composition	%
Cellulose	40-50
Hemicellulose	20-35
Lignin	20
Foreign substance	0-5

Table 2. Mechanical properties of maleic anhydride

Maleic anhydride	Value
Purity wt %	99.5
Solidification point (°C)	52.4
Boiling Point (°C)	202
Density g/cm^3	1,48

Maleic anhydride is used to enable the binding effect at interfaces of the polymer-wood flour mixtures. Mechanical properties of maleic anhydride material are shown in Table 2. Maleic anhydride is procured from As Kimya (İstanbul, Turkey).

Mechanical properties of polypropylene (PP) material are shown in Table 3. Polypropylene block copolymer was procured from Sabic (SABIC PP 48M40).

Phenolic antioxidant material with Anox20 serial is used to prevent the degradation due to temperature during the injection processes of Polymer-Wood flour mixtures. It has very low volatility and provides a better resistance in polymer extraction. Antioxidant Anox 20 has been procured from Addivant (USA). Mechanical properties of antioxidant are given in Table 4.

2.2 Production of polymer-beech flour composites

Five composite samples have been prepared in the ratios given in Table 5. Each sample mixed in vertical type mixer with three blades (DMS DER-SAN Vertical Type) with 700 dev/min. speed for 15 minutes. The mixture was molded with the injection molding method which can be seen in Figure 1 by using Arburg 50T brand injection machinery. Sizes of single axis tensile test sample (ASTM D412) produced as a result of the molding process is given in Figure 2. Injection molding parameters are given in Table 6. For each parameter, 10 units of samples were molded and tensile test is applied to five of them. Tensile and hardness tests were carried out within ISO 294 standards.

Figure 1. Plastic injection mold.

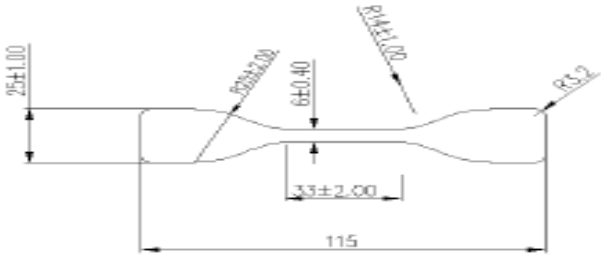

Figure 2. Tensile test sample.

Table 3. Mechanical properties of polypropylene block copolymer (PP) [20]

Polymer Properties	**Unit(SI)**	**Values**	**Standard**
Density	kg/cm^3	0.905	ISO 1183
MFR at 230 ^{o}C and 2.16 kg	g/10 min	15	ISO 1133
Mechanical Properties			
Tensile Test			
Stress at yield	MPa	29	ISO 527
Stress at break	MPa	20	
Strain at break	%	300	
Flexural Test			
Flexural Modulus	MPa	1650	ASTMD790
Izod impact notched			
at 23^{0}C	kJ/m^2	7.0	ISO 180/4A
at 0^{0}C	kJ/m^2	4.5	
at -20^{0}C	kJ/m^2	3.5	
Charpy impact notched			
at 23^{0}C	kJ/m^2	7.0	ISO 179
at 0^{0}C	kJ/m^2	4.0	
at -20^{0}C	kJ/m^2	2.5	
Hardness Shore D	-	70	ISO868
Thermal Properties			
Head Deflection Temperature			
at 1.80 MPa (HDT/A)	^{0}C	56	ISO 75/A
at 0.45 MPa (HDT/B)	^{0}C	88	ISO 75/B
Vicat Softening Temperture			
at 10 N (VST/A)	^{0}C	147	ISO306/A
at 50 N (VST/B)	^{0}C	79	ISO306/B

Tensile test is applied to the composite samples which are in accordance with the ASTM D412 standard by using ZWICK Z010 brand single axis tensile test device. Preloading time, preload and test speed for all samples in tensile test are kept at a fixed rate. Preloading time is used as 50 sec. and preload is used as 1 N/mm^2. Tensile tests are performed with 50 mm/min speed. Tensile test is applied to all the samples in line with these parameters.

Table 4. The properties of Anox 20 antioxidant

Antioxidant	Value
Bulk density (kg/m^3)	Powder 650/Granular 570
Flash point (°C)	299
Melting range (°C)	110-125
Molecular weight	1178
Appearance	White, free-flowing solid
Thermogravimetric analysis (10 mg 10^{o}C /min. under N_2)	350 (Weight loss %5)

Table 5. Mixture ratios of the wood flour and additives added to polypropylene

Samples	Group1 (wt%)	Group 2 (wt%)	Group 3 (wt%)	Group 4 (wt%)	Group 5 (wt%)
PP	PP	PP	PP	PP	PP
Wood flour	-	5	10	15	20
Maleic Anhydride	-	2	2	2	2
Antioxidant	-	0.10	0.10	0,10	0,10

Table 6. Conditions injection molding for PP-wood flour mixture

Parameters	Value
Injection temperature (°C)	190-210
Injection pressure (bar)	1400-1500
Waiting Ttme in Mold (sec)	15

Also, the hardness of the composite material is measured with ZWICK Shore D durometer. ZWICK (Shore D) durometer is given in Figure 3.

The specimens were coated with Au/Pd by using Sputter coater Q150R and transferred to FE-SEM for imaging. The microstructures of specimens were observed using a field emission scanning electron microscope (FESEM) Carl Zeiss Ultra Plus machine with an energy-dispersive X-Ray spectroscopy (semi-quantitative EDX) analysis system.

Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA) studies were carried out in nitrogen at scanning rates 10^0C min^{-1} in nitrogen atmosphere using module of a Tetra Hıtachı DSC 7000x and STA 7300 Thermal Analyzer with 10-11 mg of samples on ceramic pans. The thermal degradation of the samples was studied from a temperature 40 to 700^0C.

Differential scanning calorimetry (DSC) studies were carried out scanning rates 10^0C min^{-1} in nitrogen atmosphere using module of a Tetra Hıtachı DSC 7000x and STA 7300 Thermal Analyzer with 10-11 mg of samples on alumina pans. The thermal degradation of the samples was studied from a temperature 40 to 500^0C.

3.RESULTS AND DISCUSSION

3.1. Mechanical properties

In the study, composite samples are produced by increasing the wood ratio by 5 wt.% regularly (in a range of 5%~20%). 5 of the samples produced from each mixture are subjected to tensile test. Elasticity Module in accordance with the wood ratio, % Elongation and Tensile Stress graphics are given in Figure 4. Average of Elasticity module for composites, elongation, tensile stress values is taken and they are shown in Table 7.

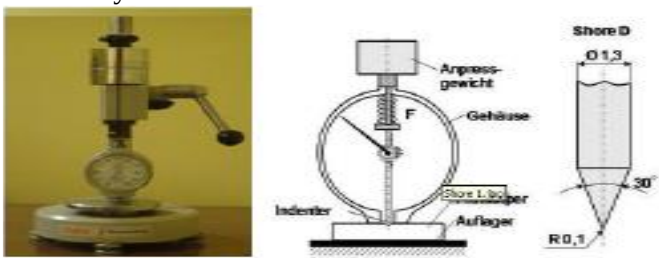

Figure 3. ZWICK durometer.

Table 7. Mechanical properties of the materials wich have different wood flour ratios

Mechanical Properties	PP	PP - 5% Wood Flour	PP -10% Wood Flour	PP -15% Wood Flour	PP -20% Wood Flour
Elasticity Modulus *(*MPa)	440.66	667.17	709.40	726.26	748.52
Tensile Strength (MPa)	39.27	29.25	27.60	25.73	23.84
Elongation (%)	19.62	7.75	6.76	4.96	4.21

In the study elasticity module of Polypropylene is found to be 440,66 MPa, elongation is found to be 19,62% and tensile stress is found to be 39,27 MPa.

When the Beech flour is added in a ratio of 5% to Polypropylene, Elasticity Module increased to 667,17MPa, elongation is found to be 7,75% and tensile stress is found to be 29,25MPa. Highest elasticity module is achieved from PP-%20 mixture containing wood Flour as 748,52MPa. Elongation value of this composite is 4,21% and tensile stress is 23,84 MPa.

Tensile and % elongation graphic belonging to the samples are shown in Figure 5. As it can be seen from the graphic, elongation percent is decreased and mechanical resistance of the composites are increased based on the increasing wood flour ratio.

Hardness graphic and its values are given in Figure 6 and Table 8 for PP-wood flour composites in different ratios. Five measurements were made from the samples belonging to each parameter and average of the values gained as a result of the measurement are taken and evaluated.

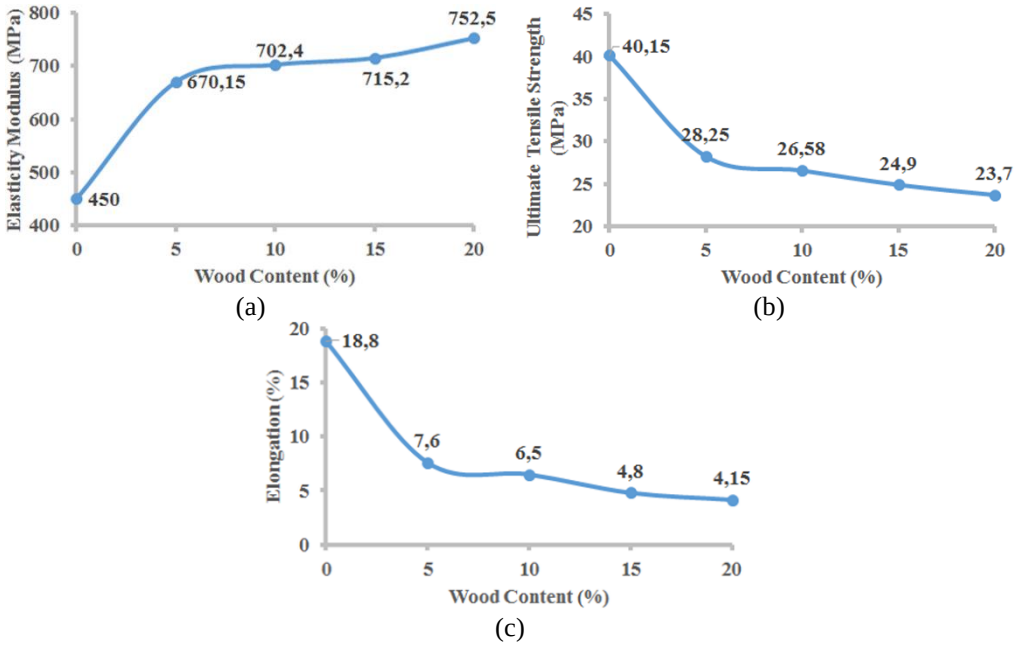

Figure 4. Tensile curves in accordance with increasing wood ratios a) Elasticity Module - %Wood flour content, b) %Elongation - %Wood flour content, c) Tensile Strength - %Wood flour content.

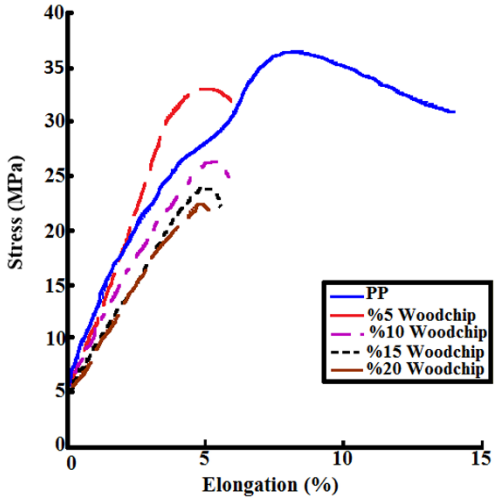

Figure 5. Tensile-% elongation graphic.

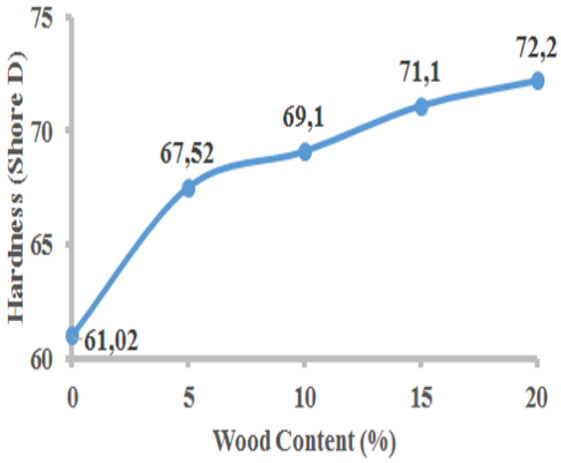

Figure 6. Hardness graphic for polypropylene-wood flour composite.

When the hardness values of the samples are analyzed after wood dust ratio is increased in a ratio of 5% regularly, it is found out that the highest hardness value belongs to PP-%20 Wood Flour mixture with 71,36 Shore D value. Hardness value of the composite material gained from the PP-%15 wood flour is 70,50 Shore D. Hardness value of the material gained from the PP-%10 Wood Flour is 69,20 ShoreD. Hardness value of the material gained from the PP-%5 Wood Flour is 66,54 Shore D. Hardness value for polypropylene is 60,89 Shore D.

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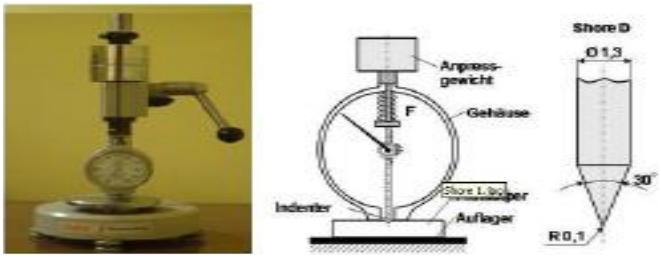

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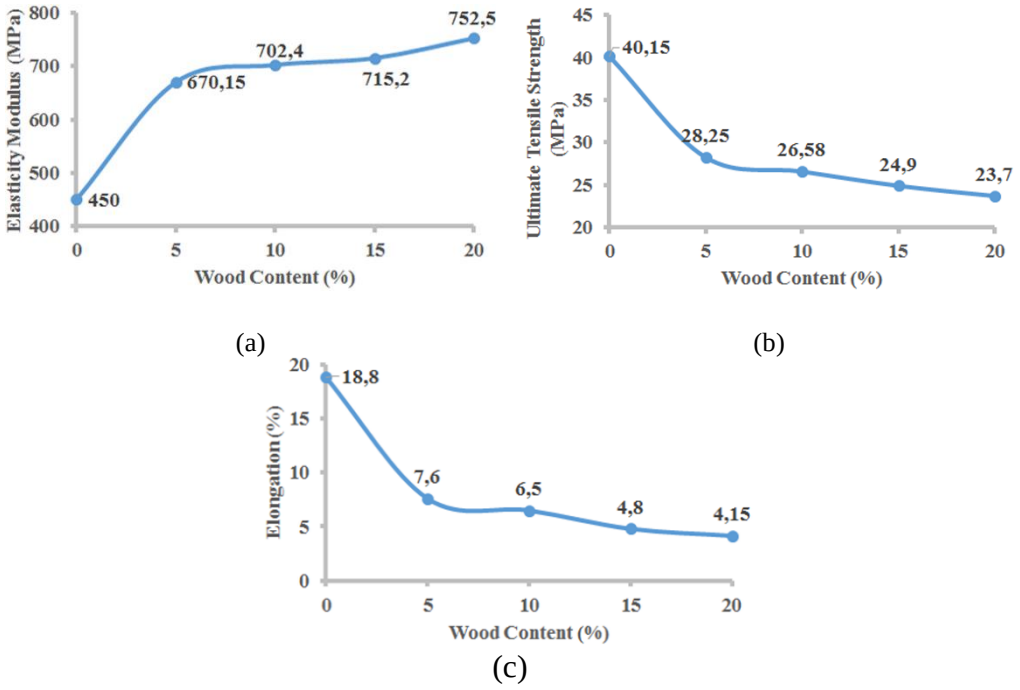


Figure 4. Tensile curves in accordance with increasing wood ratios a) elasticity module - % wood flour content, b) % elongation - %wood flour content, c) tensile strength - %wood flour content.

Table 8. Hardness values of polypropylene-wood flour composites

Mixture	Standard Deviation	Average (Shore D)
PP	0.71	60.89
PP - 5% Wood Flour	0.87	65.54
PP - 10% Wood Flour	0.45	69.20
PP -15% Wood Flour	0.42	70.50
PP- 20% Wood Flour	0.45	71.36

3.2. SEM analysis

In this study microstructure images are taken from the composite samples which have different wood flour ratios. Images were taken by SEM from both the surface and fractured surface with 500X zoom in order to understand the effect of the wood flour.

Figure 7a shows the SEM image of polypropylene. As it can be seen from Figure 7b, PP and wood flour is blended in a homogenous way. In Figure 7c, when the fractured surface SEM image of the PP-%20 wood composite is analyzed, it is seen that gaps are caused by wood flour which are not completely bonded to the composite and which are ruptured. However, the number of the gaps is few and in general terms a composite which is compatible with polymer is formed.

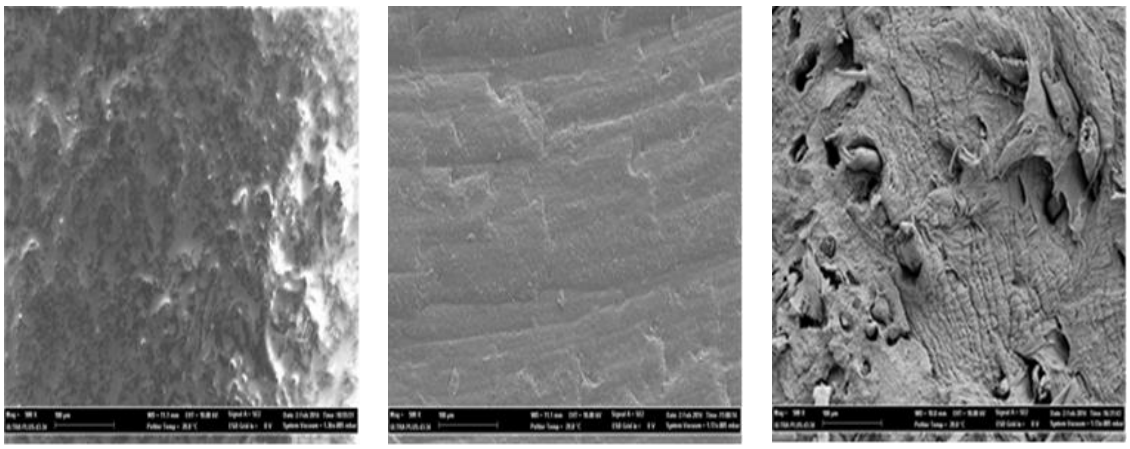
3.3. Thermal properties

DSC and TGA thermal analyses are evaluated for PP and PP-Wood flour composites. Thermal properties of the materials produced from PP under

different conditions were analyzed by other researchers [20-25].

Table 9 shows the thermal analysis result of the PP and PP-20% wood composite.

When we have a look at the TGA curve of the PP in Figure 8a there is a single decomposition in 98,5% between 254-473^{0}C. Polypropylene starts to degrade at a temperature over 253^{0}C



a) b) c)

Figure 7. Scanning electron microscope (SEM) micrographs of samples (magnification 500X) . a) PP , b) PP-20% wood flour composite, c) PP-20% fractured surface SEM image of wood flour Composite

Table 9. Thermal analysis results of the PP and PP-20% wood flour composite

Polymer	DSC(^0C)			TGA(^0C)		
	T*m*	T*d*	ΔH_m	Td_1	Td_2	Td_3
PP	168	190	79.0	-	254	473
PP-wood comp.	168	203	88.3	114	377	537

T*m* - melting temperature, T*d* - decomposition temperature, ΔH_m *(mJ/mg)* - melting enthalpy .

In Figure 8 b, single mass degradation of the PP-wood flour composite occurred between the temperatures of 114 and 537^{0}C. First decrease occurred between 114.4-377^{0}C as 7.3% (1,23mg mass loss) and second weight decreased occurred between 377-537,4^{0}C as (96.46%) (15,53mg mass loss).

In thermogram, in the temperature range up to 377^{0}C, there is only 7% loss of mass arising out of the water contained in the composite structure, removal of volatile molecules and degradation of the wood flour and additives over this temperature. Composite material from Figure 8 b is completely degraded at 537^{0}C.

When Figure 8a and 8b is compared, pure PP lost 98.8% of its total and PP-wood composite lost 96% of its total within the range of 170-500^{0}C. Also when the Td_2 degradation temperatures of pure PP and Pp-wood composite in Table 9 are compared, it has been observed that the degradation temperature is increased from 253^{0}C to 473^{0}C with the effect of additives. Degradation temperatures increased when wood flour and additives are added to polymer while the loss of mass is decreased. This shows that the thermal resistance of the composite is good.

When the DSC thermal analysis results in Figure 8c and 8d are compared, it is seen that melting and decomposition temperatures are not changed that much. While the PP melting temperature is (T*m)* 167.9; melting temperature of PP-wood composite (T*m)* is 167.8^{0}C, decomposition temperatures (T*d*) are; 190^{0}C for PP and 203^{0}C for PP-wood composite. Comparison of these two melting temperatures belonging to PP and PP-wood composite can be seen in Fig.8e.

The ΔH_m of the PP increased with increasing wood flour content. The ΔH_m of the PP increased from 79.0 to 88.3 mJ/mg as the wood flour content increased to 20%.

Our results are conclusive with the studies made with regard to the thermal properties of PP [16-24].

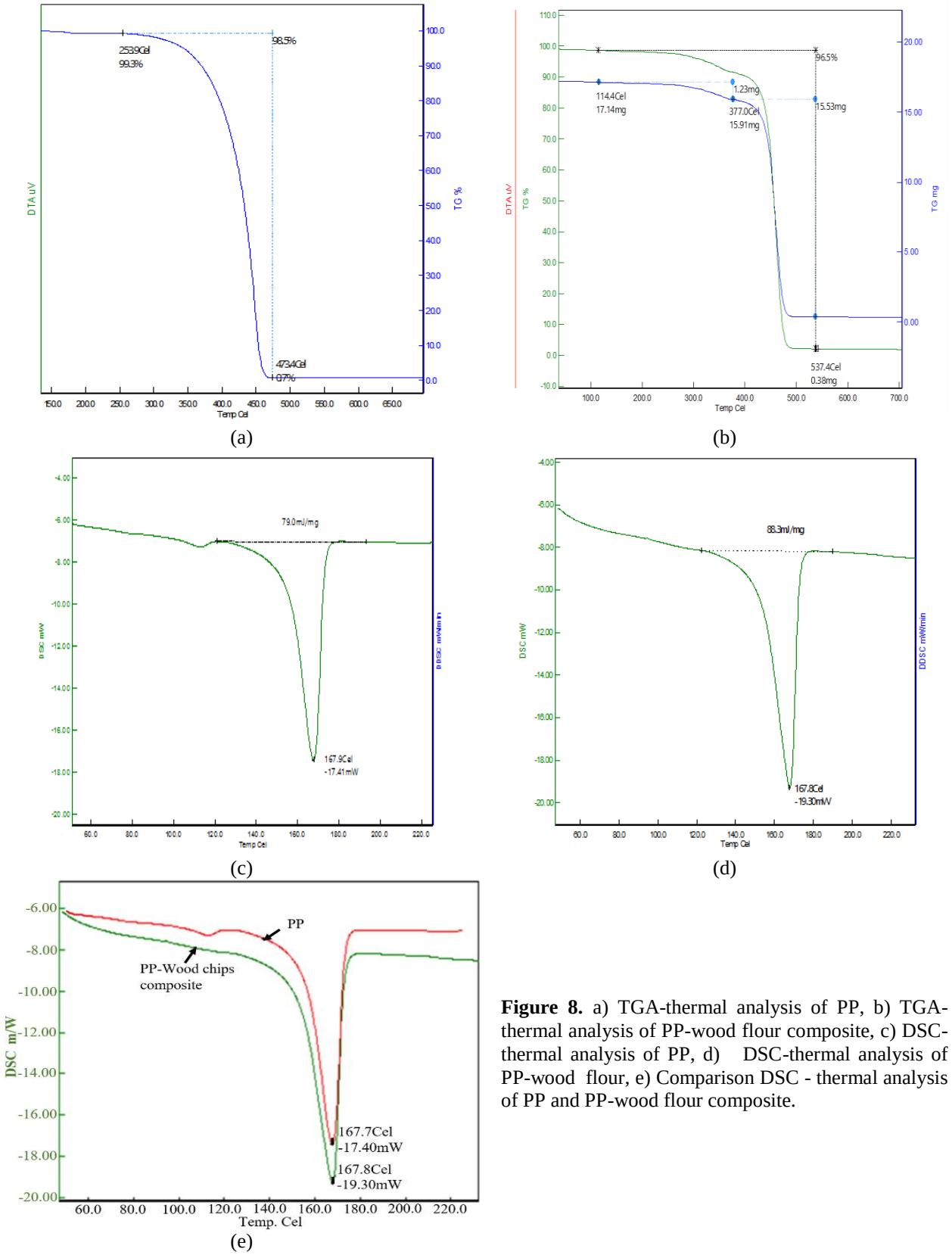


Figure 8. a) TGA-thermal analysis of PP, b) TGA-thermal analysis of PP-wood flour composite, c) DSC-thermal analysis of PP, d) DSC-thermal analysis of PP-wood flour, e) Comparison DSC - thermal analysis of PP and PP-wood flour composite.

4. CONCLUSION AND DISCUSSION

Mechanical properties of the composite materials produced from the mixture of polypropylene with wood flour are analyzed in this study. Wood flour is added to increase the strength and hardness of the polypropylene material.

Ratio of wood flour is increased by 5% regularly within the mixture in the composite material produced. Hardness and tensile test are applied to the new mixtures produced and their mechanical properties are analyzed.

When the wood ratio is increased regularly it has been observed that the elasticity module of the composites has increased as well. While the Polypropylene has high ductility and low elasticity module, increase in the wood ratio by mixing it with wood flour caused an increase in the Elasticity module, decrease in the elongation percent and decrease in the tensile stress. It has been determined that stress of composite material increased per unit of elongation when compared to polypropylene.

It has been observed that when the amount of wood within the mixture is regularly decreased the hardness of the composite material is decreased. The highest hardness value is achieved from the mixture with PP-20% Wood flour and the lowest hardness value belongs to pure Polypropylene material.

It has been observed from the SEM images taken from the material that wooden flour bonds to plastic appropriately and it becomes integrated with the plastic.

Thermal decomposition and melting temperature of the composite materials were investigated by TGA and DSC. Composites have shown high thermal decomposition temperature at 377^0C in a nitrogen atmosphere. Most of the weight loss occurred between the temperature range of 377-537^0C.

In order to achieve a good and accurate mechanical property homogenous mixture of the composite material is an important matter. For a homogenous microstructure, wood flour particles and polypropylene should be blended well and should be combined. Usage of mixer is important for well blended mixtures and for achieving a homogenous microstructure. Also, gaps created by the wood flour should be refrained and wood flour should be in a size of small sieve size which is at least 250μm.

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