DEU FMD 21(62), 395-408, 2019

Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi
Dokuz Eylul University Faculty of Engineering Journal of Science and Engineering

Basılı/Printed ISSN: 1302-9304. Elektronik/Online ISSN: 2547-958X

The Effects of Agro-Waste Reinforcing Fillers as Single and Hybrid on Mechanical and Thermal Properties of Polypropylene

Tek ve Hibrit Olarak Tarımsal Atık Takviyelendirici Dolguların Polipropilenin Mekanik ve Isıl Özellikleri Üzerindeki Etkileri

Kutlay Sever[1*], **Yaşar Aycan** [2]

[1]Izmir Katip Celebi University, Mechanical Engineering Department, Izmir, Turkey
[2]Izmir Katip Celebi University, Graduate School Of Natural And Applied Sciences, Izmir, Turkey
Sorumlu Yazar / Corresponding Author *: kutlaysever@gmail.com

Geliş Tarihi / Received: 07.08.2018 *DOI:10.21205/deufmd.2019216207*
Kabul Tarihi / Accepted: 15.11.2018 *Araştırma Makalesi/Research Article*
Atıf şekli/ How to cite: SEVER, K., AYCAN, Y. (2019). The Effects of Agro-Waste Reinforcing Fillers as Single and Hybrid on Mechanical and Thermal Properties of Polypropylene. DEUFMD, 21(62), 395-408.

Abstract

After agricultural harvests and pruning, billions of tons of agro-wastes are occurred on Earth. Only a small amount of the agro-waste is used as fertilizer and fuel and the rest is not evaluated. The remaining waste can cause air pollution if it is burned in the field. For this reason, this large amount of waste can be used as a reinforcement or filler to produce polymeric composite products. In last decade, the development of natural fiber/polymer composites has gained popularity in many applications such as decking, siding, and automotive indoor parts due to their environment friendly characteristics, low cost, low density etc. In this study, the effective utilization of rice husk (RH) and vine stem (VS) as natural reinforcing fillers in polypropylene (PP) based composites was evaluated. PP matrix composites containing different weight fraction of RH (10%, 20% and 30 %) and hybrid RH-VS-PP matrix composites were manufactured to observe the mechanical (tensile and flexural strengths, and Young's and flexural moduli) and thermal (degradation, melting, and crystallization temperatures etc.) properties of the composites. The RH-PP and RH-VS-PP composites exhibited much better mechanical and thermal properties compared to neat PP. Tensile strength of PP was increased by 10 wt.% of RH addition from 22.3 MPa to 31.0 MPa. The highest flexural strength which is about 55.0 MPa, was obtained by 3RH-7VS-90PP among all composites. Increases in storage modulus of 10RH-90PP, 20RH-80PP, and 30RH-70PP are 21.7, 29.0, and 33.4 %, respectively, when compared to that of PP at 35 °C. When 3wt% VS filled into RH-PP composite, degree of cristallinity (X_c) of the composite was increased approximately 2% as compared to that of 10RH-90PP.

Keywords: *Rice husk, vine stem, polypropylene, hybrid, thermal and mechanical properties.*

Öz

Tarımsal hasatlardan ve budamadan sonra, Dünya'da milyarlarca ton tarımsal atık meydana gelir. Yalnızca az miktarda tarımsal atık gübre ve yakıt olarak kullanılmakta olup, geri kalanı değerlendirilmemektedir. Kalan atık, sahada yakıldığında hava kirliliğine neden olabilir. Bu nedenle, bu büyük miktarda olan bu atıklar, polimerik kompozit ürünler üretmek için bir takviye veya dolgu malzemesi olarak kullanılabilir. Son on yılda, doğal elyaf/polimer kompozitlerin gelişimi çevre dostu karakteristikleri, düşük maliyet, düşük yoğunluk vb. nedeniyle zemin kaplaması, dış cephe kaplaması ve otomotiv iç parçaları gibi birçok uygulamada kullanım olanağı kazanmıştır. Bu çalışmada, polipropilen (PP) esaslı kompozitlerde doğal takviyelendirici dolgu malzemeleri olarak pirinç kabuğu (RH) ve asma çubuğu'nun (VS) etkin kullanımı değerlendirilmiştir. Bu çalışmada, kompozitlerin mekanik (çekme ve eğilme dayanımları ve Young's ve eğilme modülleri) ve termal (bozunma, erime ve kristalleşme sıcaklıkları vb.) özelliklerini incelemek için farklı ağırlık oranlarda RH (% 10,% 20 ve% 30) içeren RH-PP kompozitler ve hibrit RH-VS-PP matris kompozitler üretilmiştir. RH-PP ve RH-VS-PP kompozitler, saf PP'ye kıyasla çok daha iyi mekanik ve termal özellikler sergilemiştir. PP'nin çekme dayanımı, ağırlıkça %10 RH ilave edilmesiyle 22.3 MPa'dan 31.0 MPa'ya arttırılmıştır. Tüm kompozitler arasında en yüksek eğilme dayanımı yaklaşık 55MPa olarak RH-7VS-90PP ile elde edildi. 35 ° C'de, 10RH-90PP, 20RH-80PP ve 30RH-70PP'nin depolama modülündeki artışlar, PP'ninki ile karşılaştırıldığında, sırasıyla 21.7, 29.0 ve % 33.4'tür. % 3 oranında VS, RH-PP kompozit içine katıldığında, kompozitin kristallik derecesi (Xc), 10RH-90PP'ye kıyasla yaklaşık % 2 artmıştır.

Anahtar Kelimeler: *Pirinç kabuğu, asma çubuğu, polipropilen, hibrit, termal ve mekanik özellikler.*

1. Introduction

Scientists are working on new and eco-friendly alternative products, due to the increasingly extreme depletion of oil resources and increased environmental problems at global level. Most of the developing countries have rich agricultural resources and large amounts of agro-wastes are generated after agricultural harvest or pruning. Only a small amount of the agro-wastes is used as fertilizer and fuel and the rest is not evaluated. Turkey produces more than 55 million tons of agricultural waste, such as wheat straw, barley straw, corn stalk, vine stem, rice husk, nutshell and other wastes. Agricultural sector in Turkey annually produces around 600,000 tons of the vine stem and 400.000 tons of the rice husk [1]. Vine stem and rice husk has not been used in any manufacturing of value-added products for industrial and domestic usage in Turkey. Generally, the natural fibers such as wood, cotton, flax, hemp, jute, sisal, and sugarcane fibers are used to reinforce thermoplastics [2-3]. Agricultural wastes are potential alternative waste materials to produce polymer based composite products would help protect the environment [4]. New bio-products derived from renewable plants and agricultural wastes have various advantages, such as biodegradable, low density, high specific stiffness and strength, their low processing energy in the case of chopped fibers, less tool wear, availability, and eco-efficiency [5-6]. Agricultural wastes are also produced abundantly in a large volume at low cost [7]. Value-added and ultralight composite products for the automotive and transportation industries were produced from wheat straw. With natural fiber/polymer composites, it was possible to reduce car weight by up to 35%. This was translated into lower fuel consumption and the lower environmental impact [8]. Agro-wastes have been also used as fillers in polymers to achieve cost savings and to impart some desirable properties [9]. Natural fiber/PP composite materials have been used in automotive applications and have recently been investigated for use in construction products such as building profiles, decking, railing products, etc. [10]. However, the use of agro-fibers exhibits some drawbacks such as thermal degradation at relatively low temperature because of the presence of cellulose and hemicellulose. The thermal degradation limits the allowed processing temperature to lower than 200 °C and restricts the type of thermoplastics that can be used with agro-fibers to some commodity thermoplastics such as PP, PE, PS, and PVC [11]. Due to their poor resistance to moisture, moisture absorbed by the composite leads to dimensional changes and decrease in mechanical performance [12-13]. Besides, its incompatibility between the hydrophilic properties of natural fibers and the hydrophobic nature of the polymer matrix generally leads to poor fiber–matrix interfacial adhesion [14-15]. Moreover, many scientific studies have continued to develop thermoplastic composite with agricultural wastes. One of them is studies on hybrid composites. The incorporation of two or more natural fibers into a single matrix has led to the developing hybrid composites [16]. Hybrid composites prepare by hybridization of natural fibers with natural or synthetic fibers in order to achieve the best utilization of the positive attributes of one fiber and to reduce its negative attributes as far as practicable [17]. The concept of hybridization provides flexibility to the engineers to tailor the material properties according to specific requirements [18]. With hybrid natural fiber polymer composites, the properties in a more cost-effective way that cannot be attained in binary systems containing one type of fiber/filler dispersed in the matrix can achieve [15]. However, further research on the hybridization of natural fibers is needed to explore the potential of hybrid composites. Hybrid composite exhibits an interesting properties not found in single natural fiber reinforced composites.

The objective of this study was to investigate the influence of single rice husk and hybrid rice husk/vine stem on the morphological, mechanical, and thermal properties of polypropylene as a function of the single RH content (10, 20 and 30 wt.%) and the hybrid RH/VS weight fractions (3:7/5:5/7:3) in the composite. The mechanical, thermal, and morphological characterization of the RH-PP and RH-VS-PP composites were performed by universal testing, dynamical mechanical analysis (DMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

2. Materials and Method

2.1. Materials

The matrix material used in this study, which was provided by İzmir Makine Sanayi (Turkey), is polypropylene copolymer (PP, LG Chem M 1500, Korea) with a melt flow rate of 16 g/10 min (230 °C/2.16 kg) and a density of 0.9 g/cm^3. Rice husk (RH) as an agricultural waste was obtained from İzmir Makine Sanayi (Turkey). Vine stem (VS) waste collected from Manisa city of Turkey was broken into small pieces with an axe. RH and VS were ground with a laboratory type knife mill (Mertest LB160, Turkey). Afterwards, particles were passed through a 60 and 140 mesh sieves, respectively. Particles greater than 100 µm and less than 250 µm were taken for composite production. Particles were oven-dried at 70°C for 48 h to remove moisture and then were stored in plastic bags before preparing the composites. The agricultural waste materials were used without any surface treatment.

2.2. Manufacturing of composite materials

Manufacturing of RH-PP composites and RH-VS-PP hybrid composites was achieved by using a laboratory scale high-speed thermokinetic mixer (Gülnar Makine, Turkey). In a thermo-kinetic mixer, blades on a high-speed shaft accelerate the chopped fibers/particles and give them high kinetic energy. When they hit the chamber wall, thermal energy emerges [19-20]. Seventy grams of agricultural wastes as reinforcing fillers and PP (as plastic granules) were firstly mixed physically and the mixture was processed for 25-30 s at 2000 rev/min speed in the high-speed thermokinetic mixer to obtain compound in the form of dough. PP based composites with 10, 20, 30 wt% of RH (10RH-90PP, 20RH-80PP, 30RH-70PP, respectively) were prepared. According to mechanical test results, RH-VS-PP hybrid composites were produced. Weight fractions of VS into RH-90PP were selected as 3, 5, 7 wt%. Composite plates were prepared by compression molding technique. (Gülnar hot and cold hydraulic press with controlled heating, cooling and pressure, Turkey). The composite plates were produced by the help of hydraulic hot and cold press with controlled heating, cooling and pressure at 180 °C for 180 s at 120 bar pressure in hot press, then composite plates were cooled at 25 °C for 120 s at 120 bar pressure in cold press. The concentrations of the reinforcing fillers in the composites are shown in Table 1.

Table 1. Reinforcing filler loading levels for polypropylene

Formulations	RH	VS	PP
PP	N/A	N/A	100
10RH-90PP	10	N/A	90
20RH-80PP	20	N/A	80
30RH-70PP	30	N/A	70
7RH-3VS-90PP	7	3	90
5RH-5VS-90PP	5	5	90
3RH-7VS-90PP	3	7	90

2.3. Characterization

Particle size analyses of the ground rice husk and vine stem were performed by a particle size analyzer (Malvern Mastersizer 3000, Malvern Panalytical, UK), based on laser scattering and the average particle size was measured. Tensile properties such as tensile strength and Young's modulus of PP and its composites were determined according to ASTM D-638 standard.

Tensile tests were carried out at a universal testing machine having 5 kN load cell (Shimadzu Autograph AGS-X Series precision universal tester, Japan) at a cross-head speed of 50 mm/min at room temperature. For each composite, five specimens were tested to obtain reliable tensile properties and their corresponding standard deviations.The three-point bending tests were conducted by using ASTM D-790 standard on a universal testing machine (Shimadzu Autograph AGS-X Series precision universal tester, Japan). Three-point bending tests were performed at a cross-head speed of 1 mm/min and a span length of 32 mm at room temperature. Three samples from each group were tested. The storage moduli, loss moduli and Tan δ of PP and its composites were evaluated using a dynamic mechanical analyser (DMA Q800, TA Instruments Inc.,USA). Single cantilever and multi frequency-strain modulus mode were utilized in DMA which were made in the temperature range from 35 and 140 °C in air atmosphere. Thermogravimetric analyses of the vine stem and rice husk particles, and the composites were conducted by using thermogravimetric analyzer (SDT Q600, TA Instrument Inc., USA). The analyses were performed by a heating rate of 10 °C/min in the range of 30-600 °C under nitrogen atmosphere. DSC analyses were made by using a differential scanning calorimeter (DSC Q2000, TA Instruments Inc., USA). Specimens were firstly heated from 20°C to 200°C at a heating rate of 10°C/min under a nitrogen atmosphere and held for 3 min to erase the thermal history. The specimens were cooled to 20°C at a cooling rate of 10 °C/min. Then, a second heating was performed to 200°C with a heating rate of 10 °C/min. The surface of vine stem and rice husk particles, and the fractured surfaces of PP based composites were gold coated by using a plasma sputtering apparatus. Then, SEM analyses of particles, and fracture surfaces of composites were carried out by using a scanning electron microscope (300 VP FE-SEM, Carl Zeiss AG, Germany) operated at an acceleration voltage of 3 kV for particles and 5 kV for composites.

3. Results and Discussion

3.1. Particle size analysis

Particle size distributions of the ground VS and RH were presented in Figure 1 a-b. When the particle size distribution of VS was observed, D(10), D(50), and D(90) values of VS were determined to be 116, 217, and 412μm, respectively. According to Figure 1a, the particle volume distribution of VS particles shows a gaussion or normal distribution. Besides, D(10), D(50) and D(90) values of RH were obtained to be 68.6, 238 and 512 mm, respectively. From Figure 1b, the curve shows the presence of some particles smaller than 100 μm and larger than 1000 μm.

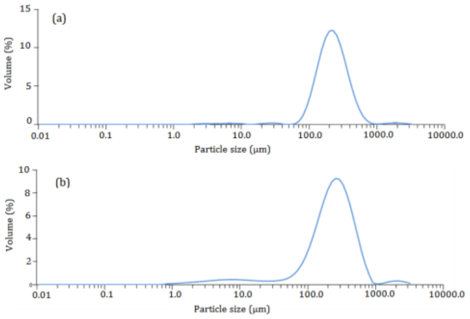

Figure 1. Particle size distributions of (a) VS and (b) RH particles

3.2. Tensile properties

The effects of RH and VS loading on the tensile strength and the Young's modulus values of the PP and its composites are shown in Figure 2. Table 2 shows the tensile strength and Young's modulus values of the neat PP, RH-PP composites, RH-VS-PP hybrid composites.

Table 2. Mechanical properties of the neat PP, RH-PP composites, RH-VS-PP hybrid composites.

	TS (MPa)	***YM (MPa)***	***FS (MPa)***	***FM (MPa)***
PP	22.3	819.9	33.8	971.2
10RH-90PP	31.0	1335.7	45.2	1369.6
20RH-80PP	25.9	1329.3	51.8	2326.3
30RH-70PP	22.2	1371.0	38.2	1536.3
7RH-3VS-90PP	29.7	1264.6	46.7	1392.9
5RH-5VS-90PP	30.3	1231.9	53.5	1599.3
3RH-7VS-90PP	30.4	1248.8	55.0	2055.8

TS: Tensile Strength, YM: Young's Modulus, FS: Flexural Strength, FM: Flexural Modulus.

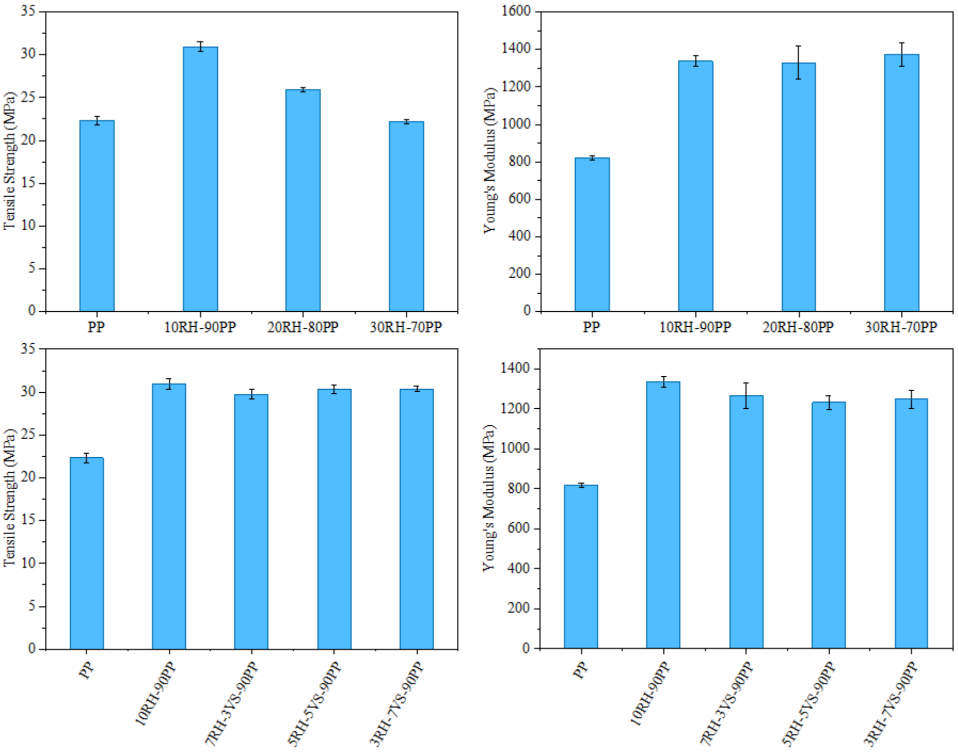

Figure 2. The effects of RH and VS loading on the tensile strength and Young's modulus of the PP and its composites.

It was observed that tensile strength of neat PP is 22.3 MPa. It is clearly seen that 10 wt% RH adding into the PP matrix considerably increased the tensile strength of PP. Among RH-PP composites, 10RH-90PP showed the best improvement in terms of tensile strength, the reason of which could be the good dispersion of RH into PP matrix. In hybrid composites, VS and RH loadings have a similar effect on tensile strength as well as 10RH-90PP. However, beyond the RH weight fraction of 10 wt% in PP, tensile strength began to decrease. The decrease in tensile strength may be explained by the increase of the interfacial surface area with filler loading. Since the fillers are very small, a high interfacial surface area exists between the polar fillers and the non-polar matrix. As this interfacial surface area increases, the worsening bonding between them decreases the tensile strength [10]. With the increase in filler, stress concentration zones in the matrix may occurs due to sharp corners of irregularly-shaped filler particles during tensile loading [21].

Young's modulus of PP considerably increased with the addition of RH weight fraction of 10 wt% into PP. When 10 wt% RH was added into PP, the Young's modulus is increased by about 62.9 %. Young's modulus of the filler is higher than the that of the matrix and this leads to an increase in Young's modulus of PP[22]. It is interesting to note that Young's moduli of 20RH-80PP and 30RH-70PP composites have a similar value as compared to that of 10RH-90PP composite. Besides, Young's modulus values of hybrid composites are lower than that of 10RH-90PP. It can be said that with adding of VS filler in RH-PP, PP hybrid composites become less stiffer. Young's modulus of the VS filler may be lower than the that of the RH.

3.3. Flexural properties

The flexural properties of neat PP, RH-PP and RH-VS-PP composites at different filler loading are shown in Figure3. Flexural strength and flexural modulus values of neat PP and its composites are given in Table 2.

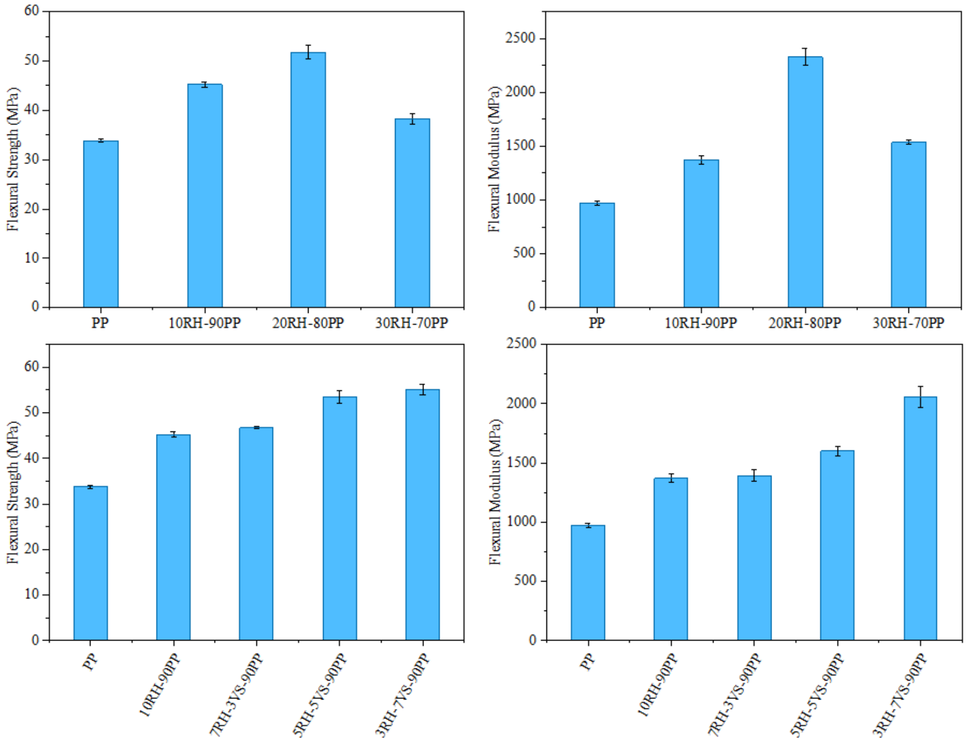

Figure 3. The effects of RH and VS loading on the flexural strength and flexural modulus of PP and its composites.

It was found that neat PP has flexural stength and flexural modulus values around 33.8 MPa and 971.2 MPa, respectively. The flexural strength values of PP composites containing RH were higher than that of PP. It was concluded that among RH-PP composites, the best flexural strength is found in 20RH-80PP which is approximately 51.8 MPa. The presence of silica in the rice husk enhanced the stiffness of the composites which was evidenced by a maximum increase in the flexural strength value compared to the tensile strength value [23]. Higher than 20 wt% of RH, flexural strength of composite decreased, which may be related to the agglomeration. Flexural strength values of 10RH-90PP, 7RH-3VS-90PP, 5RH-5VS-90PP, 3RH-7VS-90PP composites were obtained to be 45.2, 46.7, 53.5, and 55.0 MPa, respectively. Among all composites, 3RH-7VS-90PP hybrid composite has the highest flexural strength value which is approximately 55.0 MPa. This behaviour can be attributed to hybridization effect as both fillers contributed higher flexural strength to the composite. The flexural properties depend on the hybrid composition and an arrangement of the fiber piles [24].

It has clearly shown that flexural modulus values of PP increased with addition of RH up to 20 wt % and then flexural modulus decreased as the weight fraction of RH increased from 20 to 30 wt %. This decrement is due to the possible agglomeration of the RH, which can act as a stress concentration point. It was observed that incorporation of VS into RH-PP made an increase in flexural modulus. It can be reported that the highest flexural modulus value among hybrid composites was obtained to be 2055.8 MPa for 3RH-7VS-90PP. Moreover, the flexural modulus of the3RH-7VS-90PP composite was approximately 50% higher than that of 10RH-90PP. The flexural modulus of the PP matrix hybrid composites shows the similar trends as the flexural strength.

3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analyses were performed to understand the viscoelastic behavior of neat PP and agricultural waste particulate (RH, VS) reinforced PP composites. Variations of storage modulus (E′), loss modulus (E″), Tan delta of RH-PP and RH-VS-PP composites as a function of temperature are represented in Figures 4 and 5.

The storage modulus values are given in Table 3. DMA results clearly indicate that the storage modulus values of RH-PP and RH-VS-PP (except for 5RH-5VS-90PP) composites are higher than that of PP throughout the whole temperature scale. Increases in storage modulus of 10RH-90PP, 20RH-80PP, and 30RH-70PP are 21.7, 29.0, and 33.4 %, respectively, when compared to that of PP at 35 °C. Storage modulus increases due to mechanical limitation posed by increasing filler content embedded in the polymer [25].

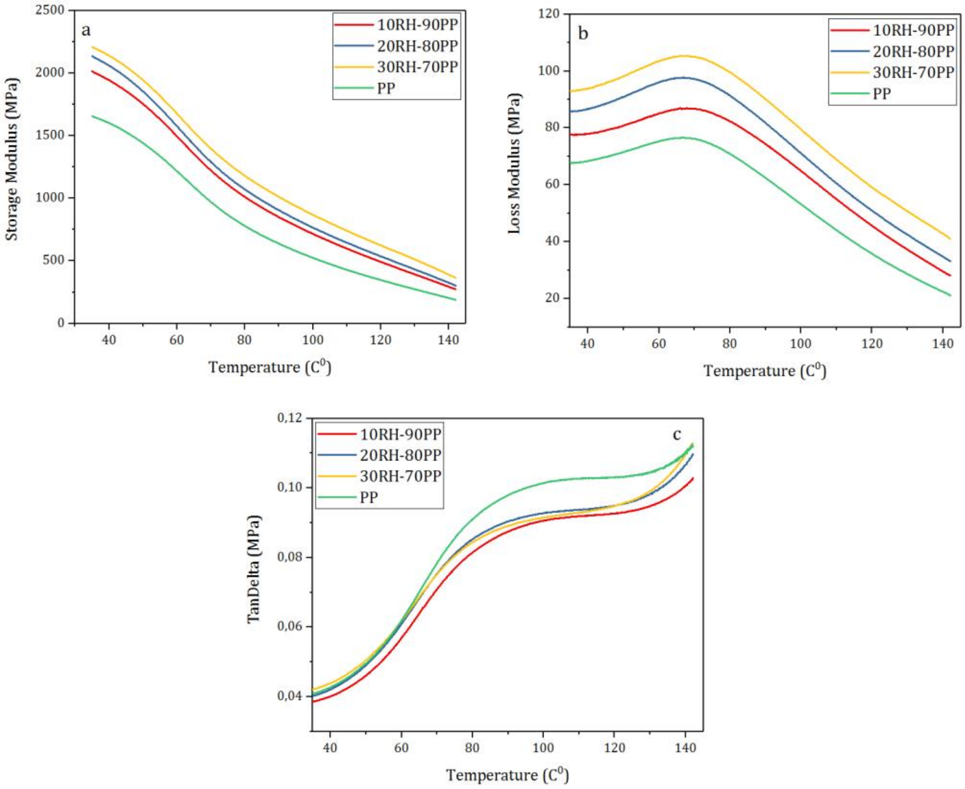

Figure 4. Variation of a) storage modulus (E′) b) loss modulus (E″) c) Tan delta of PP and RH-PP composites as a function of temperature.

Table 3. Storage modulus values of the PP and its composites as a function of temperature.

	Storage Modulus (MPa)					
Sample Name	**35°C**	**50°C**	**75°C**	**100°C**	**130°C**	**SM_{130}/SM_{30}**
PP	1656.0	1440.4	866.6	524.13	273.53	0.165
10RH-90PP	2015.5	1753.0	1105.8	715.89	392.29	0.195
20RH-80PP	2136.1	1851.5	1171.0	764.93	431.09	0.202
30RH-70PP	2209.0	1940.5	1278.1	868.86	511.88	0.232
7RH-3VS-90PP	1835.6	1586.9	989.4	641.79	359.07	0.196
5RH-5VS-90PP	1608.6	1420.2	899.7	562.38	309.84	0.193
3RH-7VS-90PP	1780.7	1544.4	959.8	624.78	352.37	0.198

The retention ratio can be defined as the ratio of the storage modulus at 130 °C to that at 35 °C. The retention ratios of PP, 10RH-90PP, 20RH-80PP, and 30RH-70PP were obtained to be 0.165, 0.195, 0.202, and 0.232, respectively. It can be seen from Table 3 that the RH-PP composites have improved mechanical properties with respect to PP at high temperatures. The storage modulus values of

RH-VS-PP composites are lower than that of 10RH-90PP throughout the whole temperature scale. Namely, the storage modulus decreased when VS was loaded into RH-PP. Among hybrid composites, 5RH-5VS-90PP composite has generally minimal effect on storage modulus versus temperature as compared to that of PP. The retention ratios of PP, 10RH-90PP, 7RH-3VS-90PP, 5RH-5VS-90PP, and 3RH-7VS-90PP were obtained to be 0.165, 0.195, 0.196, 0.193, and 0.198, respectively. RH-VS-PP composites have similar retention ratios. As can be seen from Figures 4a and 5a, as expected, storage modulus values of all composites decreased with the increase in temperature. The decrease in the storage modulus due to the increase in the molecular mobility of the polymer chains with increasing temperature [26].

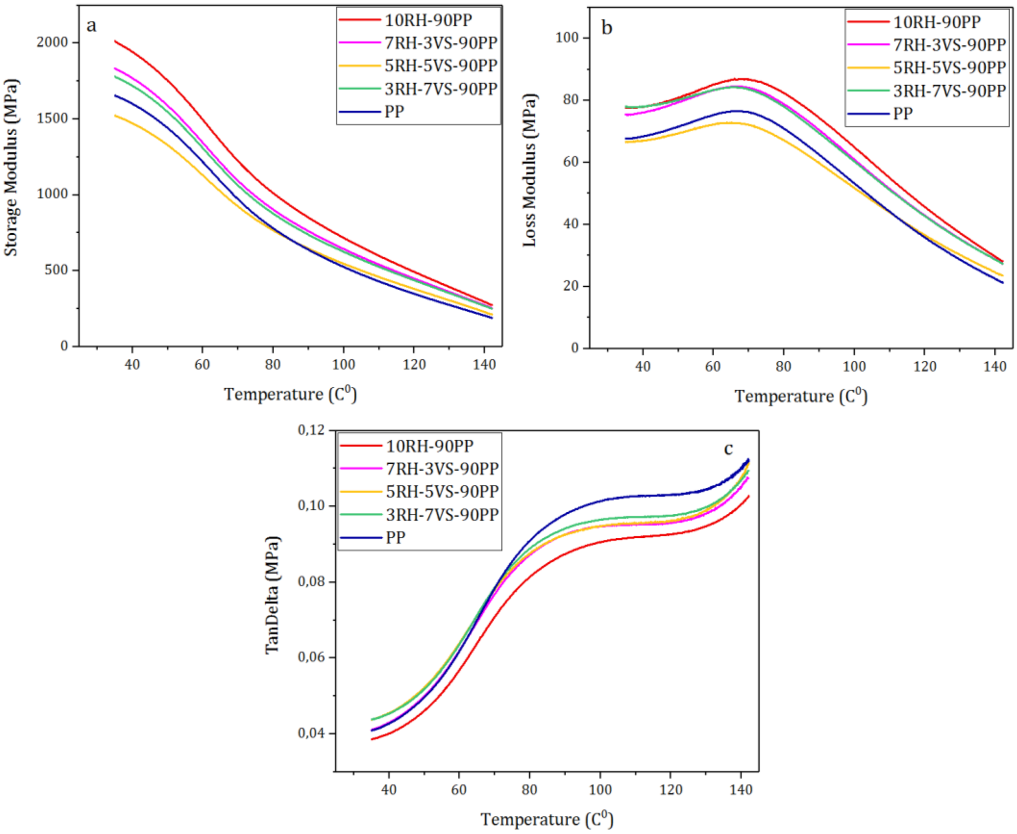

Figure 5. Variation of a)storage modulus (E′) b) loss modulus (E″) c) Tan delta of PP and RH-VS-PP composites as a function of temperature

Figures 4b and 5b display the loss modulus (E″) values of PP and its composites. As seen in Figures 4b and 5b, the E″ of RH-PP and RH-VS-PP composites was much higher than that of the PP in the whole temperature range. The loss modulus continued to increase as the RH weight fraction was increased. The increase in loss modulus values with increase in RH content may be attributed to the decrease in energy absorption [27]. Besides, the loss modulus values of RH-VS-PP composites are generally lower than that of 10RH-90PP throughout the whole temperature scale. The tan delta curves for all the composites are shown in Figures 4c and 5c. Tan delta can be related to interfacial properties between filler and polymer matrix. If stress is applied to particle filled polymeric material, energy dissipation takes place in the polymer matrix and interface between filler and matrix [28]. Relatively stronger interface can be described by less energy dissipation and lower intensity of tan delta peak [29-30]. Tan delta peak height is lower after RH and VS loading. Strong interaction of RH particles and PP matrix may be occur at higher RH loading, which decreased the mobility of molecular chains at the interface and the tan delta peak is decreased accordingly [31]. However, it can be seen from

Fig. 5c, for hybrid composites, VS particles are less effect on Tan delta peak height.

3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analyses of PP, RH-PP, and RH-VS-PP composites are shown in Figures 6 and 7. Degradation temperatures, and mass losses of PP and its composites are also given in Table 4. PP exhibited one-step degradation process up to 600 °C. The degradation of RH-PP and RH-VS-PP composites takes place in a two-step degradation process. First step is due to decomposition of agricultural waste filler and the second step is due to PP decomposition [25]. Lignocellulosic materials are thermally decompose between 150°C and 500°C. While the mass loss of PP occurs mainly between 300 °C and 500 °C, the thermal decomposition of hemicelluloses, cellulose, and lignin occurs between 150-350°C, 275-350°C and 250-500°C, respectively [32-34]. It can be seen from the Table 4 that T_{onset1} of the RH-PP composites decreases with increasing RH weight fractions. However, when VS was added to the RH filled PP composites by keeping the total weight fraction at 10 wt.%, it was seen that initial decomposition temperatures are higher that that of 10RH-90PP composite. T_{onset1} of the RH-VS-PP hybrid composites increases with increasing VS weight fractions. It could be said that addition of VS causes a delay in the degradation process and increases the initial decomposition temperatures. Maximum degradation temperatures of PP, 10RH-90PP, 20RH-80PP, and 30RH-70PP are 443.1, 465.4, 465.3, and 466.8 °C, respectively. In particular, as 10wt.% RH was added into PP, there was a shift upward of the thermal degradation temperature. It can be said that RH loading affects the maximum degradation temperature of PP. Besides, the maximum degradation temperatures for 7RH-3VS-90PP, 5RH-5VS-90PP, and 3RH-7VS-90PP were obtained to be 464.6, 465.5, and 465.2 °C, respectively.

Table 4. Degradation temperatures and mass losses of PP and its composites.

Samples	$T_{onset\ 1}$ (°C)	Mass Loss to T_{onset1}(%)	T_{onset2} (°C)	Mass Loss to T_{onset2}(%)	T_{max} (°C)	Mass Loss to 600°C(%)
PP	-	-	283.78	97.60	443.07	97.60
10RH-90PP	236.82	6.80	368.99	90.71	465.35	97.51
20RH-80PP	236.38	10.84	382.22	82.76	465.29	93.60
30RH-70PP	227.08	14.42	384.17	74.24	466.77	88.66
7RH-3VS-90PP	238.83	5.39	368.51	91.66	464.58	97.05
5RH-5VS-90PP	244.70	5.96	371.94	90.22	465.47	96.18
3RH-7VS-90PP	254.49	6.44	392.49	89.88	465.20	96.32

*T_{onset1}: First Degredation Temperature, T_{onset2}: Second Degredation Temperature, T_{max}: Maximum Degredation Temperature.

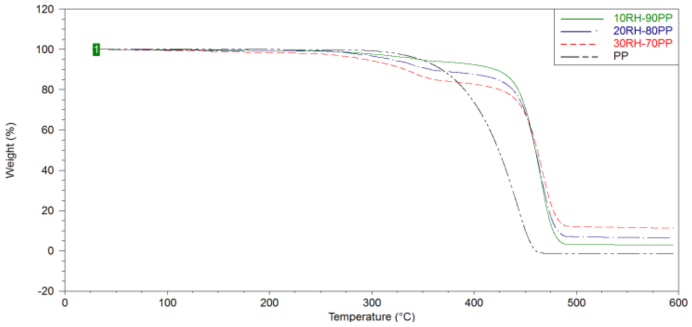

Figure 6. TGA thermograms of PP and RH-PP composites.

VS loading into RH-PP had not remarkably effect on maximum degradation temperature. On the other hand, it can be said that RH-PP and RH-VS-PP composites showed an increase in thermal stability, which is indicated by shifting in maximum degradation temperature to a higher degradation temperature, as compared to that of PP. TGA results also show that mass losses up to 600°C are 97.6, 97.5, 93.6 and 88.7 % for PP, 10RH-90PP, 20RH-80PP, and 30RH-70PP, respectively. It can be noted that as the weight fraction of RH in composites was increased, mass losses up to 600°C decreased. Carbonaceous layer produced from the thermal degradation of cellulosic fibers can enhance the thermal stability of the PP [35]. As RH is added into PP, the mass losses are decreased. When PP and 30RH-70PP are compared, PP lost 97.6% of its total weight and 30RH-70PP lost 88.7% of its total weight within the temperature range of 20-600 °C. This indicates that the thermal resistance of the 30RH-70PP is good. Also, mass losses up to 600°C for 7RH-3VS-90PP, 5RH-5VS-90PP, and 3RH-7VS-90PP were found to be 97.1, 96.2, and 96.3%, respectively. Mass losses up to 600°C of RH-VS-PP composites lightly decreased as compared to that of 10RH-90PP.

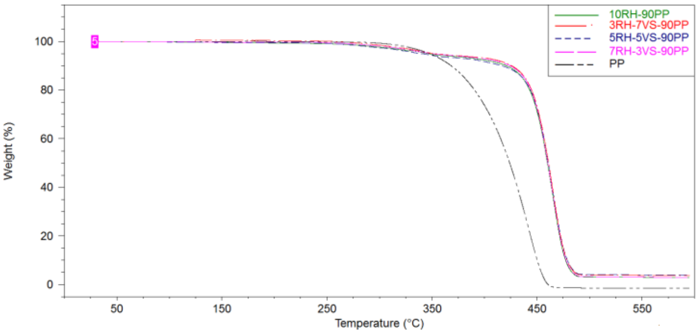

Figure 7. TGA thermograms of RH-VS-PP composites.

3.6. DSC analysis

DSC data are summarized in Table 5. DSC data includes the melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), and degree of crystallinity (X_c).The degree of crystallinity (X_c) of samples were calculated [36]. Melting enthalpy of 100% crystalline PP was taken as 209 J/g [37]. The incorporation of RH or/and VS is investigated to have little effect on the melting temperature of PP. Small variation in the melting temperature of PP indicates that the crystal size of PP did not change remarkably [25]. As can be seen from Table 5, all T_c values of the PP based composites are higher than that of PP. Increase in T_c can be considered to be due to the nucleation effect of the RH [38]. Natural fibers directly act as sites for heterogeneous nucleating thus inducing the crystallization of the matrix material [39]. RH loading into PP improved the crystallization of PP because T_c of RH-PP composites enhanced by 2.8-3.1 °C with respect to that of PP. RH-PP composites could begin to crystallize at higher temperature due to the effect of the RH particles in the PP matrix. As noted above, if the RH particles can play the role of heterogeneous nucleation sites in the PP matrix, it would be useful to increase the crystallization of the composite melts. However, the increase in weight fraction of VS in RH-PP composite caused to reduce T_c. Also, ΔHc and ΔHm increased by adding %10 RH into PP. However, ΔHc and ΔHm decreased gradually with increasing of RH loading. It can be also said that to ΔHc and ΔHm increased with hybrid filler effect for 7RH-3VS-90PP. It can be seen that X_c increases with increasing RH filler weight fraction. RH loading into PP increased the X_c of PP by 4.9-7.7%. 30RH-70PP exhibited the highest crystallinity in the composites. This shows the nucleation role played by the RH. When 3wt. %VS and 5wt. %VS are added into RH-PP composites, the degree of crystallinity of RH-VS-PP composite increases as compared to that of 10RH-90PP. Moreover, the incorporation of 3wt.% VS into RH-PP composite caused the increase in X_c of the composite (about 2%) as compared to that of 10RH-90PP. 7RH-3VS-90PP had the highest crystallinity in the hybrid composites.

Table 5. DSC data of PP, RH-PP and RH-VS-PP composites

Samples	Tm, °C	Tc, °C	ΔHc, J/g	ΔHm, J/g	Xc, %
PP	165.6	122.4	98.0	87.4	41.8
10RH-90PP	166.5	125.2	100.6	87.9	46.7
20RH-80PP	165.6	125.5	93.0	81.6	48.8
30RH-70PP	165.6	125.2	79.7	72.5	49.5
7RH-3VS-90PP	166.1	125.7	102.6	91.6	48.7
5RH-5VS-90PP	166.7	124.1	98.0	88.7	47.2
3RH-7VS-90PP	164.9	123.7	100.8	87.7	46.6

3.7. SEM analysis

SEM images of VS and RH particles were shown in Figure 8 a-b. VS particles have generally a high aspect ratio. Morphologies of VS and RH particles show irregularly-shaped and the surfaces are rough. Sharp corners of these irregularly-shaped particles may occurs stress concentration areas in the PP matrix during mechanical loading. However, rough surfaces can increase the mechanical bonding between the particles and PP matrix. SEM micrographs of the fractured surfaces of RH-PP and RH-VS-PP composites after tensile tests were shown in Figure 9 and 10, respectively. The good dispersion of RH into PP matrix can be seen from Figure 9 a-b. However, the interfacial surface area between the RH particles and the PP matrix increased with the higher RH loading.

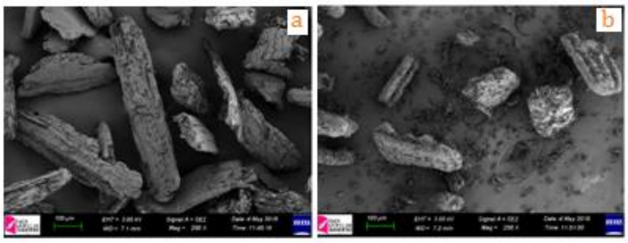

Figure 8. SEM images of a) VS and b) RH particles.

It can be seen that the increase in interface surface area worsened the interfacial bonding between the hydrophilic RH particles and the hydrophobic PP matrix (Figure 9c). RH particles were pulled out from the PP matrix the fracture process. The good dispersion of RH and VS particles into PP matrix can be seen from Figure 10 a-c.

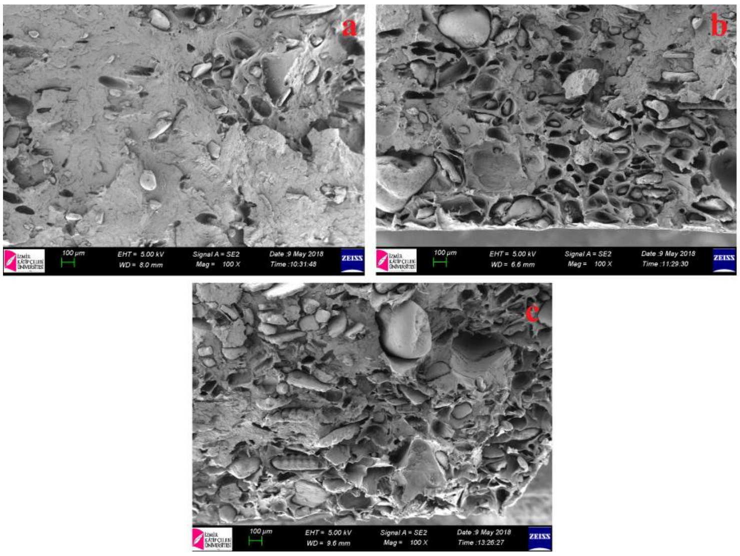

Figure 9. SEM images of a) 10RH-90PP, b) 20RH-80PP. and c) 30RH-70PP.

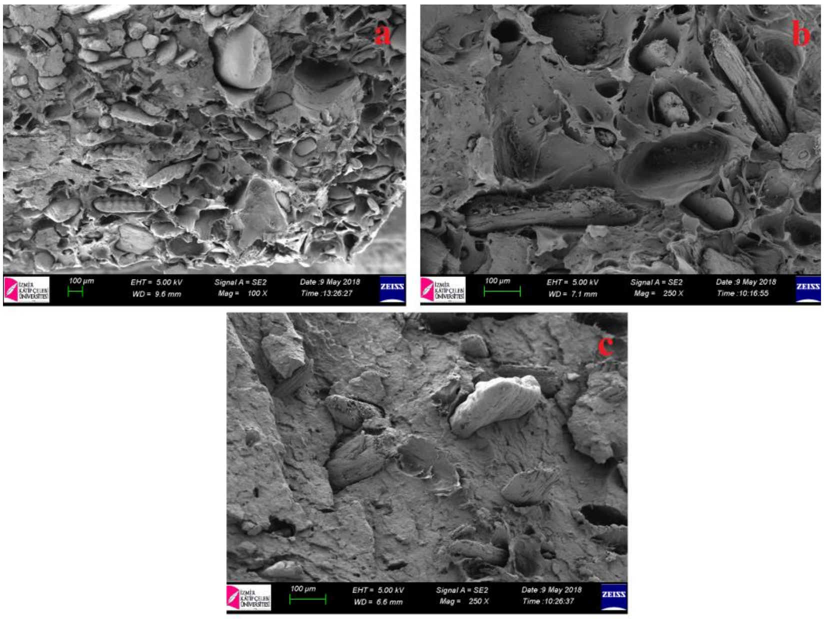

Figure 10. SEM images of a) 7RH-3VS-90PP, b) 5RH-5VS-90PP. and c) 3RH-7VS-90PP.

4. Conclusion

This study gives feasibility of using agro-waste like rice husk and vine stem in the fabrication of polypropylene matrix composites. It was observed that the hybridization of rice husk and vine stem into polypropylene enhanced the flexural strength, onset degradation temperatures and X_c of the composite. The incorporation of 3wt.% VS into RH-PP composite caused the increase in X_c of the composite (about 2%) as compared to that of 10RH-90PP. In hybrid composites, VS and RH loadings have a similar effect on tensile strength as well as 10RH-90PP. Beyond the RH weight fraction of 10 wt% in PP, tensile strength began to decrease. The flexural strength values of PP composites containing RH were higher than that of PP. Among RH-PP composites, the best flexural strength is found in 20RH-80PP which is approximately 51.8 MPa. Among all composites, 3RH-7VS-90PP hybrid composite has the highest flexural strength value which is approximately 55.0 MPa. This behaviour can be attributed to hybridization effect as both fillers contributed higher flexural strength to the composite. The storage modulus values of RH-PP composites increase with increasing RH loading throughout the whole temperature scale. However, the storage modulus decreased when VS was loaded into RH-PP as compared to that of 10RH-90PP. T_{onset1} of the RH-PP composites decreases with increasing RH weight fractions. However, T_{onset1} of the RH-VS-PP hybrid composites increases with increasing VS weight fractions. RH-PP and RH-VS-PP composites showed an increase in thermal stability, which is indicated by shifting in maximum degradation temperature to a higher degradation temperature, as compared to that of PP. This study showed that rice husk and vine stem particles can work well with PP as reinforcing filler. The rice husk and vine stem particles have great potential to boost the mechanical and thermal properties of PP as demanded in many structural applications.

Acknowledgemet

This study was financially supported by Izmir Katip Celebi University, Department of Scientific Research Projects (BAP project no: 2017-TYL-FEBE-0050).

References

[1] Acar, H., Salan, T., Altuntaş, E., Alma, M. H., 2014. Yüksek Yoğunluklu Polietilen (YYPE) ve Atık Pirinç Saplarından Üretilen Kompozitlerin Bazı Mekanik ve Fiziksel Özelliklerinin Belirlenmesi. II. Ulusal Akdeniz Orman ve Çevre Sempozyumu, 22-24 Ekim, Isparta, 808-818.

[2] Bledzki, A.K., Gassan, J., 1999. Composites Reinforced with Cellulose Based Fibres, Progress in Polymer Science, Cilt. 24, s.221–274. http://dx.doi.org/10.1016/S0079-6700(98)00018-5

[3] Bledzki, A.K., Sperber, V.E., Faruk, O. 2002. Natural and Wood Fibre Reinforcement in Polymers. Rapra Review Reports Volume 13 (8), UK, 144s.

[4] Bujjibabu, G., Chittaranjan Das, V., Ramakrishna, M., Nagarjuna, K. 2018. Mechanical and Water Absorption Behavior of Natural Fibers Reinforced Polypropylene Hybrid Composites, Materials Today: Proceedings, Cilt. 5, s. 12249–12256. https://doi.org/10.1016/j.matpr.2018.02.202

[5] Edhirej, A., Sapuan, S.M., Jawaid, M., Zahari, N.I. 2017. Cassava/Sugar Palm Fiber Reinforced Cassava Starch Hybrid Composites: Physical, Thermal and Structural Properties, International Journal of Biological Macromolecules, Cilt. 101, s. 75–83. Doi: 10.1016/j.ijbiomac.2017.03.045.

[6] Reis, K. C., Pereira, L., Melo, I. C. N. A., Marconcini, J. M., Trugilho, P. F., Tonoli, G. H. D. 2015. Particles of Coffee Wastes as Reinforcement in Polyhydroxybutyrate (PHB) Based Composites, Materials Research, Cilt. 18(3), s. 546-552. DOI: http://dx.doi.org/10.1590/1516-1439.318114

[7] Islam, Md. S., Hasbullah, N. A. B., Hasan, M., Talib, Z. A., Jawaid, M., Haafiz M.K.M. 2015. Physical, Mechanical and Biodegradable Properties of Kenaf/Coir Hybrid Fiber Reinforced Polymer Nanocomposites, Materials Today Communications, Cilt. 4, s. 69–76. https://doi.org/10.1016/j.mtcomm.2015.05.001

[8] El Messiry, M. El Deeb, R. 2016. Analysis of the Wheat Straw/Flax Fiber Reinforced Polymer Hybrid Composites, Journal of Applied Mechanical Engineering, 5:6, doi:10.4172/2168-9873.1000240

[9] Sanjay, M.R., Madhu, P., Jawaid, M., Senthamaraikannan, P., Senthil, S., Pradeep, S. 2018. Characterization and Properties of Natural Fiber Polymer Composites: A Comprehensive Review, Journal of Cleaner Production, Cilt. 172, s. 566-581. DOI: 10.1016/j.jclepro.2017.10.101

[10] Rosa, S. M. L., Santos, E. F., Ferreira, C. A., Nachtigall, S.M.B. 2009. Studies on the Properties of Rice-Husk-Filled-PP Composites-Effect of Maleated PP, Materials Research, Cilt. 12 (3), s. 333-338. http://dx.doi.org/10.1590/S1516-14392009000300014

[11] Silva, R.V., Aquino, E.M.F. 2008. Curauá Fiber: A New Alternative to Polymeric Composites, Journal of Reinforced Plastics and Composites, Cilt. 27(1), s. 103-112. https://doi.org/10.1177/07316844080270010301

[12] Wang, W., Sain, M. Cooper, P.A. 2006. Study of Moisture Absorption in Natural Fiber Plastic Composites, Composites Science and Technology, Cilt. 66(3-4), s. 379-386. doi:10.1016/j.compscitech.2005.07.027

[13] Sanadi, A.R., Caulfield, D.F., Rowell. R.M. 1994. Reinforcing Polypropylene with Natural Fibers, Plastics Engineering, Cilt. 50(4), s. 27-28.

[14] Merajul, H.M., Hasan, M. 2018. Influence of Fiber Surface Treatment on Physicomechanical Properties of Betel Nut and Glass Fiber Reinforced Hybrid Polyethylene Composites, Advances in Materials and Processing Technologies, Cilt. 4 (3), s. 511-525. https://doi.org/10.1080/2374068X.2018.1465322

[15] Haque, M.M., Hasan, M. 2016. Mechanical Properties of Betel Nut and Glass Fibre Reinforced Hybrid Polyethylene Composites, International Journal of Automotive and Mechanical Engineering (IJAME), Cilt. 13 (3), s. 3763-3772. DOI: https://doi.org/10.15282/ijame.13.3.2016.18.0308

[16] Zainudin, E.S., Yan,L.H., Haniffah, W.H., Jawaid, M., Alothman, O.Y. 2014. Effect of Coir Fiber Loading on Mechanical and Morphological Properties of Oil Palm Fibers Reinforced Polypropylene Composites, Polymer Composites, Cilt. 35, s. 1418-1425. https://doi.org/10.1002/pc.22794

[17] Jawaid, M., Abdul Khalil, H.P.S. 2011. Cellulosic/Synthetic Fibre Reinforced Polymer Hybrid Composites: A Review, Carbohydrate Polymers, Cilt. 86, s. 1-18. DOI: 10.1016/j.carbpol.2011.04.043

[18] Velmurugan, R., Manikandan, V. 2007. Mechanical Properties of Palmyra/Glass Fiber Hybrid Composites, Composites Part A Applied Science and Manufacturing, Cilt. 38(10), s. 2216-2226. DOI: 10.1016/j.compositesa.2007.06.006

[19] Faraz, M.I., Bhowmik, S., De Ruijter, C., Laoutid, F., Benedictus, R. , Dubois, Ph., Page, J.V.S., Jeson, S. 2010. Thermal, Morphological, and Mechanical Characterization of Novel Carbon Nanofiber-Filled Bismaleimide Composites, Journal of Applied Polymer Science, Cilt. 117 (4), s. 2159-2167. https://doi.org/10.1002/app.31842

[20] Gopakumar, T.G., Page, D.J.Y.S. 2005. Compounding of Nanocomposites by Thermokinetic Mixing, Journal of Applied Polymer Science, Cilt. 96, s. 1557-1563. https://doi.org/10.1002/app.21597

[21] Deka, P.P., Samanta, S. 2015. Experimental Investigation on Mechanical Properties of Rice Husk Filled Jute Reinforced Composites, International Journal of Materials and Metallurgical Engineering, Cilt. 9 (12), s. 1431-1436.

[22] Shumigin, D., Tarasova, E., Krumme, A., Meier, P. 2011. Rheological and Mechanical Properties of Poly(Lactic) Acid/Cellulose and LDPE/Cellulose Composites, Materials Science, Cilt. 17(1), s. 32-37. http://dx.doi.org/10.5755/j01.ms.17.1.245

[23] Prithivirajan, R., Jayabal, S., Bharathiraja, G. 2015. Bio-Based Composites From Waste Agricultural Residues: Mechanical and Morphological Properties, Cellulose Chemistry and Technology, Cilt. 49(1), s. 65-68.

[24] Phanindra Varma, D., Rama Krishna, T., Madhukiran, J., Lakshmi Poornima, C.H. 2015. Estimation of Mechanical Properties on Pineapple/Jute Hybrid Natural Fiber Composites, International Journal of Modern Engineering Research (IJMER), Cilt. 5(9), 43-47.

[25] Kaya, N., Atagür, M., Akyüz, O., Seki, Y., Sarıkanat, M., Sütçü, M., Seydibeyoğlu, M.O., Sever, K. 2017. Fabrication and Characterization of Olive Pomace Filled PP Composites, Composites Part B: Engineering, In press. https://doi.org/10.1016/j.compositesb.2017.08.017

[26] Palanivel, A., Veerabathiran, A., Duruvasalu, R., Iyyanar, S., Velumayil, R. 2017. Dynamic Mechanical Analysis and Crystalline Analysis of Hemp Fiber Reinforced Cellulose Filled Epoxy Composite, Polímeros, Cilt. 27(4), s. 309-319. DOI: 10.1590/0104-1428.00516

[27] Nagarajan, T.T., Suresh Babu, A., Palanivelu, K., Nayak, S.K. 2016. Mechanical and Thermal Properties of PALF Reinforced Epoxy Composites, Macromolecular Symposia, Cilt. 361, s. 57-63. https://doi.org/10.1002/masy.201400256

[28] Mohanty, S., Verma, S.K., Nayak, S.K. 2006. Dynamic Mechanical and Thermal Properties of MAPE Treated Jute/HDPE Composites, Composites Science and Technology, Cilt. 66, s. 538–547. DOI:10.1016/j.compscitech.2005.06.014

[29] Sever, K., Atagür M., Tunçalp, M., Altay, L., Seki Y., Sarıkanat, M. 2018. The Effect of Pumice Powder on Mechanical and Thermal Properties of Polypropylene, Journal of Thermoplastic Composite, In press. DOI: 10.1177/0892705718785692

[30] Idicula, M., Malhotra, S.K., Joseph, K., et al. 2005. Dynamic Mechanical Analysis of Randomly Oriented Intimately Mixed Short Banana/Sisal Hybrid Fibre Reinforced Polyester Composites, Composites Science and Technology, Cilt. 65, s. 1077–1087. https://doi.org/10.1016/j.compscitech.2004.10.023

[31] Romanzini, D., Ornaghi Jr, H.L., Amico, S.C., Zattera, A. J. 2012. Influence of Fiber Hybridization on the Dynamic Mechanical Properties of Glass/Ramie Fiber-Reinforced Polyester Composites, Journal of Reinforced Plastics and Composites, Cilt. 31(23), s. 1652–1661. DOI: 10.1177/0731684412459982

[32] Cheewawuttipong, W., Fuoka, D., Tanoue, S., Uematsu, H., Iemoto, Y. 2013. Thermal and Mechanical Properties of Polypropylene/Boron Nitride Composites, Energy Procedia, Cilt. 34, s. 808-817. doi: 10.1016/j.egypro.2013.06.817

[33] Jeske H, Schirp A, Cornelius F. Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wood flour and polypropylene in wood plastic composites (WPC). Thermochimica Acta. 2012;543:165-71.

[34] Kılınc A, Atagur M, Ozdemir O, Sen I, Kucukdogan N, Sever K, et al. Manufacturing and characterization of vine stem reinforced high density polyethylene composites. Composites Part B: Engineering. 2016;91:267-74.

[35] Bodîrlău R, Teacă C-A, Spiridon I. Thermal investigation upon various composite materials. Rev Roum Chim. 2007;52(1-2):153-8.

[36] Gwon JG, Lee SY, Kim JH. Thermal degradation behavior of polypropylene base wood plastic composites hybridized with metal (aluminum, magnesium) hydroxides. Journal of Applied Polymer Science. 2014;131(7)

[37] Selvakumar, V., Manoharan, N. 2014. Thermal Properties of Polypropylene/Montmorillonite Nanocomposites, Indian Journal of Science and Technology, Cilt. 7(S7), s. 136–139.

[38] Rosa, S.M.L., Nachtigall, S.M.B., Ferreira, C.A. 2009. Thermal and Dynamic-Mechanical Characterization of Rice-Husk Filled Polypropylene Composites, Macromolecular Research, Cilt. 17 (1), s. 8-13. https://doi.org/10.1007/BF03218594

[39] Mohamed, M. M. F., Mohamed, R., Azız, N. Z. A., 2016. Effect of Flexural and Thermal Properties of Sustainable Kenaf Fibre and Rice Husk with Mineral Filled PP Hybrid Composite, 63rd The IIER International Conference, 28 February, Phuket, Thailand, 25-29.