The influence of coupling agents on mechanical properties of lignin-filled polypropylene composites

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Abstract: Natural fiber filled/reinforced composite materials are heavily studied in the academy and industry. Lignin is both a natural filling material and a side product of cellulosic bioethanol and paper industries. Lignin has been used as a filling/reinforcing material for twenty years in order to create value-added products. In this study, 10 % wt. soda lignin reinforced polypropylene composites with and without coupling agents was produced by using twin-screw extruder in order to investigate the effect of coupling agent type and the effect of coupling agent content (0.1 %, 0.3 %, and 0.5 % wt.). Mechanical, thermal and morphological properties of the composites were investigated. The results showed that the optimum amount of coupling agents in composites was 0.3% for the best interaction with lignin and polymer. According to TGA analysis, it can be concluded that lignin filled composite is more stable compared to neat copolymer.
Keywords: Lignin, Polypropylene, Mechanical properties, Thermal properties

Lignin polipropilen kompozitlerinde ara yüzey kimyasallarının mukavemete etkisi

Özet: Doğal elyaf ile takviye edilen kompozit malzemeler akademide ve endüstride yoğun çalışılan bir konudur. Lignin doğal bir dolgu maddesi olarak kullanılmasının yanı sıra selüloz esaslı biyoetanol ve kağıt endüstrilerinin de yan ürünüdür. Lignin çok farklı uygulamalarda 20 yıla yakındır kullanılmaktadır. Bu çalışmada soda lignin ve polipropilen kompozitleri çift vidalı polimer işleme makinasında karıştırılmıştır ve 2 farklı ara yüzey ajanı da % 0.1, % 0.3 ve % 0.5 oranlarında karıştırılmıştır. Mekanik özellikler, ısıl özellikler ve morfolojik etkileri incelenmiştir. Sonuçlar göstermiştir ki en iyi sonuçlar % 0.3 yüzey kimyasal oranı ile yapılmıştır. Termogravimetrik analizler lignin katkılı polipropilen kompozitlerinin ısıl kararlılığının daha yüksek olduğunu göstermiştir.
Anahtar kelimeler: Lignin, Polipropilen, Mekanik özellikler, Isıl özellikler

1. Introduction

A strong interest in the use of renewable resources for energy and material production is increasing day by day because of different reasons mainly economic, modest investments and human impacts on the environment (Luong et al. 2012). Use of renewable sources such as sun, wind, hydropower, and biomass for energy and materials have been seen the solution of global problems such as climate change, environmental pollution and security of supply of fossil fuels (De Wild et al. 2012). This growing interest about a green and sustainable chemistry has also contributed to call attention to biomass and specifically on lignocellulosic feedstock as a promising, renewable and vast resource for chemicals (Laurichesse and Averous 2014). Lignocellulosic biomass can be used as renewable feedstock for the co-production of materials, energy, chemicals, and fuels via integral bio-refinery concepts(De Wild et al. 2012).

As a lignocellulosic biomass, lignin has called attention and was started to use in different areas. Among these areas, interest in the development of lignin-containing polymeric

materials has been upheld more or less continuously for the past 20 years (Fan et al. 2011; González Sánchez and Alvarez 1999; Kadla and Kubo 2004; Kharade and Kale 1999; Košíková et al. 1995; Li et al. 2011; Li et al. 1997; Mariotti et al. 2013; Olsson et al. 2011; Sailaja and Deepthi 2010). The study made by Peng et al., (2014) wood flour, lignin and cellulose were chosen to blend with polypropylene (PP) matrix at different loading levels to evaluate the influence of accelerated ultra violet weathering. It is found that the presence of high lignin content caused an acceleration in the discoloration of composites. Moreover, lignin filled composites gave less loss of flexural strength, modulus and cracks (Peng et al. 2014). Zhong et al., (2011) fabricated PP blend with 70 wt% lignin content. According to tensile and flexural test, if lignin content increases, modulus and strength values decreases. The impact strength was enhanced by blending up to 40 wt% alkylated lignin. SEM images has showed that alkylated lignin is homogeneously dispersed in the PP. TGA analysis showed that high lignin content improved the thermal stability (Zhong et al. 2011). The aim of paper made by Pouteau et

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al. (2004) is to investigate good polymer candidates displaying good compatibility with Kraft lignin. It was found that only low molecular weight lignins were compatible with apolar and very polar matrices (Pouteau et al. 2004). Toriz et al. (2002) studied lignin filled (between 10 wt. % and 60 wt. %) polypropylene composites by blending. Tensile and flexural strength were reduced and it was seen a spectacular decrease in un-notched Izod impact strength compared with the properties of neat polypropylene, although Young's modulus and flexural modulus were improved. It was concluded that maleic anhydride grafted polypropylene (MAPP) as a coupling agent improved strength properties (Toriz et al. 2002).

The purpose of this study is the production and characterization of lignin filled polypropylene composites for industrial applications by using different coupling agents in order to decrease the interface mismatch between lignin and polypropylene.

2. Material and methods

2.1. Materials

Protobind 2400 was provided as a gift by GreenValue SA Company. Heterophasic polypropylene copolymer Moplen 2000 HEXP (Tm=165°C, ρ=0.9 g/cm^{3}, Melt flow rate (230°C/2.16 kg) =16g/10 min) produced by Lyondell Basell Company, was used as the polymeric material. PG1190 (POSS) and the commercial coupling agent FUSABOND®E265 (FUSE) were used as a coupling agent.

2.2. Preparation of the materials for extrusion process

Copolymer was grinded by using micronized device with 1400 rpm speed during 15 minutes in order to decrease the particle size of the pellets. Lignin and copolymer were mixed for five minutes until observing the proper mixing in order to produce composites without coupling agent. Lignin and copolymer were mixed with POSS and FUSE respectively with the compositions 0.1%, 0.3% and 0.5% (by weight) when composites with coupling agent was produced.

2.3. Extrusion process

Lignin filled composites with and without coupling agents were manufactured by using twin-screw extruder (co-rotate) branded Labtech. The prepared mixture was placed to the hopper of extruder and feed with 20 rpm. Zone temperatures of extruder were selected between the temperatures 170°C and 185°C. Screw speed is adjusted as 190 rpm. The extruded strand was passed through a water bath and granulated. The granules were dried at 80 ± 2 °C for 1 h to remove any moisture. Table 1 shows produced composites and their sample codes.

Table 1. Produced composites and their samples codes

Composites	Sample codes
Copolymer	cPP
10% Lignin	cPP10L
10% Lignin-0.1% FUSE	cPP10L-0.1F
10% Lignin-0.3% FUSE	cPP10L-0.3F
10% Lignin-0.5% FUSE	cPP10L-0.5F
10%Lignin-0.1% POSS	cPP10L-0.1P
10% Lignin-0.3%POSS	cPP10L-0.3P
10% Lignin-0.5% POSS	cPP10L-0.5P

2.4. Thermokinetic mixer

Melt mixing of the pellets was achieved using a Gelimat, a high-speed laboratory thermokinetic mixer. Composite samples of 50 g were mixed for 15-20 seconds at 2000 rpm in order to get mixture in the form of dough.

2.5. Fabrication of composite plate

After heating the hot press until processing temperature (200°C), produced composite pellets were placed into the mold cavity (15 cm x 15 cm) between Teflon sheets which were used to avoid direct contact of PP composites with the hot press metal platens during heating and pressing. Plates were obtained from the mixture by using Hydraulic Laboratory Press (Labtech) with heating and cooling plates. Samples were pressed under 40 bar pressure at 200°C for 20 seconds and pressed under 120 bar pressure at 20 ^{o}C for 2 minutes.

2.6. Fourier transform infrared (FTIR) analysis

Copolymer, lignin and their composites prepared with FUSE and POSS were investigated with FTIR analysis. Thermo Scientific™ FTIR spectrometer in Attenuated Total Reflection Infrared (ATR-IR) mode was used to obtain the spectra of lignin and lignin composites. Attenuated total reflection infrared (ATR-IR) spectra of the materials were collected at a resolution of 4 cm-1 with a range of 400–4000 cm^{-1} and a number of 16 scans per sample. Spectral outputs were recorded in transmittance mode as a function of wave number.

2.7. TGA analysis

Thermogravimetric analysis (TGA) was carried with Perkin Elmer STA 8000 TG/DTA by heating from room temperature by 10°C/min to 700°C under N$_2$ atmosphere.

2.8. Tensile testing

Tensile testing samples were obtained by using a mold which cut the plate with blades according to the American Society for Testing and Materials (ASTM) D638 standard. SHIMADZU AGS-X 5kN tensile test machine was used for lignin reinforced composites at room temperature with a crosshead speed of 50 mm/min. 6 specimens were tested for each composite formulation to obtain a reliable average of tensile properties as well as their corresponding standard deviations. Young's modulus (E, deduced from the initial slope of the strength-strain curve), the strength (σ_{max}) and the elongation at break are evaluated.

2.9. Dynamic mechanical analysis (DMA)

The storage modulus and tan δ of neat PP and its composites were evaluated using a DMA Q800 (TA Instruments Inc., USA). Single cantilever was used and multi frequency-strain modulus mode was selected to test all specimens between the temperatures 30°C and 120°C in air atmosphere.

2.10. Scanning electron microscopy (SEM) analysis

TESCAN VEGA3 SEM device was used to observe the microstructure of lignin, copolymer and polymer composites. SEM images were taken from the fracture surfaces of the tensile specimens. The samples were coated with gold and the images and accelerated voltage was adjusted as 30 kV and images were taken at different magnifications.

3. Results and discussion

3.1. FTIR analysis

Figure 1 shows that the FTIR spectra of copolymer, lignin, coupling agent and their composites modified with FUSE between the wave numbers 4000 cm^{-1} and 500 cm^{-1}. FTIR spectra of lignin showed that lignin had peaks at 3351, 2941 and 2879 cm^{-1}. The peak at 3351 cm-1 is H-bonded O-H stretch. In the study made by Yeo et al. (2015), the hydroxyl groups was selected among the various functional groups. Because the hydroxyl groups as functional organic moiety on the lignin surface are the reactive sites and change the polarity of lignin surface that can hinder their dispersion in hydrophobic polymer matrices (Yeo et al. 2015). Also, the peaks at 2941 and 2879 cm^{-1} are attributed to the C-H stretch. One of the important peaks is to mention is the band at 3351 cm^{-1} which become invisible in all lignin filled composites. Copolymer had peaks which represented C-H stretching at 2949, 2916, 2866 and 2837 cm^{-1} and also 1375 cm^{-1} and 1358 cm^{-1}. The peak at 1375 cm^{-1} is syringyl group and the peak at 1358 cm^{-1} is the C-H_3 bonding and C-O stretch. Composites have these peaks like copolymer. But, it is seen that addition of lignin to copolymer makes a decrease in the intensity of these peaks. Also, there was a decrease in the intensity of copolymer peaks at 1375 cm^{-1} and 1358 cm^{-1} due to addition of lignin in all composites spectra. Lignin had the peaks at 1595 cm^{-1} which is aromatic functionality, aromatic C=C stretching, 1513 cm^{-1} which is aromatic skeletal vibration (Sahoo et al. 2011b). FTIR spectra showed that these peaks came from lignin became visible in its composites. Lignin also gave a peak at 1211 cm^{-1} which represented C-O-C soft segments. It was considered that the peak at 1247 cm^{-1} observed in the spectrum of the composite sample comes from the lignin peak at 1211 cm^{-1}.

Figure 2 shows the FTIR spectra of copolymer, lignin, coupling agent and their composites modified with POSS. The peak of lignin at 3351 cm^{-1} became invisible in all composites. But, the addition of lignin to copolymer made a decrease in the intensity of the peaks at 2949, 2916, 2866 and 2837 cm^{-1}.The peak of lignin at 1681 cm^{-1} which his C=O stretch became visible in all composites. Also, the peaks of lignin at 1595 cm^{-1} and 1513 cm^{-1}became visible in

all composites. Copolymer had the peak at 1453 cm^{-1} which is C-H deformation. Lignin had peak at 1455 cm^{-1} which also represented C-H deformation. There was a decrease in the intensity of the peaks of the composites when these two peaks come together. Also, there is a decrease in the intensity of copolymer peaks at 1375 cm^{-1} and 1358 cm^{-1} due to addition of lignin in all composites spectra. Compared with %10lignin filled composite which had no modification, C-O-C soft segment peak at 1211 cm^{-1} could be seen only in all composites modified with POSS, especially in the composite modified with 0.5% POSS with higher intensity.
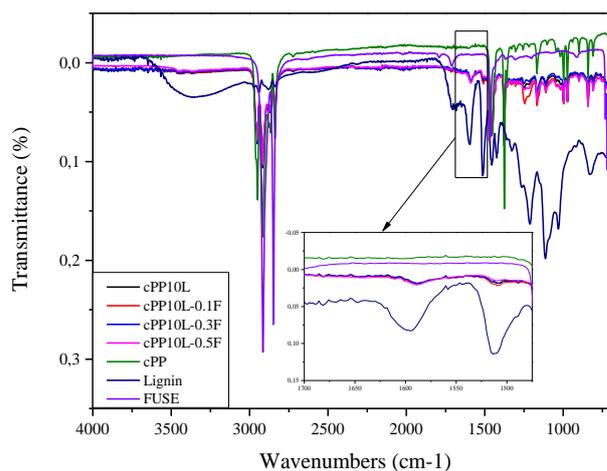

Figure 1. FTIR spectra of copolymer, lignin, coupling agent and their composites modified with FUSE
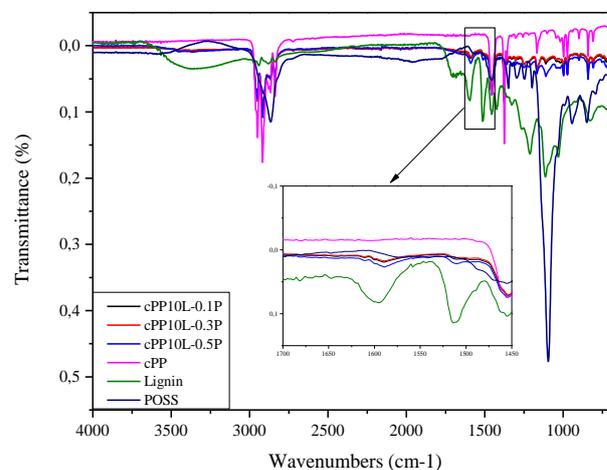

Figure 2. FTIR spectra of copolymer, lignin, coupling agent and their composites modified with POSS

3.2. TGA analysis

Table 2 shows onset temperature, degraded weight, end temperature and charred residues of lignin, extruded neat copolymer and all composites.

In TGA curve of lignin, which is showed in Figure 3, it was seen that initial weight loss around 2.3% wt. occurs at 49.3 ^{o}C and continues until the temperature 75.3 ^{o}C.

The reason of this weight loss could be attributed to loss of moisture from lignin. The study (Sahoo et al. 2011a) found the similar result as well. Weight loss at the onset temperature explained as the degradation correspond to the scission of weak ether bonds present in lignin inter units (b-O-4 linkage) in this study. Main degradation of lignin was observed at 286 ^{o}C and 57.1% wt. is lost and this degradation continues until the temperature around 430 ^{o}C.

Table 2. Onset temperature, degraded weight, end temperature and Maximum Degradation Temperature of the specimens

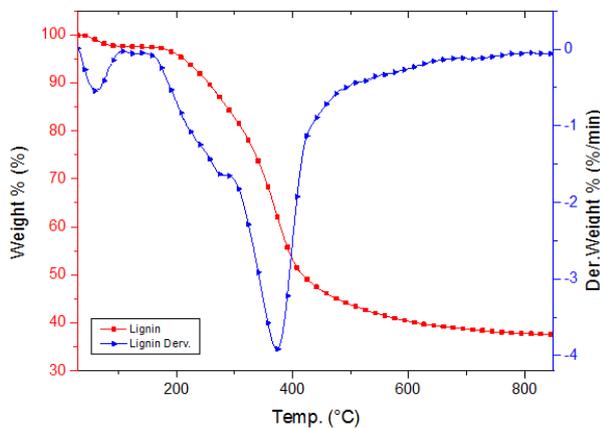| Specimens	T_{onset} (^{o}C)	Weight Loss (%)	T_{end} (^{o}C)	Charred residues at 600°C (%)
Lignin	286.0	57.1	429.9	42.9
cPP	443.1	97.7	472.8	2.3
cPP10L	438.9	93.1	477.1	6.9
cPP10L-0.1F	439.8	89.0	477.4	11
cPP10L-0.3F	439.7	91.5	478.1	8.5
cPP10L-0.5F	438.7	92.3	477.3	7.7
cPP10L-0.1P	441.3	91.9	478.9	8.1
cPP10L-0.3P	439.3	90.4	476.9	9.6
cPP10L-0.5P	430.2	89.4	476.3	10.6

Figure 3. TGA curve of lignin

Pyrolytic degradation of lignin was explained in the study (Sun and Tomkinson 2001)as involved fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase. Practically, extruder barrel temperatures were set between 170 ^{o}C and 185 ^{o}C for the production of lignin filled composites. According to TG curve, the onset degradation temperature of lignin is 286 ^{o}C and lignin lost 3% wt. of its weight between these temperature ranges. In TGA analysis of lignin, the charred residue was found around 43%. The result is similar to the literature which concluded that the non-volatile residue at 600 °C was large, amounting to 45.5% of the lignin material (Sun and Tomkinson 2001) and it explains the reason based on the structure of lignin which reflected a high degree of branching and substantial condensation of the lignin preparations.

According to the TG curve, copolymer degraded between the temperatures around 443.1^{o}C and 472.8^{o}C. Copolymer lost 97.7% wt. between these temperature ranges. When TGA analysis data of the composites produced was investigated, it was seen that when copolymer was filled with 10 % wt. lignin, the composite started to degrade around 439°C. It means that addition of lignin increases the onset temperature and could be concluded that makes the composite more stable compared to copolymer itself. The addition of lignin to copolymer without modification decreased the weight loss percentage approximately 6 %. There was no significant difference in onset temperatures which was around 439°C between the composites modified with FUSE when compared with the 10 % wt. lignin filled composites. It means FUSE has no effect on onset temperature. On the other hand, addition of 0.1% POSS increased the onset temperature approximately 3°C when compared with the composite without coupling agent. By increasing the POSS content of the composites, onset temperature decreased.

When FUSE concentration increased, the degraded weight of the composites slightly increased. On the other hand, when POSS concentration increased, the degraded weight of the composites slightly decreased. End temperature of the composites was approximately the same with each other but higher than the temperature of copolymer which is 474.8^{o}C.

3.3. Tensile testing

Tensile test results of neat copolymer and lignin composites with and without coupling agent are shown in Table 3. Standard deviations were in an acceptable range for all samples.

Table 3. Elongation at break, Young's Modulus and tensile strength data of copolymer and the composites

Samples	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)
cPP	43.5±3.809	583.3±13.94	13.88±2.150
cPP10L	17.5±2.092	744.4±13.641	14.132±1.879
cPP10L-0.1F	33.8±2.095	740.2±13.603	13.978±1.869
cPP10L-0.3F	34.4±2.931	723±15.524	14.256±1.887
cPP10L-0.5F	27±2.999	722±15.513	13.8525±2.148
cPP10L-0.1P	23.6±2.803	677±15.022	13.56±2.126
cPP10L-0.3P	42.8±3.271	672.6±12.967	13.48±1.835
cPP10L-0.5P	40.5±3.182	652.8±12.774	13.702±1.850

Figure 4 shows tensile strength and elongation at break graph of copolymer and lignin filled composites. When the data was analyzed, it was seen that tensile strength of 10% lignin filled composite is almost the same with copolymer. Without using any coupling agents, only the addition of lignin had no minute effect on tensile strength. This outcome was attributed to the weak interfacial adhesion between the hydrophilic filler and the hydrophobic polymer matrix. (Sahoo et al. 2011b).

For the composites produced with FUSE coupling agent, it was thought that maleic anhydride graft in the structure of FUSE coupling agent could ensure an improvement in the tensile properties but significant differences could not be observed between values of copolymer and composites containing FUSE. The reason of that was explained the literature (Yeo et al. 2015);MAPP is one of a compatibilizer for lignocellulosic-polymer composites due to the interaction through chemical bonds between the pendant anhydride of MAPP and hydroxyl group of lignin, which would form ester linkages in the melt-mixed composites. However, the ester bonds between MAPP and lignin were too few to improve their mechanical properties compared with those of neat cPP.

Among the composites produced with FUSE coupling agent, the highest tensile strength is belong to 0.3 % FUSE added composite. Although the tensile strength of the composite prepared with 0.1 % FUSE addition is higher than copolymer's strength, it is lower than the composite coupled with 0.3 % FUSE. Tensile strength of the composite produced with 0.5 % FUSE is almost the same with copolymer, it has lower strength comparing with 0.3% FUSE added composite.

These results were also supported by the data of the SEM images of the samples. The reason of being higher strength of 10 % lignin filled composite compared with the composite containing 0.1 % FUSE is thought that because less voids in the structure in 0.1 % FUSE added composite. Also, it was seen that in SEM images, the voids decreased with the contribution of 0.3 % FUSE to the structure compared with the sample coupled with 0.1 % FUSE addition.
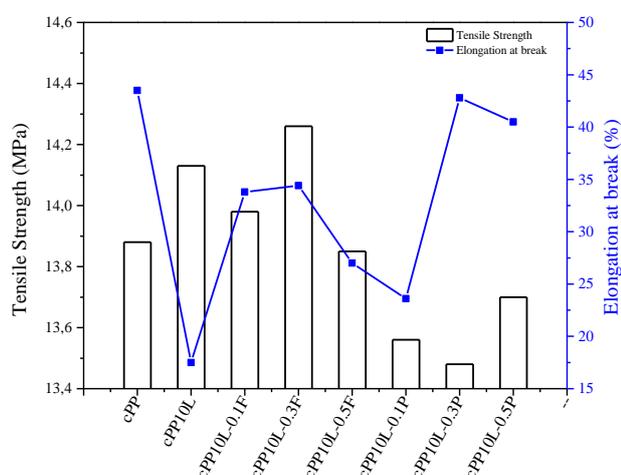

Figure 4. Tensile strength and elongation at break graph of copolymer and lignin filled composites

Similar trends in tensile properties of composite containing POSS was reported as there is no significant differences observed between values of copolymer and composites with POSS coupling agent. 0.1 % POSS, 0.3 % POSS and 0.5 % POSS added composites have tensile strength values 13.56 MPa, 13.48 MPa and 13.70 MPa, respectively.

When the elongation at break data of copolymer and all composites is investigated, large variability in % elongation was observed. It was found that addition of lignin to neat copolymer made a decrease of 60% in elongation at break values of copolymer which has 43.5%. The cause of this decline was explained as due to the mismatch between the polymer matrix interfaces with lignin particles(Sahoo et al. 2011a). Elongation at break value, which shows a significant decrease with the addition of 10% lignin to neat copolymer, had improved with the use of FUSE and POSS coupling agents. When the elongation at break values of composites containing FUSE coupling agent, it was observed that the highest value was belong to 0.3 % FUSE added composite. Elongation at break value of the composite containing 0.1 % FUSE is very close to value of 0.3 % FUSE containing composite. But the increase of FUSE addition to 0.5 % deteriorated the elongation at break value and it was observed a decrease of about 22 % comparing with 0.3 % FUSE added composite.

When it was investigated the elongation at break values of the composites containing POSS coupling agent, the composite containing 0.3 % POSS has the closet elongation at break value (42.8 %) to copolymer's value (43.5 %). 0.1 % POSS content in lignin composite improved %strain of lignin filled composite but it could not be as good as 0.3 % POSS addition. It was seen that % strain value could not be improved with the 0.5 % POSS addition to lignin filled composite, on the contrary a decline was observed in comparison with 0.3 % POSS used composite. Elongation at break values are concerned, the optimum POSS amount in composites could be selected as 0.3 % for the best interaction with lignin and polymer.

Young's modulus of copolymer was found as 583.30 MPa. It was observed that 10 % wt. lignin addition to neat copolymer made an increase of 28 % in Young's modulus of copolymer itself. The improvement in the properties of lignin filled composites could be indicated an interaction, possibly polar–polar interaction between lignin and polyolefin matrix. It is determined that not only Young's Modulus of 10 % lignin added composite but also all composites produced with coupling agents are quite higher than the modulus value of copolymer.

This significant increase in Young's modulus and decreasing of elongation at break with lignin addition indicates that stiffer material obtained. The composite filled 10% lignin without any coupling agents has the highest Young's Modulus value as 744.40 MPa. In the composites produced with FUSE coupling agent, it was seen a decrease in Young's modulus while increasing FUSE content in the composites. This decrease is about 6 % with the addition of 0.1 % FUSE and about 3.1 % with the addition of 0.3 % and 0.5 % FUSE added composites when comparing with 10 % lignin filled composite. This result was interpreted in the study made by Pucciariello et al.(2004) as; As far as the

modulus is concerned, it generally increases, after the addition of lignin (Pucciariello et al. 2004).

3.4. DMA analysis

DMA analysis was performed between the temperatures 30°C and 100°C in order to investigate the viscoelastic behavior and the impact of the modification with coupling agents on lignin-matrix adhesion. Dynamic mechanical analysis helps to understand the mechanical performance of the materials with regards to change in frequency and temperature. It measures storage modulus which gives information about stiffness of the material and damping which is a measure of how well the material absorbs energy. Damping measurement called as Tan δ which is the ratio of loss modulus over storage modulus (Seydibeyoğlu 2012).

The storage modulus of neat copolymer decreases when the temperature increases. The same result was found in the study made by (Sahoo et al. 2011a) and explained as "The reduction of storage modulus with temperature can be attributed to the softening of the polymer due to the increase in the chain mobility of the polymer matrix at high temperatures". This interesting result was observed with the addition of 10% wt. lignin without modification to copolymer, the storage modulus of neat copolymer decreased throughout the whole temperature scale. That means lignin incorporation decreases the stiffness of the material. Also, the results showed that the storage modulus values of the lignin composites modified with FUSE and POSS at their each compositions showed a decreasing trend between the temperatures 30°C and 100°C. The results showed that the deformation of composites increases as the temperature increases.

As it is seen in Figure 5, when the storage modulus values of lignin filled composites modified with FUSE coupling agent were investigated at 30°C, it is seen that 0.1% wt. FUSE addition to 10% wt. lignin filled composite made a decrease in storage modulus of 10 %wt. lignin filled composite. Then the increasing content of FUSE amount to 0.3 % made another decrease in the storage values of the composites. This decreasing trend ended with the addition of 0.5 %wt. FUSE to the structure and storage values of composites increased again. This interesting result could be observed for other temperatures as well with the same trend.

Figure 6 shows the storage modulus of copolymer and its composites modified with POSS coupling agent. At 30 °C, the addition of 0.1 %wt. POSS to the structure of 10 %wt. lignin filled composite decreases the storage modulus of the composite but it has been observed that POSS coupling agent had adverse effects for other temperatures and it was observed an increase in the storage modulus.

The results were different from the FUSE added composites in terms of the increasing and decreasing trends. When the Table 3. is investigated, it is seen that storage modulus decreased with the increasing POSS amounts in the composites modified with POSS at 30°C. Contrary to this, the result differs at the temperatures 50°C and 70°C. At these two temperatures, storage modulus increased with the increasing POSS amount in the composite structures. At 100°C, whereas storage modulus of composite material included 0.1% wt. POSS was 358.28 MPa, with the increasing POSS amount, storage modulus of composite material included 0.3% POSS was found as 361.96 MPa.

This interesting trend didn't valid for the composite incorporated with 0.5 % wt. POSS, it is seen that the storage modulus of 0.5 %wt. POSS composite was less than the storage modulus of composite modified with 0.1 %.

As the test data starts from room temperature, the glass transition temperature was not observed at these temperature scales. This is also reflected in Tan δ values as well. Lignin reinforced composites modified with FUSE and POSS coupling agents showed a broad single damping curve. The damping behavior was explained in the study made by (Pouteau et al. 2004) as "It is measured by the magnitude of tan d since it is the ratio of loss modulus to storage modulus or energy dissipated to energy stored during a dynamic loading cycle."

According to this result, dissimilar observation could be reported as lignin filling may help the molecular mobility of copolymer matrix. Hereby, Tan δ increased since there is reduced inter friction between molecular chains. This interesting effect of lignin filling observed also in the composites throughout the whole temperature scale. Only the composite sample modified with 0.5 % POSS was different as its Tan δ has a decreasing trend after 100°C.
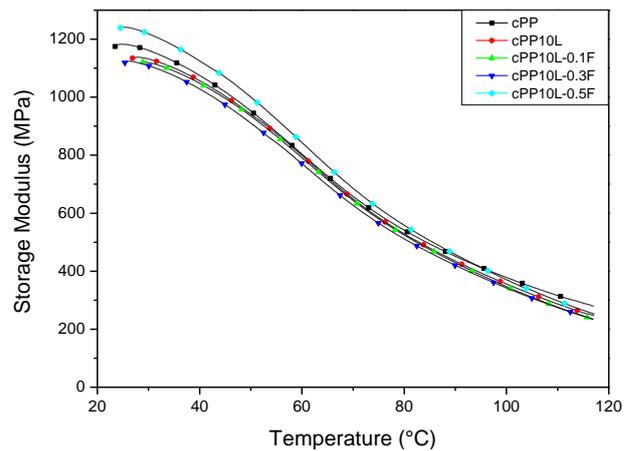

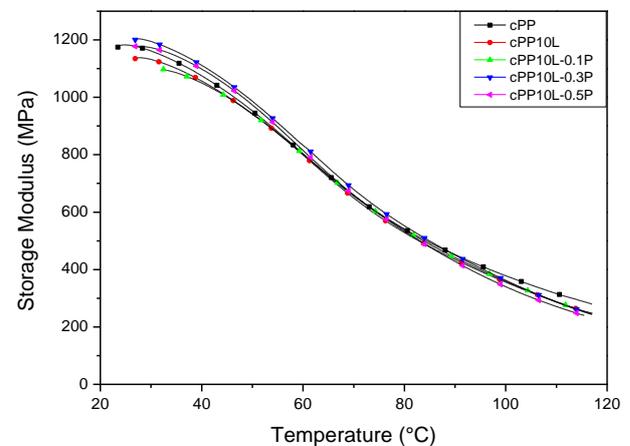Figure 5. Storage modulus of FUSE composites

Figure 6. Storage Modulus of POSS composites

3.5. SEM analysis

Figure 7 shows that the SEM images of copolymer, lignin and composites. SEM analysis has been performed by imaging the fracture surfaces of the tensile specimens of lignin filled composites. In the Figure 7 (a), air gaps were observed in copolymer surface. The reason of air voids within the structure could be explained as copolymer was not subjected to drying process prior to extrusion, and therefore the copolymer would absorb moisture from the air. In the typical SEM micrographs of lignin which is seen in Figure 7 (b), also it can be observed in fact that lignin has not homogeneous in size. The particle size of lignin changes between 5-35 μm. When the SEM images of composites with and without modification was analyzed, it was considered that the gaps in SEM images of 10% wt. lignin composite without modification and composite modified with 0.1% wt. with FUSE and POSS cause due to interface mismatch between lignin and polymer matrix interface. In the composites modified with FUSE, it was observed that the number of gaps decreased in composites modified with 0.3 % and 0.5 % concentration. In the composites modified with POSS, the number of gaps decreased in composites modified with 0.5 % concentration. As a result, it was concluded that coupling agent had an improvement in composites compared with the 10 % wt. lignin filled composite without modification.

3.6. Application of optimized coupling agent content for automotive parts

The optimized formulation was produced in large scale and the optimized composition was in injection molded to obtain an automotive part (Figure 8). One of the most important outcome was to be used by a commercial company, namely Farplas Auto Spare Parts Production Company in their product portfolio. For future studies, the use of side product lignin from paper industries and cellulosic bioethanol industries will create an important sustainable material from renewable resources. This study will also help increased usage of the bio based materials in industrial applications.
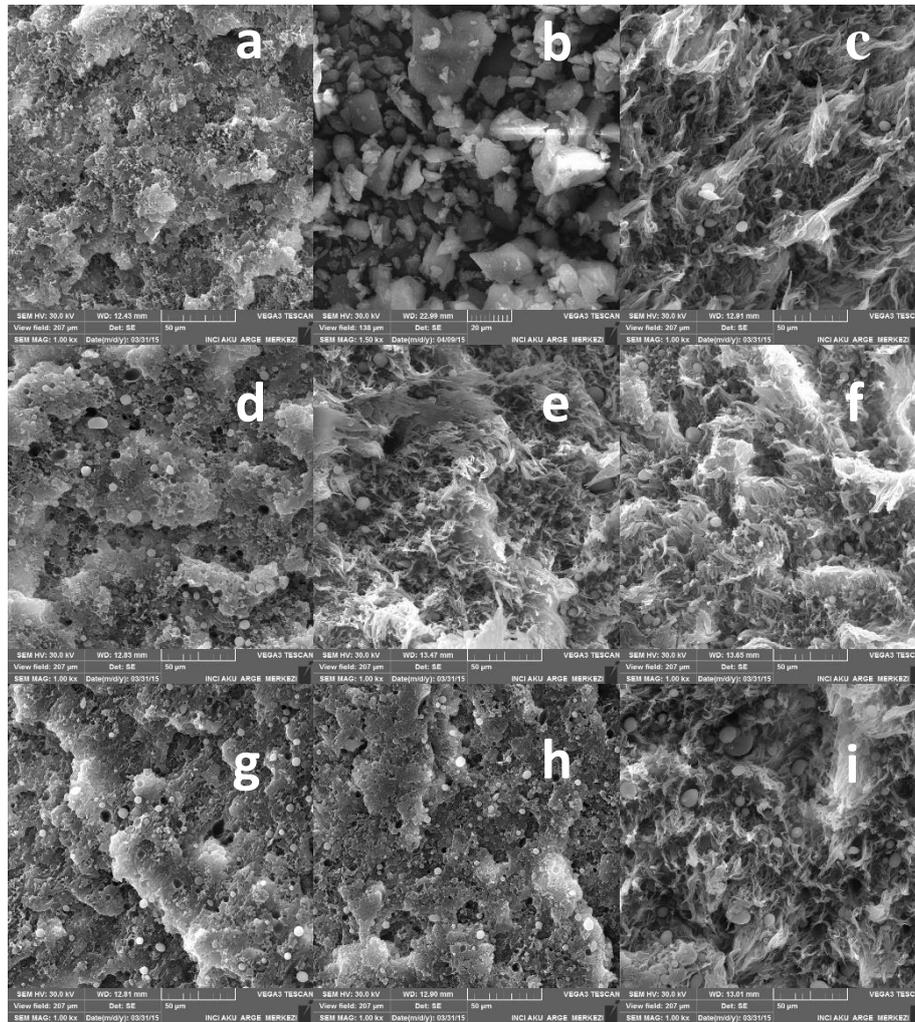

Figure 7. SEM images; a) cPP, b) Lignin c) cPP10L, d) cPP10L-0.1F, e) cPP10L-0.3F, f) cPP10L-0.5F, g) cPP10L-0.1P, h) cPP10L-0.3P, i) cPP10L-0.5P

Figure 8. Final products of lignin filled PP composites

4. Conclusion

This is a very critical study on the utilization of lignin materials for the manufacturing of eco-friendly polymeric materials. In this study, we could achieve a new formulation being low-cost and environment friendly by using lignin. The processing conditions for preparing lignin based composites are optimized with mechanical properties improvement. Furthermore, it was shown that these materials can be used in certain automotive applications.

To conclude, lignin which is a side product of paper and cellulose based bioethanol industry has been utilized in polymeric materials creating an important value and this study will help the use of lignin in various polymer studies.

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