IZMIR KATIP CELEBI UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

ENVIRONMENTALLY-FRIENDLY, HIGH STRENGTH LIGNIN FILLED POLYPROPYLENE COMPOSITES

M.Sc. THESIS

Tuğçe UYSALMAN

Department of Material Science and Engineering

Thesis Advisor: Assoc. Prof. M. Özgür SEYDİBEYOĞLU

NOVEMBER 2015

IZMIR KATIP CELEBI UNIVERSITY★ GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

ENVIRONMENTALLY-FRIENDLY, HIGH STRENGTH LIGNIN FILLED POLYPROPYLENE COMPOSITES

M.Sc. THESIS

Tuğçe UYSALMAN
Y130111031

Department of Material Science and Engineering

Thesis Advisor: Assoc. Prof. Dr. M. Özgür SEYDİBEYOĞLU

NOVEMBER 2015

İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇEVREYE DUYARLI, YÜKSEK MUKAVEMETLİ POLİPROPİLEN LİGNİN KOMPOZİTLERİ

YÜKSEK LİSANS TEZİ

Tuğçe UYSALMAN
Y130111031

Malzeme Bilimi ve Mühendisliği Anabilim Dalı

Tez Danışmanı: Doç. Dr. M. Özgür SEYDİBEYOĞLU

KASIM 2015

Tuğçe UYSALMAN, a **M.Sc.** student of **İzmir Katip Çelebi University** student ID Y130111031, successfully defended the **thesis** entitled "**Environmentally-Friendly, High Strength Lignin Filled Polypropylene Composites**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor: Assoc. Prof. Mehmet Özgür SEYDİBEYOĞLU
İzmir Kâtip Çelebi University

Jury Members : Prof. Dr. Sevgi Ulutan
Ege University

Assist. Prof. Mustafa Erol
İzmir Kâtip Çelebi University

Date of Submission: 16.11.2015

Date of Defense : 16.11.2015

To my family,

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Assoc. Prof. Mehmet Özgür Seydibeyoğlu for his guidance and his constructive suggestions and to Assoc. Prof. Kutlay Sever from Mechanical Engineering Department for good advices and letting me use some of the facilities in their research laboratories.

I present my thanks to Dr. Altan Yıldırım and Burcu Girginer from Farplas Auto Spare Parts Production Company for their support in SAN-TEZ project and timely help during the work. I would like to present thanks for lignin supply to Jairo Lora. Also I would like to thank to Deniz Taşkın, Mert Yücetürk and Vahap Emektar from Budin Akarca Company for extrusion process and hot press production.

I would like to endless thanks for understanding and their continuous moral support during my thesis to my family. I am grateful to Res. Assis. Metehan Atagür for his help for performing characterization and criticism from time to time during the course of progress of my work. I also express my sincere thanks to my lab members Hilal Kara, Ece Yakkan for their help during laboratory work and Sibel Demiroğlu for her support during the writing of my thesis.

The work presented in this thesis has been supported and funded by SAN-TEZ project which was realized with the cooperation of İzmir Katip Çelebi University located in İzmir, Ministry of Science, Industry and Technology in Turkey and Farplas Auto Spare Parts Production Company.

16 November 2015 Tuğçe UYSALMAN

Table of Contents

List of Tables

List of Figures

Page

List of Figures (continued)

Abbreviations

POSS	Polyhedral Oligomeric Silsesquioxane
FUSE	Fusabond®E265
FTIR	Fourier Transform Infrared Spectroscopy
DMA	Dynamic Mechanic Analysis
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy

List of Symbols

σ_{max}	Maximum Strength
E	Young’s Modulus

ENVIRONMENTALLY-FRIENDLY, HIGH STRENGTH LIGNIN FILLED POLYPROPYLENE COMPOSITES

SUMMARY

Natural fiber filled/reinforced composite materials are studied in the literature as an emerging area. Lignin is both a natural filling material and a waste material of 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 soda lignin was used as a natural filler. Soda lignin has no sulphur content structurally and it's the closest to native lignin structure compared to that of the other lignin types.

In the literature, lignin filled/reinforced composites with difference matrix materials and lignin types produced by using blending, single screw extrusion, twin-screw extrusion or solvent casting methods. It is seen that there are only three studies about lignin filled/reinforced composite production made by using twin-screw extruder. Among these three studies, only there is one study used PP as a matrix component and in another study a coupling agent used in order to enhance the mechanical properties of the composites. The studies in the literature were investigated, there is only one study that matrix material used is PP and production method is twin-screw extruder in the production of lignin filled polymer composite. This indicates the subject of the study is up to date and promising.

In this study, PP-lignin composites were prepared via twin-screw extruder. Addition of coupling agent was needed because of the interface mismatch created by the combination of lignin which has more hydrophilic than polypropylene matrix. Therefore, 10 wt. % 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 in this study. Coupling agent was used with the concentrations of 0.1%, 0.3% and 0.5% by using POSS (Polyhedral Oligomeric Silsesquioxane) and a commercial coupling agent FUSABOND®E265.

Fourier Transform Infrared Spectroscopy (FTIR) was used to observe interaction between the components. Thermal stability was measured with the help of thermogravimetric Analysis (TGA). Mechanical properties were evaluated by tensile and 3-point bending tests. Thermomechanical analysis was characterized by using dynamic mechanic analysis (DMA). Morphology of interface was observed by scanning electron microscopy (SEM).

The results showed that the optimum amount of FUSE and POSS in composites could be selected as 0.3% for the best interaction with lignin and polymer. DMA results showed that the deformation of composites increases by the temperature increases. The linkages of the lignin filled composites determined by (FTIR) for the interactions of neat copolymer, lignin and coupling agents.

According to TGA analysis, the degraded weight of the composites slightly decreased with using FUSE and POSS coupling agents in the composite structure.

Morphology of interface was observed by SEM analysis. It is seen that lignin has not homogeneous in size and also, the composites produced has air voids and proper lignin dispersion could not be achieved. According to mechanical testing results, the tensile strength of the composites is almost the same with tensile strength as copolymer. With the addition of lignin and coupling agents, more rigid composites are produced.

ÇEVREYE DUYARLI, YÜKSEK MUKAVEMETLİ LİGNİN POLİPROPİLEN KOMPOZİTLERİ

ÖZET

Gelişmekte olan bir alan olarak doğal elyaf katkılı kompozit malzemeler, literatürde yaygın olarak çalışılmaktadır. Lignin hem doğal bir dolgu malzemesi hem de biyoetanol ve kâğıt endüstrilerinin atığıdır. Lignin, katma değerli ürünler yaratmak için son yirmi yıldır çalışılmakta olan bir takviye malzemesidir. Bu çalışmada, doğal elyaf olarak Soda lignin kullanılmıştır. Soda lignin yapısal olarak sülfür içermeyen ve diğer lignin tiplerine kıyasla ligninin doğal yapısına en yakın olanıdır.

Lignin dolgulu/takviyeli kompozitler literatürde farklı matris malzemeleri ve lignin tipleri kullanılarak; karıştırma, tek vidalı eriyik harmanlama, çift vidalı eriyik harmanlama veya çözeltide harmanlama ile üretilmiştir. Yapılan çalışmaların sadece üçünde çift vidalı harmanlama yöntemi kullanılarak lignin katkılı kompozit üretildiği görülmüştür. Bu üç çalışma içerisinde sadece bir çalışmada Polipropilen matris malzemesi olarak kullanılmış ve bir diğer çalışmada da kompozitlerin mekanik özelliklerini iyileştirmek amacıyla birleştirici ajan kullanılmıştır. Yapılan çalışmalar incelendiğinde lignin katkılı polimer kompozit malzeme üretiminde matris malzemesinin polipropilen olup üretim yöntemi olarakda çift vidalı extrüder kullanılan yalnızca bir çalışma bulunmaktadır. Bu durum konunun hali hazırda çalışılan güncel ve gelişmeye açık olduğunun göstergesidir.

Bu çalışmada, PP-lignin kompozitleri çift vidalı ekstrüder ile üretilmiştir. Polipropilen matrisden daha hidrofilik olan lignin birleşiminin yarattığı arayüzey uyumsuzluğundan dolayı birleştirici ajan kullanılmasına ihtiyaç duyulmuştur. Bundan dolayı farklı birleştirici ajanın etkisini incelemek amacı ile kütlece 10% lignin katkılı kompozitler yüzey modifikasyonlu ve modifikasyonsuz olarak çift vidalı ekstruder kullanılarak üretilmiştir. POSS (oligomerik yüzlü silseskioksan) ve ticari bir birleştirme ajanı olan FUSABOND® E265 kullanılarak 0.1%, 0.3% ve 0.5%'lik konsantrasyonlarda birleştirici ajan kullanılmıştır. Yapısal özellikleri görmek amacıyla kompozit malzemelere Fourier Kızılötesi Spektroskopisi (FTIR) analizi yapılmıştır. Termal kararlılık ısıl kütle kaybı analizi (TGA) yardımı ile belirlenmiştir. Mekanik özellikler çekme testi ve üç nokta eğme ile değerlendirilmiştir. Termomekanik özellikler dinamik mekanik analiz (DMA) kullanılarak karakterize edilmiştir. Taramalı elektron mikroskopisi (SEM) ile arayüz morfolojisi gözlenmiştir.

Sonuçlar kompozitlerdeki FUSE ve POSS'un optimum miktarının lignin ve polimer arasında en iyi etkileşim olması için 0.3% olarak seçilebileceğini göstermiştir. DMA sonuçları kompozitlerin deformasyonun sıcaklıkla arttığını göstermektedir. Lignin dolgulu kompozitlerin bağ özellikleri, katkısız kopolimer. lignin ve bağlayıcı ajanların arasındaki etkileşimlerin FTIR ile analiz edilmesiyle belirlenmiştir. TGA analizlerine göre kompozitlerin bozunan kütlesi, kompozit yapısında FUSE ve POSS bağlayıcı ajanların kullanılmasıyla nispeten azalmıştır. Arayüzey morfolojisi SEM analizi ile incelenmiştir. Lignin boyutlarının homojen olmadığı ve ayrıca üretilen kompozitlerde hava boşlukları bulunduğu ve düzgün lignin dağılımının elde edilemediği görülmüştür. Mekanik test sonuçlarına göre kompozitlerin çekme mukavemeti neredeyse kopolimerin çekme mukavemeti ile aynıdır. Lignin ve birleştirici ajan ilave edilmesi ile daha rijit kompozitler üretilmiştir.

1. INTRODUCTION

1.1 Background

A powerful interest in the usage of renewable resources for material and energy production is increasing day by day because of several purposes mainly modest investments, economic and human impacts on the environment (Luong et al., 2011). Use of sustainable sources, which are sun, biomass, wind and materials, have been seen the solution of global problems such as security of supply of fossil fuels, environmental pollution and climate change (de Wild et al., 2012). This increasing trend for green and renewable chemistry has also called attention to biomass and especially on lignocellulosic feedstock as a favorable and environmentally-friendly (Laurichesse and Avérous, 2014). Biomass from lignocellulosic feedstock can be utilized for the development of materials and chemicals (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 (Y. A. N. Li and Mlyna, 2004). Under the light of this trend, lignin is used in this study for production of bio-composites with the use of coupling agents in order to improve the interfacial linkage and compatibility with the matrix.

1.2 Definition and Classification of Composite Materials

Composite materials are formed by using two (or more) individual materials. The main purpose of producing a composite is to accomplish a combination of properties which is not exhibited by any single material and also to combine the best features of each of the component materials. Most of the composite materials have just two phases; one of them is named as the matrix, which is continuous and surrounds the other phase, and the other one is often called the dispersed phase. According to type of matrix material they are classified as metal, ceramic and polymer matrix composites.

According to the properties of dispersed phase, composites classified by four main divisions: Particle-reinforced, fiber-reinforced, structural and nanocomposites (Kaxiras, 2001).

The composite materials are widely used in many different application areas such as aeronautics, automotive, boats, sports parts and medical devices. The number of studies about usage of biocomposite materials for these application areas is increasing day by day especially when material costs and environmental issues are taken into consideration.

1.3 Biocomposites

Biocomposites are composite materials formed by a matrix and a reinforcement of natural fibers such as wood fibers (hardwood and softwood) or non-wood fibers. Natural fibers are grouped into three types: vegetable, animal and mineral fibers. Vegetable fibers is consisting of seed hair, bast fibers, and leaf fibers, depending upon the source. Of these fibers, jute, ramie, flax, and sisal are the most commonly used fibers for polymer composites.

Natural fibers have many advantages compared to conventional reinforcement or filling materials. Due to the benefits with the different from other reinforcing fibers; cheap, low density, high specific properties, biodegradability, abrasion resistance. However, there are some disadvantages such as: incompatibility with the hydrophobic polymer matrix, the tendency to form aggregates during processing, poor resistance to moisture and photochemical degradation because of the UV radiations (Amar et al., 2005; Bledzki et al., 1998; Chawla 1987, Hull and Clyne, 1996).

As a natural filler, lignin is one of the components of lignocellulosic biomass which contains cellulose and hemicellulose (de Wild et al., 2012). Some research is going on to use the lignin as a natural filler in thermoplastic materials.

1.4 Lignin

Lignin is the most abundant natural biopolymer after cellulose on the planet. Lignin serves as a matrix material for cellulose and hemicellulose in the plant cell walls in all vascular plants and woody materials (Y. A. N. Li and Mlyna, 2004). Lignin (20-

35% dry weight basis) is one of the components of lignocelllulosic biomass which contains cellulose (35-45% dry weight basis) and hemicellulose (25-30 % dry weight basis) (de Wild et al., 2012). The content of lignin in the world is 3 × 10^{11} tons and it is increasing annually 2 × 10^{10} tons (Peng et al., 2014). Wood species and processing conditions affect lignin's polyaromatic polyol structure (Kadla and Kubo, 2004).

1.4.1 Structure and chemistry of lignin

Lignin's complicated structure is formed of numerous polar functional groups as a polyfunctional macromolecule (Sahoo et al., 2011). It is an amorphous macromolecule consisting of phenylpropane repeat units and includes aromatic hydroxyl groups, aliphatic and carboxylic acid groups (Mousavioun et al., 2010). These phenylpropane units formed by three aromatic alcohol precursors (monolignols) which are p-coumaryl, coniferyl and sinapyl alcohol (de Wild et al., 2012). Monolignols are also called guaiacyl (G, from coniferyl alcohol), p-hydroxyphenyl (H, from coumaryl alcohol) and syringyl (S, from sinapyl alcohol) moieties. These conventional monolignols and the non-conventional ones were showed in Figure 1.1.

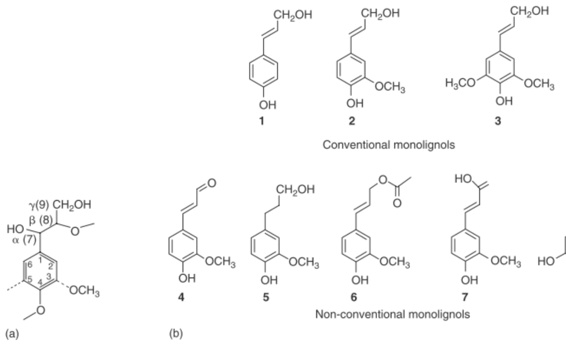

Figure 1.5: (a) Numbering system in monolignols. (b) Types of monolignols found as building blocks in lignin. (Gellerstedt andHenriksson, 2008)

The monolignols creates a complex 3D amorphous polymer that is consist of a huge variety of bonds with typically around 50% β-O-4 ether linkages during the biological lignification process (Buranov and Mazza, 2008). Carbon-carbon and ether bonds link these structural elements and form tri-dimensional network associated with the hemicelluloses polysaccharides inside the cell wall (Ibrahim et al., 2004).

1.4.2 Lignin extraction

Extraction of lignin from lignocellulosic materials is performed by different industrial and well-known processes. Standard well-defined lignins are obtained by industrial processes (Kadla and Kubo, 2004). Extraction processes of lignin has two main groups which are sulfur and sulfur-free processes. Figure 1.2 shows that there are different extraction processes in order to separate lignin from lignocellulosic biomass and productions of technical lignins (Laurichesse and Avérous, 2014).

Sulfur processes includes Lignosulfonates and Kraft lignins which are primarily manufactured by pulp and paper industries in large amounts (Lora, 2008). Lignin is a commercial by-product of paper production process. The pulp and paper industry generates 227 million tonnes of black liquor annually. Lignin is a main ingredient of black liquor and it must be took away from wood fibers in order to produce paper. Cellulosic pulp process from wood and non-wood fiber needs delignification with NaOH under pressure. Cellulosic fiber is liberated and a huge amount of black liquor is produced (Sun and Tomkinson, 2001).

Sulfur-free lignins can be categorized into two as organosolv lignin and soda lignin. Soda lignins and Organosolv are sulfur-free lignins which are handled from annual crops like straws, bagasse, flax and to some extent, softwoods and hardwoods. From the point of ecological and economical view, sulfur-free lignins as new renewable raw materials are regarded as value-added products. The best suitability for manufacturing of lignin products for polymer applications is handled in the soda process by manufacturing lignin products with the best quality (Laurichesse and Avérous, 2013).

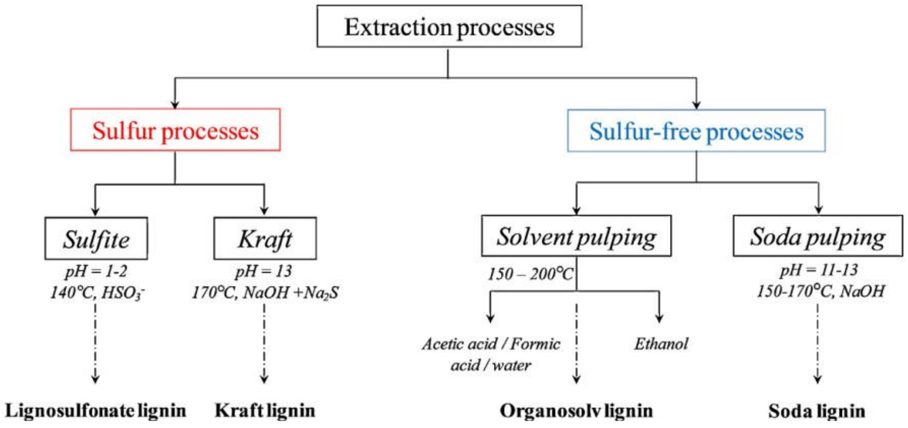

Figure 1.6: Different extraction processes to separate lignin from Lignocellulosic biomass and the corresponding productions of technical lignins (Laurichesse and Avérous, 2014).

1.4.3 Soda lignin

Soda lignin is obtained from the black spent liquor which is a by-product of soda pulping process which was the first chemical pulping method and was patented in 1845 (Ouyang et al., 2010). The pulping process involves heating the biomass in a pressurized reactor to 140–170^{o}C in the presence of 13–16 wt% alkali. High-temperature and high-pressure are applied during the chemical pulping process and this lead degradation of lignin(Doherty et al., 2011; Ibrahim et al., 2004).Lignin from biomass is dissolved by the action of solutions of NaSH or NaOH without inclusion of hydrogen sulfide anions in soda process(Duval and Lawoko, 2014; Joffres et al., 2014).

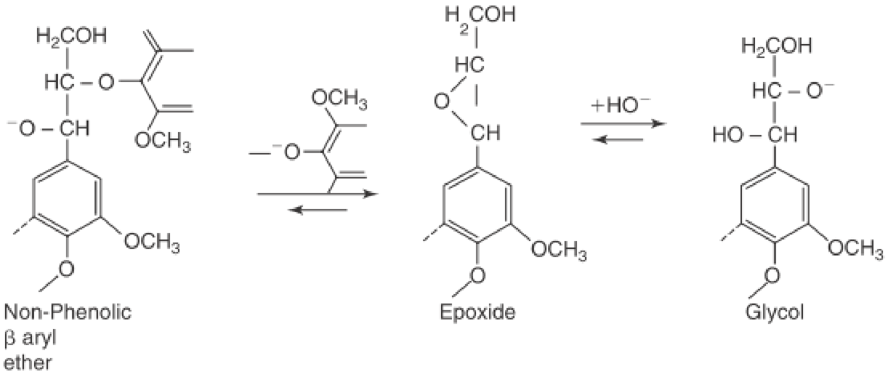

Figure 1.7: Main reactions leading to the formation of soda lignin (Gellerstedt and Henriksson, 2008)

Soda based process methods are primarily generated from non-woody plants such as bagasse, wheat straw, hemp, kenaf or sisal (Bernardini et al., 2014; Duval and Lawoko, 2014). These resources generally have similar properties such as low molecular weight, high phenolic hydroxyl content, and relatively low glass transition temperature (Thakur et al., 2014).

Soda lignins are structurally sulphur-free and close to those of native lignins compared to others lignin types. Because during the extraction of lignin by soda process, hydrolytic cleavage happens and it results in a relatively chemically unmodified lignin. During lignin depolymerization, an α ether bond can be effectively cleaved and β -O-4 ether linkage can be easily cleaved first in phenolic units and in a later part of delignification, in non-phenolic units (Chung and Washburn, 2012; Lora, 2008). The soda lignin is a low molecular weight substance with high phenolic hydroxyl content (Chauhan et al., 2014). Soda lignin from non-wood plants contain more p-hydroxyl units and carboxyl groups (Kraslawski, 2011). Soda lignin can consists of also nitrogen and high silicate contents because of its extraction procedure (Laurichesse and Avérous, 2014). Soda lignins are obtained with low levels of sugar and ash contaminants. They are also low molecular weight and insoluble in water. It is reported that glass transition temperatures of soda lignins change between 158–185 °C. Soda lignins do flow when they are heated (Lora, 2008).

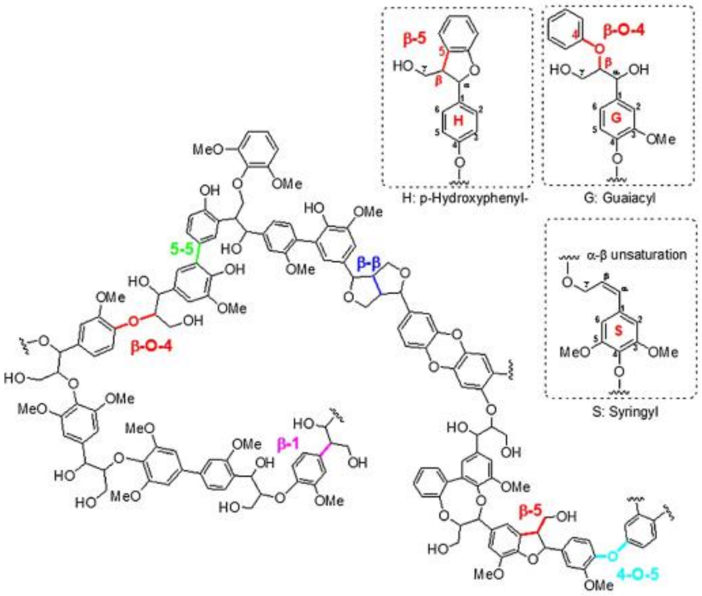

Figure 1.8: Principal linkages and functional groups in soda lignin (Joffres et al., 2014)

1.4.4 The potential and application of soda lignins

The lack of sulphur is important for applications for which thermal flow is a requirement and volatile sulphurous emissions are undesirable (Lora, 2008) It has good potential for use in high value product because soda lignin contains no sulfur and little hemicellulose or oxidized defect structures (Doherty et al., 2011).

For plastics and rubber, lignin is used as a stabilizer in the formulation of dispersants, adhesives, asphalts, polyurethanes, phenol–formaldehyde resin formulations and surfactants (Kadla and Kubo, 2004; Sahoo et al., 2011). Lignin is used and as compatibilizer because of a large number of polar functional groups for many years due to the presence of both aliphatic and polar groups which may provide compatibility between non-polar polymers and lignocellulosic fibers. The antioxidant function arises from its chemical structure similar to hindered phenols used as primary antioxidants in polymer industry (Yeo et al., 2015).

1.5 Literature Survey

The studies made in the literature between the years 1995 and 2015wereordered according the publishing year and given in Table A.1 which is in Appendix part of the study. These studies investigated the production of lignin filled/reinforced composites with different types of polymers such as PET, PLA, PEG, PU, etc. According to the thesis, only lignin reinforced PP matrix composites were investigated in detail.

The study made by Peng et al., (2014) wood flour, lignin and cellulose were chosen to blend with PP matrix at different loading levels to evaluate the influence of accelerated UV weathering. QUV accelerated weathering test was achieved. Firstly, flexural properties of the samples are analyzed. Also, the surface gloss and surface color measurement was performed.

Contact angle measurement of the samples were tested. Besides, the characterization of weathered surface was achieved by using ATR-FTIR and SEM. The results showed that the presence of high lignin content caused an acceleration in the discoloration of composites. Second important result is that lignin filled composites gave less loss of flexural strength, modulus and less cracks.

Zhong et al., (2011) alkylated parent lignin with bromododecane, which improved its compatibility with a PP matrix. PP blend with 70wt% lignin content prepared with by melt-mixing. Morphology, tensile and flexural tests and the supermolecular structure of the PP/lignin blends were investigated.

According to tensile and flexural test, it was found that if lignin content increases, modulus and strength values decreases. The impact strength was enhanced by blending up to 40wt% alkylated lignin. SEM images showed that alkylated lignin is homogeneously dispersed in the PP. TGA analysis showed that high lignin content improved the thermal stability.

The aim of this paper made by Charlyse et al, (2004) is to investigate good polymer candidates displaying good compatibility with Kraft lignin. Also, the study was performed to select very polar and apolar polymers in order to identify the structural features of good lignin candidates. Visible microscopy is used for morphology. It was found in the study that only low molecular weight lignins are compatible with apolar and very polar matrixes.

According to Kadla and Kubo, (2004) had a study for manufacturing lignin filled thermoplastics. Altering of the viscoelastic properties of lignin was aimed through polymer blending or chemical modification. Lignin/synthetic polymer blends were produced by using melt extrusion. Thermal analysis and FT-IR analysis were used. According to thermal analysis, lignin blends which contains PET and PEO, showed miscible blend behavior, whereas PP and PVA lignin blends appeared immiscible. A negative deviation from a linear mixing rule was seen from the glass transition of the lignin/PET blends and lignin/PEO. This indicated the specific intermolecular interactions.

The study made by C. Pouteau et al., (2003)in order to investigate the antioxidant properties of lignin in polypropylene. 15 lignin samples from various botanical origins (wheat straw and wheat bran) were extracted and kraft lignins used to incorporate with PP.

It is seen that the solubility in polypropylene is very low and also the antioxidant activity tends to be improved by low molecular weight and low total OH content.

Youngavb, (2002) studied with preparation of lignin filled (between 10 wt. % and 60 wt. %) polypropylene composites by blending. Tensile and flexural strength are reduced and it is seen a spectacular decrease in un-notched Izod impact strength compared with the properties of neat polypropylene, although Young's and flexural modulus were improved.

Conventional surface treated fillers, which are mica and talc, gave better results than lignin, but the strength properties were improved with respect to lignin alone when lignin and inorganic fillers were mixed. It could be probably because of a better distribution of lignin and interaction between the filler and lignin.

It was concluded that maleic anhydride grafted polypropylene (MAPP) as a coupling agent improved strength properties. Although there was substantial variance at high lignin concentration in the tensile strength (For example, %60 lignin loading.)

The objective of the present paper Alexy et al., (2000) was to produce lignin filled with polypropylene and polyethylene (low density polyethylene, LDPE) it was shown that lignin acts, mainly in PP, as a good processing stabilizer and a light stabilizer. At long-term heat strength lignin acts as an initiator of the degradation process in PP, mainly at higher concentration levels.

The mechanical properties decrease with increasing lignin content. The MFI of PP–lignin blends is stabilized up to 20 wt. % lignin content, and increases above this concentration.

In the present work Gonza, (1999), lignin was selected in order to produce composites with polypropylene matrix because of its low cost, low density and low abrasive character. Thermal and mechanical properties were investigated and it was seen that the produced composites were utile for commercial and industrial applications.

The study made by Gonza, (1999) includes compounding of lignin/PP composites by melt blending in a thermokinetic mixer. Two PPs with different molecular weights were used as matrices and lignin was incorporated in the range from 10 to 55wt%. Tensile strength, elongation at break and Young's modulus were evaluated for those composites as well as micromechanical analysis.

In the study realized by Kharade and Kale, (1999) dry lignin powder is used as a filler. It is incorporated into high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP) up to 30 wt. % content. When the tensile test was investigated, it was seen a reduction in tensile strength for all polymers.

Impact properties were not affected significantly in case of usage of PP matrix. But the properties were decreased for HDPE and LDPE. Five parts of ethylene acrylic acid copolymer (EAA) and 0.5 parts of titanate coupling agent were used in order to improve the mechanical properties. It was concluded that increasing lignin content increased the melt viscosity steadily. When the electrical properties were analyzed, it was seen that electrical resistance was increased.

The changes of electrokinetic surface properties of polypropylene was examined with various lignin preparations in the study made by (Republic, 1995). The differences were observed between in zeta potential behavior of the lignin-free and lignin filled polypropylene films.

All lignin preparations made changes on PP surface and an increase in its hydrophilicity was observed. Also, the differences in zeta potential behavior of the lignin-free and lignin-containing films were observed and this indicated that there are specific interactions between both polymer components by modifying the hydrophobic surface properties of PP and it was concluded that addition of lignin will improve the printing ability of PP film.

In the study made by Yeo et al., (2015) the pristine lignin was chemically modified by hydrolysis condensation reaction using (3-aminopropyl) triethoxysilane and was afterwards treated with polypropylene-graft-maleic anhydride in order to give MAPP anchored lignin. The modified lignin particles prepared at each steps were characterized by FT-IR, SEM-EDX and XPS measurements.

Polypropylene composites with MAPP-a-Lignin were prepared through melt-blending method. In this work, the effects of content of MAPP-a-Lignin on the properties of the polypropylene composites were investigated. From the results of mechanical properties, melting/crystallization behaviors and the morphologies of the composites, it was found that there was a stronger interfacial interaction between MAPP-a-lignin and polypropylene in the composites.

Objective of this study is the production 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 METHOD

2.1 Materials

2.1.1 Lignin

Protobind 2400 was kindly provided as gift by Green Value SA Company. Lignin (Figure 2.1) was produced as a by-product from paper industry. Typical properties of Protobind 2400 are presented in Table 2.1. Protobind 2400 is a high-purity natural polyphenolic material. This product is now being industrially produced in India in dry powder form using state-of art proprietary and patented Swiss technology.

Figure 2.4: Protobind 2400 Lignin

Table 2.2: Composition on a dry basis and Average Molecular Weight of Protobind 2400 (Datasheet of Protobind 2400).

Composition on dry basis and Average Molecular Weight	Unit (weight %)
High purity lignin	approximately 90
Hemicellulose Sugars	< 2
Ash	< 2
Number Avg. Molecular Wt.	approximately 1,000
Non-volatile content (%)	97±1
Softening Temperature (^{o}C)	130^{o}C

2.1.2 Copolymer

Heterophasic polypropylene copolymer *Moplen* 2000 HEXP (medium high fluidity, T_m=165^{o}C, ρ=0.9 g/cm3, Melt flow rate (230^{o}C/2.16 kg) =16g/10 min) produced by Lyondell Basell Company, was used as the polymeric material. The product features an outstandingly high impact performance, particularly at very low temperature, combined with stiffness. It is especially designed for injection molding applications where either a very high impact at deep-freeze conditions or a heavy duty impact performance at room temperature is critical.

Figure 2.5: Granular heterophasic polypropylene copolymer

Table 2.2: Properties of Copolymer used as a matrix material (Datasheet of Moplen 2000 HEXP).

Typical Resin Properties	**Standard**$^{(a)}$	**Unit**	**Value**$^{(b)}$
Melt Flow Rate (230°C, 2.16 kg)	ISO 1133	g/10min	16
Density	ISO 1183	g/cm^3	0.9
Flexural Modulus	ISO 178	MPa	900
Tensile strength at yield	ISO R 527	MPa	18.5
Elongation at yield	ISO R 527	%	6

(a) The property values shown are based on a limited number of tests and, therefore, should not be construed as product specifications. These values may shift slightly as additional data are accumulated.

(b) ISO test methods are the latest under the Society current procedures where applicable, specimens are prepared by injection molding (ASTM 2146).

2.1.3 Coupling Agents

Coupling agents, POSS (Polyhedral Oligomeric Silsesquioxane) and the commercial coupling agent FUSABOND$^{®}$E265, were showed in Figure 2.3a and Figure 2.3b.

Figure 2.6: a. FUSABOND E 265, b. POSS

2.1.3.1 FUSABOND E 265

DuPont™ Fusabond® is a family of functional polymers that have been modified typically by maleic anhydride grafting to help bond together different polymer. DuPont™ Fusabond® E265 is an anhydride modified high density polyethylene (Table 2.3.). It is used for compatibilizer for halogen-free flame-retarded plastic compounds containing fillers such as aluminum trihydrate or magnesium hydroxide or natural fiber.

Table 2.3: Some physical and thermal properties of FUSABOND E 265 (Datasheet of FUSABOND E 265).

Physical	**Nominal Values**
Density	0.95 g/cm^3
Melt Flow (190°C/2.16kg)	12 g/10 min
Thermal	**Nominal Values**
Melting Point (DSC)	131^{o}C
Freezing Point (DSC)	111^{o}C

2.1.3.2 POSS (Polyhedral Oligomeric Silsesquioxane)

PEG POSS coded as PG1190 was used as coupling agent in this study. POSS® is Polyhedral Oligomeric Silsesquioxane (Figure 2.4.). The key properties of PEG-POSS are shown in table 2.4. PEG POSS has a regular, often cubic, inorganic cage structure. It's chemical formula is $(C_{2m+3}H_{4m+7}O_{m+1})\ (SiO_{1.5})_n$. It is a hybrid molecule with an inorganic silsequioxane at the core and organic polyethylene glycol groups attached at the corners of the cage. PG1190 is very stable even at high loadings and temperatures. It is also useful in lithium batteries, biomaterials, cosmetics and dispersion of oxide and carbon particles.

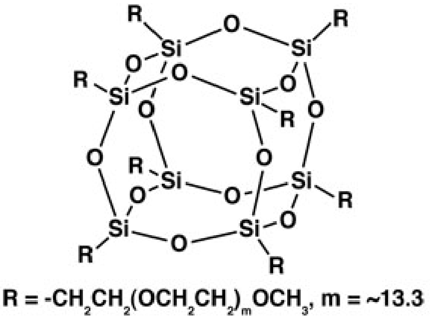

Figure 2.4: Cage mixture of PEG POSS

Table 2.4: Key properties of PEG-POSS.

Key Properties	
Formula Weight	5576.6
Appearance	Clear, Colorless liquid
Viscosity (at 25°C)	280 centipoise
Thermal Stability5% wt. loss	250˚C
Solvent Stability	Water, alcohols
Solvent Insolubility	Hexane
Resin Solubility	Polyethers and polyesters

2.2 Method

2.2.1 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 to obtain a homogeneous mixture due to lignin used as reinforcing material in the powder form. Lignin and copolymer were mixed for three or five minutes until observing the proper mixing in order to produce composites without coupling agent. Lignin and copolymer were mixed with POSS and FUSABOND respectively with the compositions 0.1%, 0.3% and 0.5% (by weight) when composites with coupling agent was produced.

2.2.2 Extrusion process

Lignin filled composites with and without coupling agents were manufactured by using twin-screw extruder (co-rotate) branded Labtech (Figure 2.5) in Budin Chemicals Industry and Trade Limited Company located in İzmir. L/D ratio of the extruder is selected as 44:1. 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.

Figure 2.5: Co-rotate twin-screw extruder

After the extruder die, composite was cooled with water in cooling bath and transferred to pelletizer to obtain pellet type composite materials. At the exit of the pelletizer, composite pellets produced had moist due to cooling process after extrusion. The oven was used in order to eliminate the moisture of the composite pellets. After extrusion, composite pellets were dried in oven for 1 hour at 80°C.

Lignin reinforced composites with or without coupling agent was produced as 1 kg in extruder. Table 2.5 shows composites and their sample codes and Table 2.6 shows the composites produced and the amounts for each.

Table 2.5: 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
20% Lignin-0.3% FUSE	cPP20L-0.3F
30% Lignin-0.3% FUSE	cPP30L-0.3F

Table 2.6: Lignin reinforced composites produced in the study.

Sample Codes	Copolymer Amount (g)	Lignin Amount (g)	Coupling Agent amount (g)
cPP	1000	-	-
cPP10L	900	100	-
cPP10L-0.1F	889	100	1
cPP10L-0.3F	887	100	3
cPP10L-0.5F	885	100	5
cPP10L-0.1P	889	100	1
cPP10L-0.3P	887	100	3
cPP10L-0.5P	885	100	5
cPP20L-0.3F	797	200	3
cPP30L-0.3F	697	300	3

2.2.3 Thermokinetic mixer

Melt mixing of the pellets was achieved using a Gelimat (Figure 2.6), a high-speed laboratory thermokinetic mixer branded as Gülnar Makina. 50 gr composite samples were mixed for 15-20 seconds with 2000 rpm speed in order to get mixture in the form of dough.

Figure 2.6: Thermokinetic Mixer

2.2.4 Hot and cold press

Hot press (Figure 2.7) was used to form the composite panels from compounded pellets.

Figure 2.7: Hot and cold press

After heating the hot press until processing temperature (200^{o}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) which has heating and cooling platens. Samples (Figure 2.8) were pressed under 39 bar pressure with 200^{o}C upper and lower temperature of heating platens for 20 seconds in hot part and 2 minutes in cold part of the press.

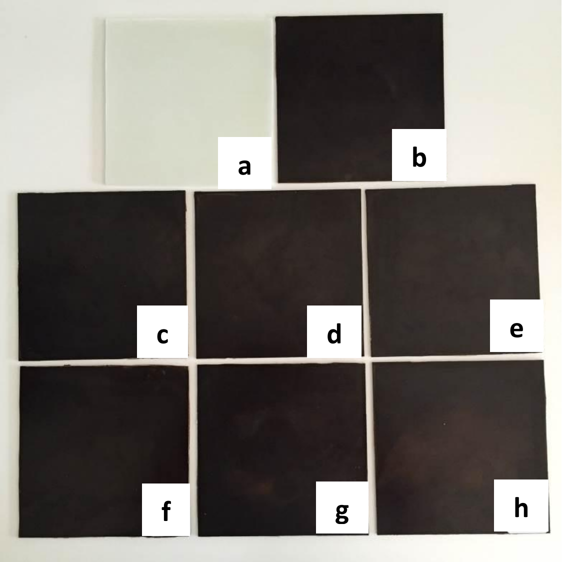

Figure 2.8: Photos of all groups of composites; a) cPP, b) cPP10L, c) cPP10L-0.1F, d) cPP10L-0.3F, e) cPP10L-0.5F, f) cPP10L-0.1P, g) cPP10L-0.3P, h) cPP10L-0.5P

2.3 Characterization

2.3.1 Tensile testing

Tensile testing samples were obtained by using a mold which cut the plate with blades according to ASTM D638 standard. SHIMADZU AGS-X 5kN tensile test machine (Figure 2.9) 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.

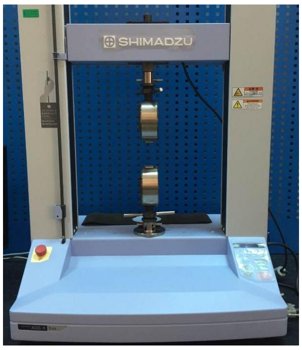

Figure 2.9: Tensile testing device

2.3.2 Three-point bending

The flexural modulus and flexural strength of samples were tested according to DIN EN ISO 178 in SHIMADZU AGS-X 5kN (Figure 2.10), which involves a three-point bending test at a crosshead speed of 1 mm/min. The size of samples was 25 mm×40 mm. Three samples of each group were tested.

Figure 2.10: Three-point bending testing device

2.3.3 Dynamic mechanical analysis (DMA)

DMA Q800 V21.1 Build 51 instrument (Figure 2.11) in Multi-Frequency-Strain Modulus was used in air atmosphere between the temperatures 25°C and 120°C. Single cantilever was used as clamp.

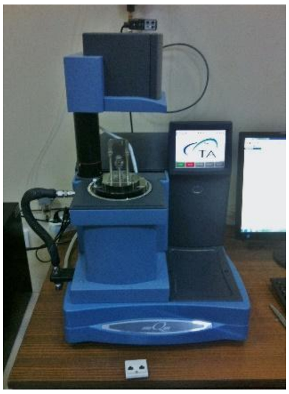

Figure 2.11: DMA device

2.3.4 FTIR analysis

Copolymer, lignin and their composites prepared with FUSE and POSS were investigated with FTIR analysis (Figure 2.12). 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.

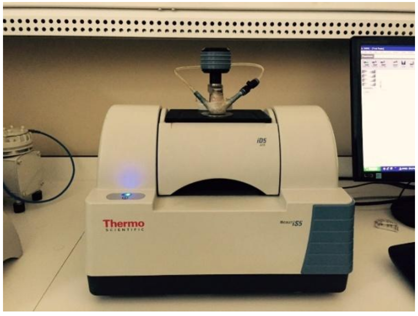

Figure 2.12: FTIR device

2.3.5 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. TGA device is shown in Figure 2.13.

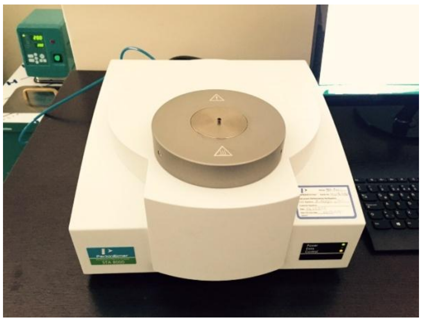

Figure 2.13: TGA device

2.3.6 SEM analysis

Scanning electron microscopy (SEM) was used to observe the microstructure of lignin, copolymer and polymer composites. SEM images were taken from the fracture surfaces of the tensile specimens. VEGA3 TC TESCAN was used as SEM. 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 Tensile Testing

Stress-strain curve of the composites coupled with FUSE and POSS after taking the average of six specimens for each composite is given in Figure 3.1 and Figure 3.2, respectively.

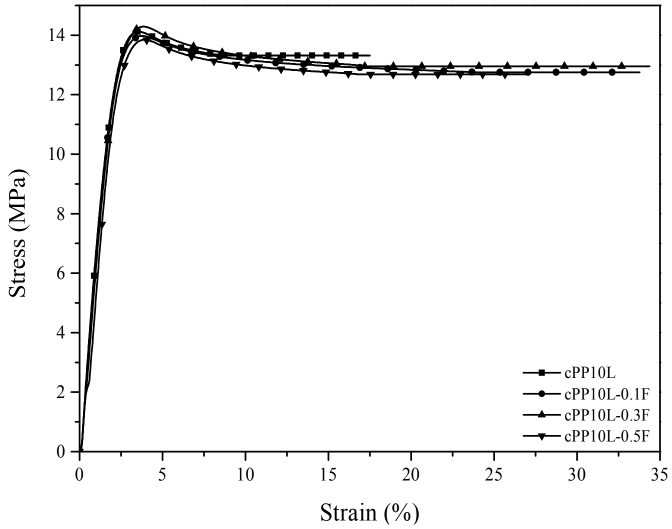

Figure 3.3: Stress-Strain curve of lignin filled composites modified with FUSE

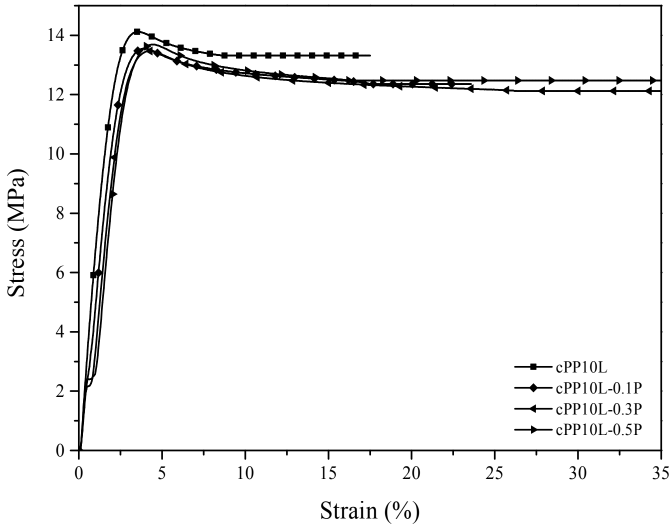

Figure 3.4: Stress-Strain curve of lignin filled composites modified with POSS

Tensile test results of neat copolymer and lignin composites with and without coupling agent are shown in Table 3.1. Standard deviations were in an acceptable range for all samples.

Table 3.4: 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 3.3 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 that there is a weak interfacial adhesion between the hydrophilic filler and the hydrophobic polymer matrix in the study made by Saswata et al., (2011).

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 by Yeo et al., (2015) based on the previous works made in the literatures. The study explains that MAPP as a coupling agent for lignocellulosic-polymer composites is used due to the interaction between the chemical bonds of the pendant anhydride of MAPP and hydroxyl group of lignin. In the melt-mixed composites, these bonds would form ester linkages. However, the ester bonds between lignin and MAPP were too few in order to improve their mechanical properties compared with those of neat cPP.

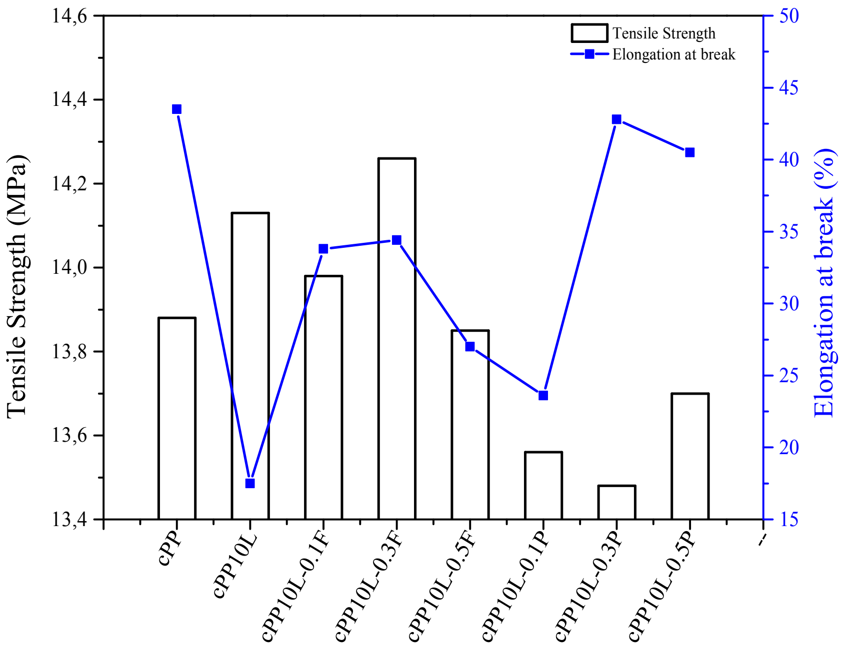

Figure 3.3: Tensile strength and elongation at break graph of copolymer and lignin filled composites.

Among the composites produced with FUSE coupling agent, the highest tensile strength belongs 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. For a better understanding of the results obtained in tensile tests, fractured samples were investigated in scanning electron microscopy.

These results are 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.

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%. In the study made by Sahoo et al., (2011), the cause of this decline was explained as due to the mismatch between the polymer matrix interfaces with lignin particles. 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. The reason of variability in data supported with SEM analysis as it was explained above.

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.

POSS coupling agent used in the study for dispersion and compatibility. It was expected that the R groups on the cage provide compatibility via the principle of "like dissolves like" and cages containing polar groups or polymerizable groups provide interaction with polymer. In this content, the amount of POSS coupling agent used in lignin filled composites became very important to ensure compatibility. 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 and composites were shown in Figure 3.4. 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.

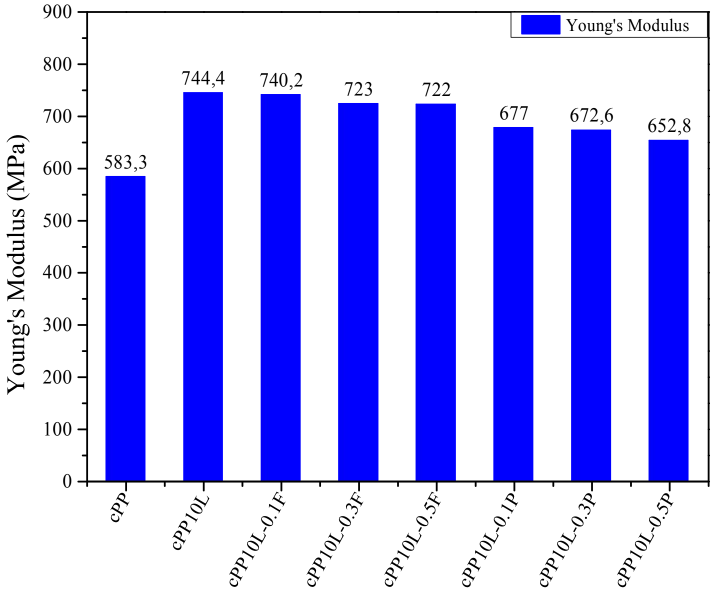

Figure 3.4: Young's modulus of copolymer and composites

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 as744.40 MPa. In the composites produced with FUSE coupling agent, it was seen a gradually 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.

To sum up, it could be concluded that Young's modulus of the composites increased and the elongation at break decreased, indicating that the composites became stiffer. 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.

This result would suggest that lignin may be used as a reinforcing agent, i.e. as a filler suitable to increase such mechanical features of the material, in general rigidity, but even the dimensional stability and the shrinkage.

3.2 Three Point Bending

Flexural strength and flexural modulus of neat copolymer and composites are shown in Table 3.2.

Table 3.5: Flexural strength and modulus values of copolymer and composites.

Samples	Flexural Strength (MPa)	Flexural modulus (MPa)
cPP	35.66 ± 8.43E-08	1385.18 ± 3.37E-07
cPP10L	36.23 ± 5.96E-08	1554.35 ± 0.00E+00
cPP10L-0.1F	20.19 ± 4.21E-08	975.56 ± 2.38E-07
cPP10L-0.3F	25.39 ± 0.00E+00	934.60 ± 0.00E+00
cPP10L-0.5F	23.24 ± 4.21E-08	955.08 ± 2.38E-07
cPP10L-0.1P	22.07 ± 4.21E-08	906.82 ± 0.00E+00
cPP10L-0.3P	23.35 ± 5.96E-08	917.98 ± 4.13E-07
cPP10L-0.5P	22.98 ± 0.00E+00	842.15 ± 2.38E-07

Flexural strength and flexural modulus of neat copolymer and the composites produced with and without FUSE and POSS coupling agents is given in Figure 3.5. When the values were investigated, it was seen that the incorporation of lignin to copolymer increased slightly the flexural strength value of copolymer.

When the composites containing FUSE were evaluated, a sharp decrease was observed with the addition of 0.1% wt. FUSE into the structure by decreasing flexural strength 36.23 MPa to approximately 20.19 MPa.

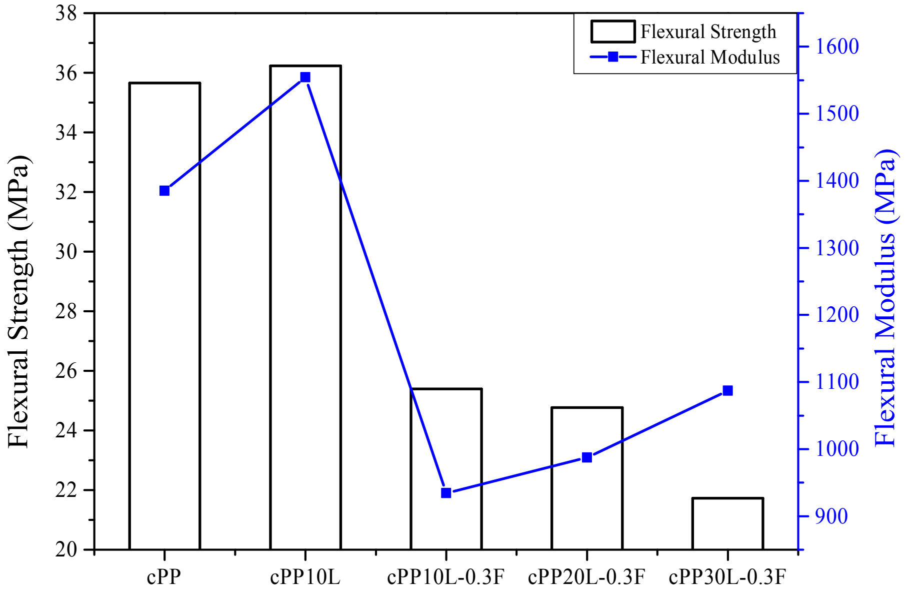

Figure 3.5: Flexural strength and flexural modulus graphs of copolymer and lignin filled composites.

However, the interesting result was obtained with the addition of 0.3% wt. FUSE coupling agent had an improvement in flexural strength of the composite around 5 MPa when comparing with the composite coupled by using 0.1% FUSE. When the FUSE content reaches the 0.5% wt., it was seen that there was a small decrease of the flexural strength value compared with the 0.3% wt. FUSE addition. According to these results, it could be said that among the composites, lignin filled composite containing 0.3% FUSE gave the best result when flexural strength was concerned.

With the addition of POSS chemical into the structure of the composites, there was a significant decrease around 14 MPa in the flexural strength value of the 0.1% wt. POSS added composite compared with the 10% wt. lignin addition to neat copolymer. 0.3% wt. POSS addition to lignin filled composite made an improvement in flexural strength and among the POSS containing composites it gave the best result. It was seen that 0.5% POSS added composites followed 0.3% wt. POSS containing lignin filled composite.

When the trend in tensile and flexural strength are compared depending on homogeneity, it could be said that lignin filled composites with and without coupling agents were non-homogeneous in structure. Because if lignin filled composites produced in the study were homogeneous, it would be expected that the flexural strength would be the same as the tensile strength. Also, the air voids trapped inside the composite could effect this result as it affects the result of tensile strength.

It was seen that there is a significant increase around 12% in modulus value of copolymer when comparing with the composite filled with 10% lignin. Flexural modulus values of all composites containing coupling agents are quite lower than copolymer’s modulus. When it is investigated the flexural modulus values of the composites containing FUSE, the modulus value of the composite containing 0.1% FUSE was found as 975,56 MPa which is the highest modulus value among the FUSE added composites. The modulus value decreased to 934.6 MPa with the addition of 0.3% FUSE and with the addition of 0.5% FUSE it was increased to 955 MPa. The modulus values of composites prepared with POSS are lower than the composites prepared with FUSE. According to these results, it was seen that addition of POSS had no improvement in flexural modulus values. 0.2% POSS containing composite (917.98 MPa) has higher modulus than 0.1% POSS added composite (906.82 MPa).

The lowest modulus belongs to (842.15 MPa) 0.5% POSS containing composite. The possible cause explained in the study Sahoo et al., (2011) as it may be the behavior of the material towards the stretching and bending forces.

According to mechanical testing results, it could be concluded in terms of application that lignin filled composites could be obviously used under tension rather than using in bending mode. While lignin filling and using of coupling agents for compatibility could not improve the ability to resist deformation under load, it provides ability to resist deformation under tension.

3.3 Dynamic Mechanical Analysis (DMA)

DMA analysis was performed between the temperatures 30^{o}C and 100^{o}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 composites was examined and given in the Table 3.3 at different temperatures.

Table 3.6: Storage modulus values of the copolymer and its composites at different temperatures

Samples	**Storage Modulus (MPa)**			
	30^{o}C	**50^{o}C**	**75^{o}C**	**100^{o}C**
cPP	1161.31	951.23	595.55	377.67
cPP10L	1131.84	941.03	583.74	355.78
cPP10L-0.1F	1118.99	934.31	578.83	346.58
cPP10L-0.3F	1108.07	910.14	564.24	341.99
cPP10L-0.5F	1217.75	999.02	617.20	369.91
cPP10L-0.1P	1094.26	942.36	593.31	358.28
cPP10L-0.3P	1193.89	985.58	610.11	361.96
cPP10L-0.5P	1177.95	994.14	612.78	352.98

The storage modulus of neat copolymer decreases when the temperature increases. The same result was found in the study made by Sahoo et al., (2011) 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 each compositions showed a decreasing trend between the temperatures 30°C and 100°C. The results showed that the deformation of composites increases by the temperature increases.

As it is seen in Figure 3.6, 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.

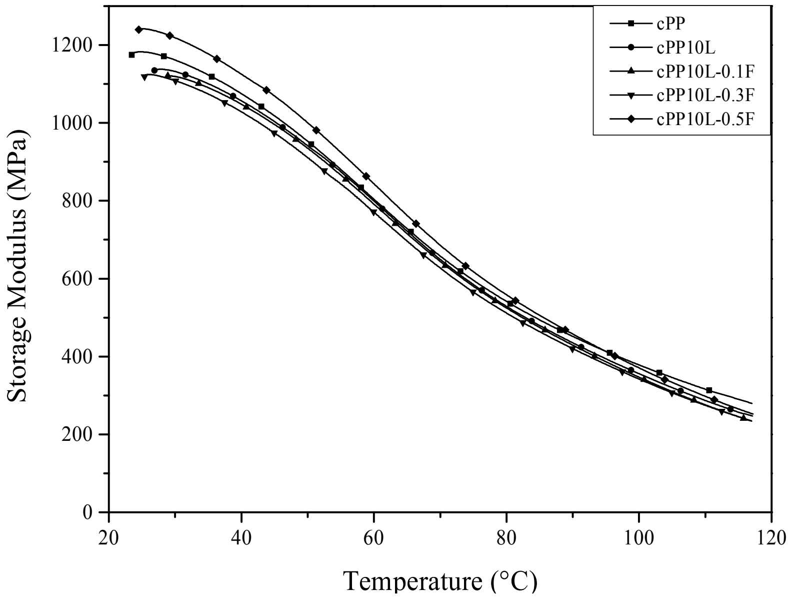

Figure 3.6: Storage Modulus of FUSE composites

Figure 3.7 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.

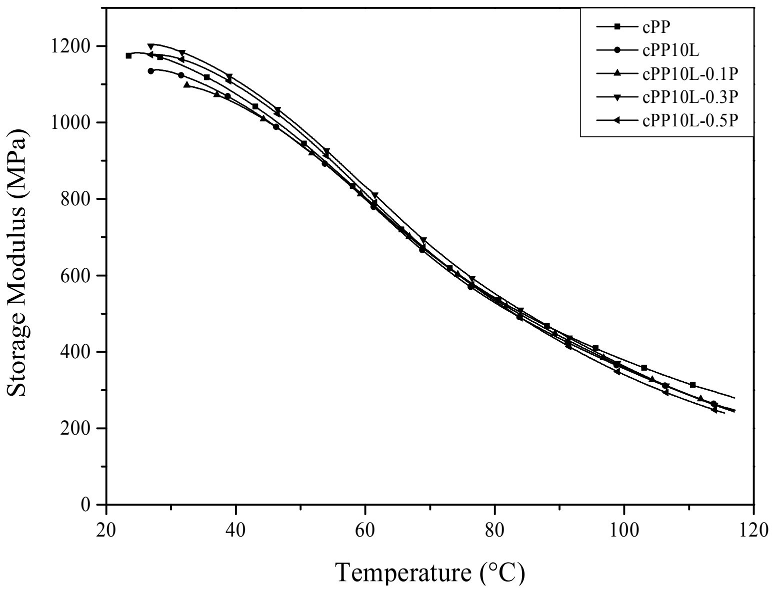

Figure 3.7: Storage Modulus of POSS composites

The results were different from the FUSE added composites in terms of the increasing and decreasing trends. When the Table 3.3 is investigated, it is seen that storage modulus decreased with the increasing POSS amounts in the composites modified with POSS at 30^{o}C. Contrary to this, the result differs at the temperatures 50^{o}C and 70^{o}C. At these two temperatures, storage modulus increased with the increasing POSS amount in the composite structures. At 100^{o}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 Sahoo et al., (2011). The damping behavior is the magnitude of tan d which is the ratio of loss modulus to storage modulus, also it can be explained as during a dynamic loading cycle, it is energy dissipated to energy stored.

Figure 3.8 shows the Tan δ values of copolymer and lignin filled composites modified with FUSE. As it is seen in the graph, lignin filled composites have higher Tan δ peak area than the neat copolymer has.

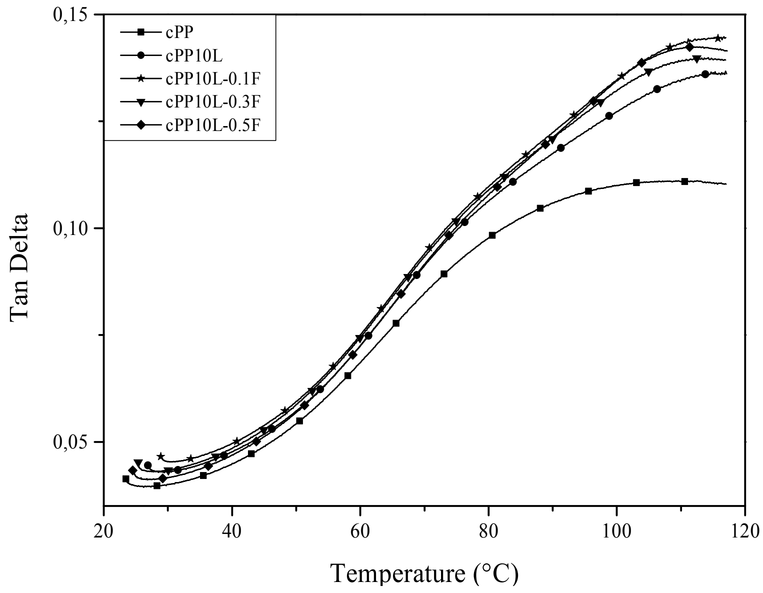

Figure 3.8: Tan delta vs. temperature graph of composites modified with FUSE

Figure 3.9 shows Tan δ values of copolymer and its composites modified with the POSS coupling agent. Addition of lignin and modification of composites with POSS made an increase in Tan δ. This result is dissimilar with the study made by Sahoo et al., (2011) because they found that Tan δ decreased with lignin incorporation to PBS matrix. They considered that this result indicated that the molecular mobility of the composite materials was decreased with addition of filler and mechanical loss occurred to overcome the interfriction between molecular chains was also reduced.

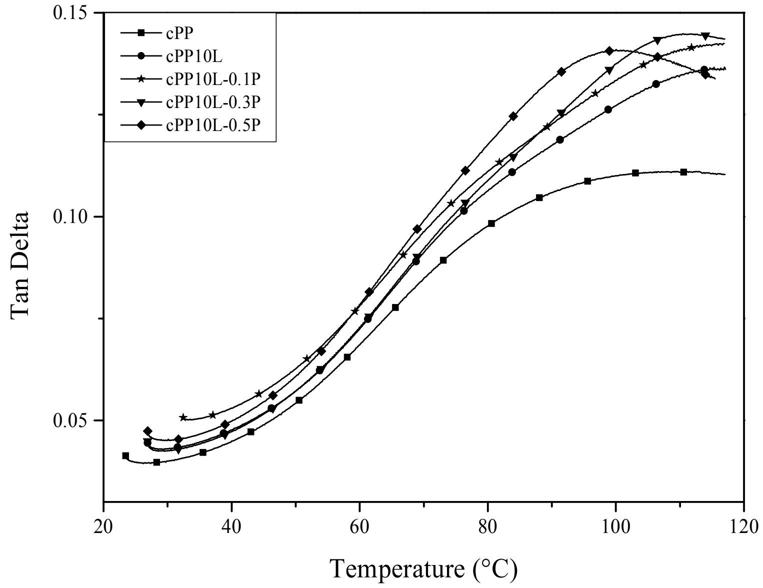

Figure 3.9: Tan delta vs. temperature graph of composites modified with POSS

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 interfriction 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 a different as its Tan δ has a decreasing trend after 100°C.

3.4 FTIR Analysis

Figure 3.10 shows that the stacked FTIR spectra of copolymer, lignin, coupling agent (Fuse) and their composites modified with FUSE between the wave numbers 4000 cm^{-1} and 500 cm^{-1}. FTIR spectra of lignin showed that lignin has 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. Also, the peaks at 2941 and 2879 cm^{-1} are attributed to the C-H stretch. One of the important peak is to mention is the band at 3351 cm^{-1}which became invisible in all lignin filled composites.

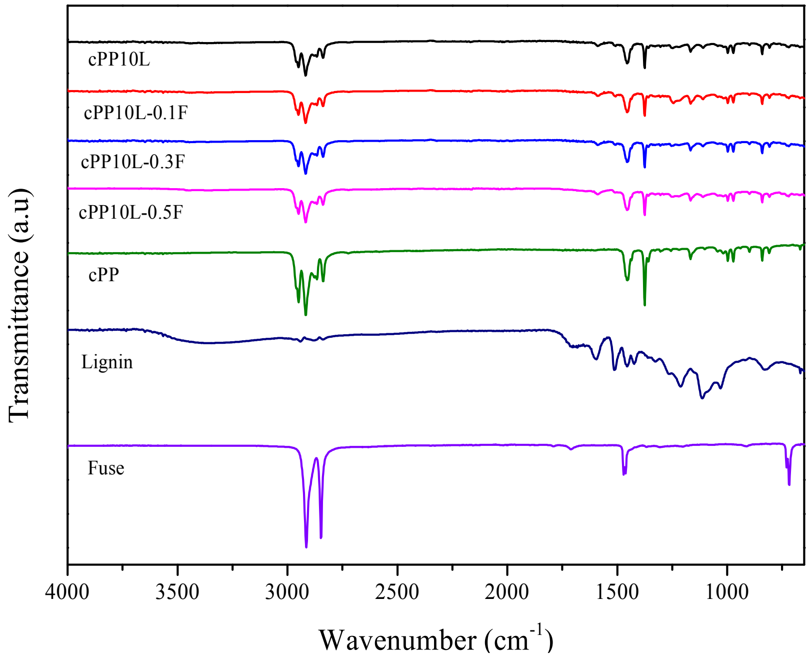

Figure 3.10: Stacked FTIR spectra of copolymer, lignin, coupling agent (Fuse) and their composites modified with FUSE.

Copolymer has peaks which represent 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 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.

Figure 3.11 shows the FTIR spectra of copolymer, lignin, coupling agent (Fuse) and their composites modified with FUSE 4000 cm^{-1} and 500 cm^{-1}. Lignin has the peaks at 1595 cm^{-1} which is aromatic functionality, aromatic C=C stretching, 1513 cm^{-1} which is aromatic skeletal vibration (S. Sahoo et al,. 2011). FTIR spectra showed that these peaks came from lignin became visible in its composites. Lignin also gives a peak at 1211 cm^{-1} which represents C-O-C soft segments. It is 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}.

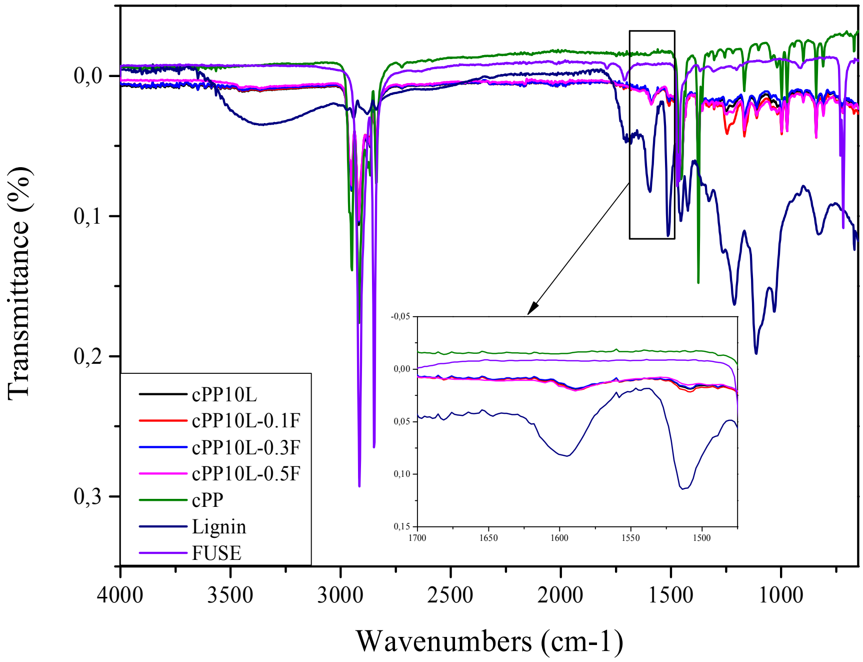

Figure 3.11: FTIR spectra of copolymer, lignin, coupling agent (Fuse) and their composites modified with FUSE.

Figure 3.12 shows the FTIR spectra of copolymer, lignin, coupling agent (POSS) and their composites modified with POSS. The peak of Lignin at 3351 cm^{-1} became invisible in all composites. But, it is seen that addition of lignin to copolymer makes a decrease in the intensity of the peaks at 2949, 2916, 2866 and 2837 cm^{-1}.

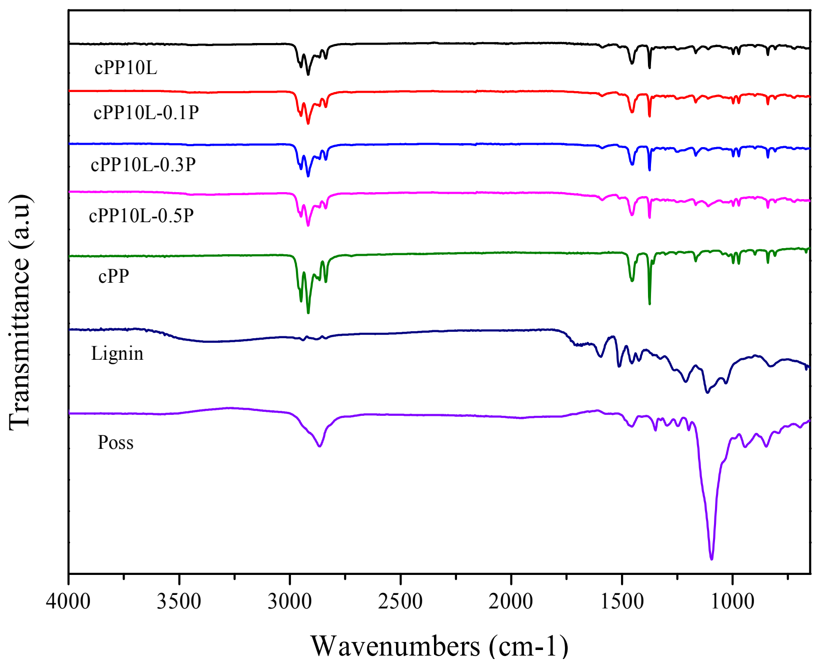

Figure 3.12: Stacked FTIR spectra of copolymer, lignin, coupling agent (POSS) and their composites modified with POSS.

Figure 3.13 shows the FTIR spectra of copolymer, lignin, coupling agent (POSS) and their composites modified with POSS. The peak of Lignin at 1681 cm^{-1} which is 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.

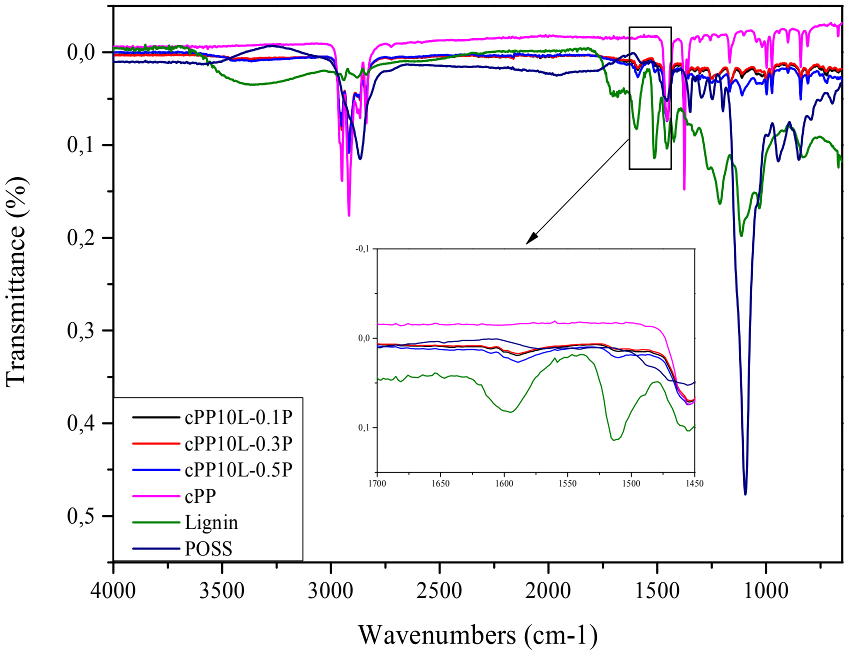

Figure 3.13: FTIR spectra of copolymer, lignin, coupling agent (POSS) and their composites modified with POSS.

Copolymer has the peak at 1453 cm^{-1} which is C-H deformation. Lignin has peak at 1455 cm^{-1} which also represents C-H deformation. There is 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 10% Lignin filled composite which has no modification, C-O-C soft segment peak at 1211 cm^{-1} can be seen only in all composites modified with POSS, especially in the composite modified with 0.5% POSS with higher intensity.

3.5 TGA Analysis

Table 3.4 shows onset temperature, degraded weight, end temperature and charred residues of lignin, extruded neat copolymer and all composites.

Table 3.4: Onset temperature, degraded weight, end temperature and Maximum Degradation Temperature of the specimens.

Specimens	T_{onset} (°C)	Degraded Weight (%)	T_{end} (°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 3.14 shows a typical mass loss curve until 700°C. In TGA graph of lignin it was seen that initial weight loss around 2.3% wt. occurs at 49.3 °C and continues until the temperature 75.3 °C. The reason of this weight loss could be attributed to loss of moisture from lignin. This result was supported in the study Sahoo et al., (2011) and 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). Main degradation of lignin was observed at 286 °C and 57.1% wt. is lost and this degradation continues until the temperature around 430 °C.

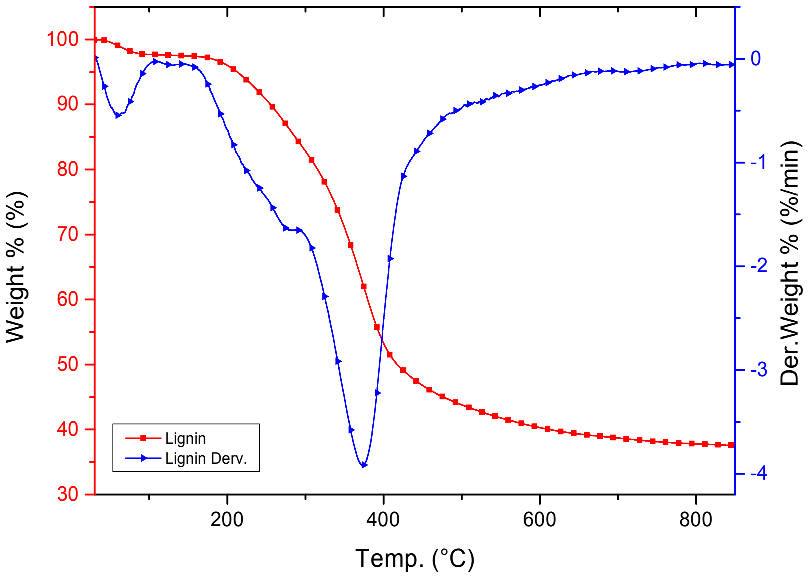

Figure 3.14: TGA analysis of Protobind Lignin 2400

Lignin degradation was also explained in the study made by Sun and Tomkinson, (2001) as "Pyrolytic degradation of lignin in the temperature region involved fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase". Practically, extruder barrel temperatures were set between 170°C and 185°C for the production of lignin filled composites. According to TGA analysis of lignin because of onset degradation temperature of lignin was found as 286°C, it was concluded that 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 article made by Sun and Tomkinson, (2001) which concluded that the non-volatile residue at 600 °C was large, amounting to 45.5% of the lignin material. The study 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 data, copolymer degraded between the temperatures around 443.1°C and 472.8°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 decreases the onset temperature. The addition of lignin to copolymer without modification decreased the degraded weight percentage app. 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 app. 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 were approximately the same with each other but higher than the temperature of copolymer which is 474.8°C. Among the composites, 10% wt. Lignin filled composite modified with 0.3% wt. FUSE and 10% wt.

3.6 SEM Analysis

Figure 3.16 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 3.17 (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. These holes indicate poor interfacial adhesion and this observation supported by tensile testing data of composites. In the typical SEM micrographs of lignin which is seen in Figure 3.17 (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.

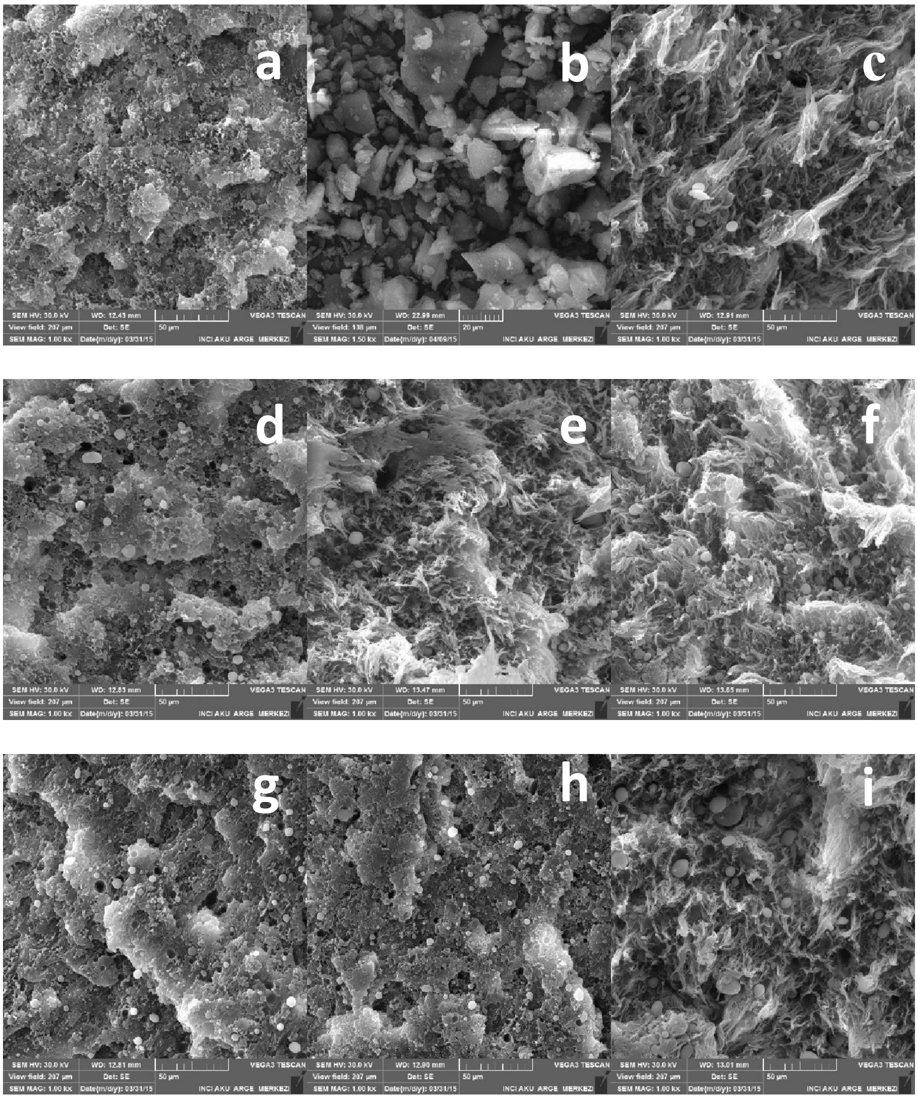

Figure 3.25: SEM images; a) cPP, b) Lignin c) cPP10L, d) cPP10L-0.1F, e) cPP10L-0.3F, f) cPP10L-0.5F, g) cPP10L-0.1P, h) cPP10L-0.3P, i) cPP10L-0.5P

3.7 Observation of mechanical properties of composites depending on lignin content by using 0.3% FUSE as a coupling agent

According to the test results given above, it was seen that 0.3% FUSE added composites gave the optimum results when taking into consideration the mechanical properties. Because of this reason, this part of the study was made in order to see the effect of lignin content in the composites prepared by using 0.3% FUSE coupling agent. The same materials were used as well in this part of the study. Tensile and three-point bending tests were performed and result were given in Table 3.5.

Table 3.5: Elongation at break, Young's Modulus and Tensile Strength of the composites

SAMPLES	ELONGATION AT BREAK (%)	YOUNG'S MODULUS (MPa)	TENSILE STRENGTH (MPa)
cPP	43.5±3.81	583.3±13.94	13.88±2.15
cPP10L	17.5±2.09	744.4±13.64	14.132±1.88
cPP10L-0.3F	34,4±2,93	723±15,53	14,256±1,89
cPP20L-0.3F	30±2.04	839,23±14.74	13,27±1.01
cPP30L-0.3F	15,65±2.15	860,47±13.81	10,83±1.23

Figure 3.16 shows tensile strength and elongation break graphs of copolymer and lignin filled composites.

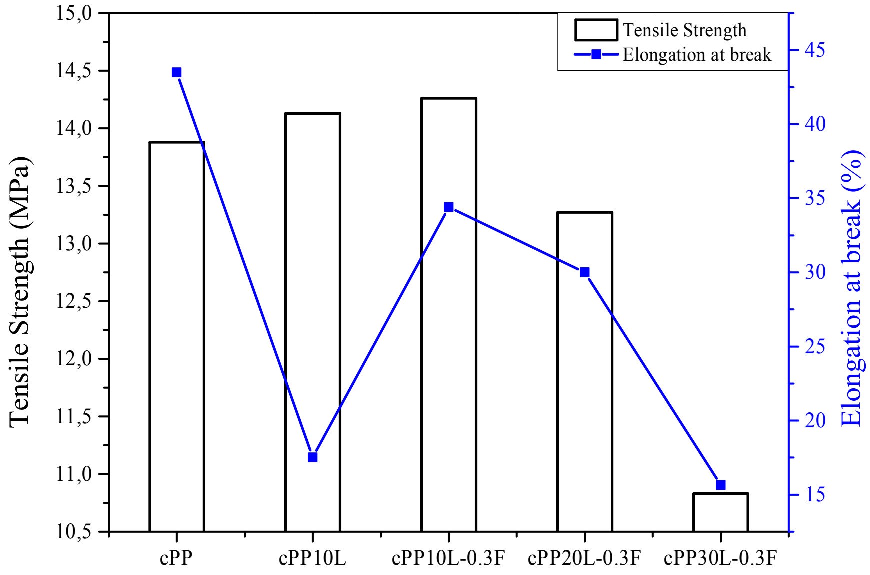

Figure 3.16: Tensile strength and elongation break of copolymer and lignin filled composites.

When the tensile test was investigated, it was observed that there was an approximately 2% increase in tensile strength with the addition of lignin to copolymer. It was concluded that similar tensile strength was obtained by the addition of 0.3% FUSE coupling agent into 10% filled composite. This case showed that there was no effect with the addition of coupling agent to tensile strength value of 10% lignin filled composite. When the tensile strength values of cPP20L-0.3F and cPP30L-0.3F were investigated, it was seen that there was a decrease in tensile strength of the composites which is inversely proportional with the increase of lignin content. The main reason of this situation is thought that agglomeration occured due to the increasing content of lignin and consequent incompatibility between the filler and the matrix.

When the elongation at break values were investigated, it was seen that lignin addition to the neat copolymer made a significant decrease which is around 76%. The possible reason could be the incompatibility in interface between lignin and matrix. The negative impact substantially removed with the addition of coupling agent to 10% lignin filled composite and only 10% decrease observed comparing with the neat copolymer. This case clearly demonstrates that use of the coupling agent has a positive effect on elongation at break values of composite materials. When the elongation at break values of cPP20L-0.3F and cPP30L-0.3F were investigated, it was seen that increase in lignin content made a decrease in strain values. The reason of this case could be the insufficient content of coupling agent and it has no effect to neutralize the negative effect of incompatibility of lignin/matrix interface.

Figure 3.17 shows Young's modulus graph of copolymer and lignin filled composites.

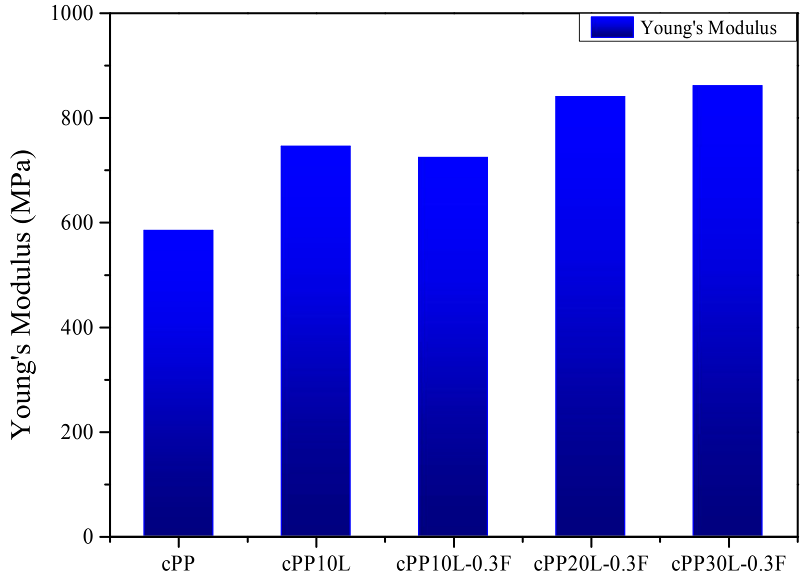

Figure 3.17: Young's modulus of copolymer and lignin filled composites.

When Young's modulus values were investigated, it was seen that there was an increase about 27% of Young's Modulus by addition of lignin to neat copolymer. Although there was a small decrease in Young's Modulus of 10% lignin filled composite by the addition of 0.3% FUSE coupling agent, generally Young's Modulus values were increased significantly by increasing lignin content.

Flexural tests were performed and result were given in Table 3.6.

Table 3.6: Flexural Strength and modulus of the composites

Samples	Flexural Strength (MPa)	Flexural modulus (MPa)
cPP	35.66 ± 8.43E-08	1385.18 ± 3.37E-07
cPP10L	36,23 ± 5,96E-08	1554,35 ± 0,00E+00
cPP10L-0.3F	25,39 ± 0,00E+00	934,60 ± 0,00E+00
cPP20L-0.3F	24,77±3,44128E-08	987,52±1,94668E-07
cPP30L-0.3F	21,73±5,96046E-08	1086,88±5,50604E-07

Figure 3.18 shows flexural strength and flexural modulus graphs of copolymer and lignin filled composites.

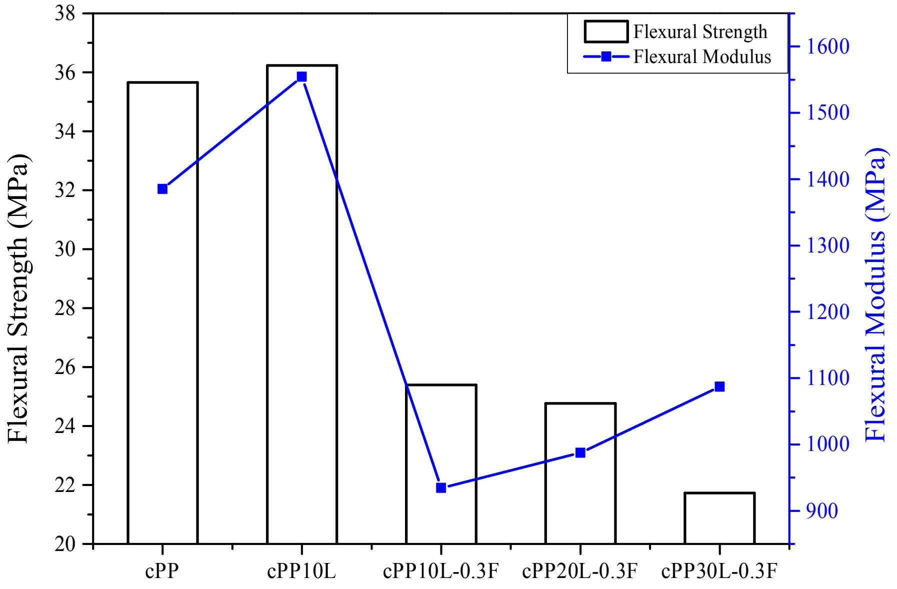

Figure 3.18: Flexural strength and flexural modulus of copolymer and lignin filled composites.

When the flexural strength values were investigated, the addition of lignin to neat copolymer had minute effect on flexural strength of copolymer. It was seen that there was a significant decrease in flexural strength with the addition of coupling agent to 10% lignin filled composite (Pe et al., 2015). There is a study in the literature which is about effect of coupling agents on the composites filled with natural fiber. In this study was concluded that the composites made with coupling agent presented lower flexural moduli than without coupling agent. The result was discussed as ‘’Incorporation of coupling agents sometimes does not produce significant improvement in flexural modulus of polymer-lignocellulose composites. Lower modulus may possibly be due to the plasticizing effect of low molecular weight MAPE which coused a reduction of the composite stiffness.’’ It was seen that there was a reduction in flexural strength values of 20% and 30% filled composites by increasing lignin content as this inverse effect was similarly observed in tensile strength of the composites.

When the flexural modulus values were investigated, there was an increase approximately 12% by the addition of 10% lignin to copolymer. It was observed a significant decrease in flexural moduli by the addition of FUSE coupling agent to 10% lignin filled composite. This decrease could be caused by the plastisizing effect of coupling agent (Pe et al., 2015). When the flexural modulus values of cPP20L-0.3F and cPP30L-0.3F were investigated, flexural modulus were increased by increasing lignin content. It was concluded that this result coincided with the Young's modulus values obtained by tensile test.

4. CONCLUSION

A series of composites has been fabricated with 10% lignin addition with two different coupling agents. The important features of the soda lignin preparations and resulting composites comprise the following:

According to tensile test, there was no improvement in tensile strength by addition of lignin and coupling agents. The decrease of 60% in elongation at break by lignin addition to neat copolymer had improved with the use of FUSE and POSS coupling agents. The optimum amount of FUSE and POSS in composites could be selected as 0.3% for the best interaction with lignin and polymer. 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.

It is concluded in flexural test, while the incorporation of lignin to copolymer increased slightly the flexural strength value of copolymer, addition of FUSE and POSS coupling agents deteriorate the flexural strength comparing with neat copolymer and lignin filled composite. There is a significant increase around 12% in modulus value of copolymer when comparing with the composite filled with 10% lignin. Flexural modulus values of all composites containing coupling agents are quite lower than copolymer's modulus.

According to mechanical testing results, almost the same tensile strength as copolymer's and more rigid composites produced with the addition of lignin and coupling agents. It could be concluded in terms of application that lignin filled composites could be obviously used under tension rather than using in bending mode.

While lignin filling and using of coupling agents for compatibility could not improve the ability to resist deformation under load, it provides ability to resist deformation under tension. Also, environmentally friendly and low-cost products were produced comparing with copolymer. The viscoelastic behavior and the impact of the modification with coupling agents on lignin-matrix adhesion investigated by DMA test. The storage modulus of neat copolymer decreases when the temperature increases. Lignin incorporation decreases the stiffness of the material. The results showed that the deformation of composites increases by the temperature increases. Lignin filled composites containing FUSE coupling agents have higher Tan δ peak area than the neat copolymer has. Addition of lignin and modification of composites with POSS made an increase in Tan δ.

Interaction in lignin filled composites were analyzed with (FTIR). The interaction of neat copolymer, lignin and coupling agents were investigated.

In TGA analysis, that addition of lignin decreases the onset temperature of copolymer. While FUSE has no effect on onset temperature, the addition of 0.1% POSS increased the onset temperature app. 3^{o}C when compared with lignin filled composite. The degraded weight of the composites slightly decreased with using FUSE and POSS coupling agents in the composite structure.

Morphology of interface was observed by SEM analysis. It is seen that lignin has not homogeneous in size which changes between 5-35 µm. Also, the composites produced has air voids and proper lignin dispersion could not be achieved.

For the future of study, a pre-treatment surface modification could be applied to lignin in order to enhance the compatibility with the polymeric matrix. In terms of processing, lignin could be feed from a side-feeder to extruder in order to enhance the dispersion of lignin in polymer melt. Additional analysis for characterization could be performed to lignin reinforced composites such as DSC (Differential Scanning Calorimetry), contact angle measurement, water absorption capacity and UV test.

5. REFERENCES

Amar, K.M., et al., (2005). Natural Fibers, Biopolymers, and Biocomposites. *CRC Press*, Tailor and Francis.

Alexy, P., et al,.(2000). The effect of blending lignin with polyethylene and polypropylene on physical properties. *Polymer*, *41*(13), 4901–4908. doi:10.1016/S0032-3861(99)00714-4

Bernardini, J., et al,.(2014). Accepted Manuscript.

Bledzki, A. K., et al,. (1998). Thermoplastics reinforced with wood fillers. *Polym. Plast. Technol. Eng.* 37, 451-468.

Buranov, A. U., and Mazza, G. (2008). Lignin in straw of herbaceous crops. *Industrial Crops and Products*, *28*(3), 237–259. doi:10.1016/j.indcrop.2008.03.008

Canetti, M., and Bertini, F. (2007). Supermolecular structure and thermal properties of poly(ethylene terephthalate)/lignin composites. *Composites Science and Technology*, *67*(15-16), 3151–3157. doi:10.1016/j.compscitech.2007.04.013

Cazacu, G., et al,.(2004). Lignin role in a complex polyolefin blend. *Industrial Crops and Products*, *20*(2), 261–273. doi:10.1016/j.indcrop.2004.04.030

Chauhan, M., et al,. (2014). Effect of functionalized lignin on the properties of lignin–isocyanate prepolymer blends and composites. *European Polymer Journal* (Vol. 52). Elsevier Ltd. doi:10.1016/j.eurpolymj.2013.12.016

Chawla, K.K. (1987). Composite Materials. Science and Engineering. *Springer* Verlag, New York.

Chen, L., et al,.(2009). Preparation and Properties of Chitosan/Lignin Composite Films. *Chinese Journal of Polymer Science*, *27*(05), 739. doi:10.1142/S0256767909004448

Chung, H., and Washburn, N. R. (2012). Chemistry of lignin-based, *1*, 137–160.

Cinelli, P., et al,. (2013). Green synthesis of flexible polyurethane foams from liquefied lignin. *European Polymer Journal*, *49*(6), 1174–1184. doi:10.1016/j.eurpolymj.2013.04.005

de Wild, P. J., et al,. (2012). Pyrolysis of wheat straw-derived organosolv lignin. *Journal of Analytical and Applied Pyrolysis*, *93*, 95–103. doi:10.1016/j.jaap.2011.10.002

Datasheet of FUSABOND E 265

Datasheet of Protobind 2400

Datasheet of Moplen 2000 HEXP

Doherty, W. O. S., et al,. (2011). Value-adding to cellulosic ethanol: Lignin polymers. *Industrial Crops and Products*, *33*(2), 259–276.

doi:10.1016/j.indcrop.2010.10.022

Duval, A., and Lawoko, M. (2014). A review on lignin-based polymeric, micro- and nano-structured materials. *Reactive and Functional Polymers*. doi:10.1016/j.reactfunctpolym.2014.09.017

Fan, D., et al, (2011). Structure and properties of alkaline lignin-filled poly(butylene succinate) plastics. *Iran. Polym. J.*, 20, 3–14. (n.d.).

Gonza, C. (1999). Micromechanics of lignin / polypropylene composites suitable for industrial applications a, *272*(4758), 65–70.

Gordobil, O., et al,. (2014). Physicochemical properties of PLA lignin blends. *Polymer Degradation and Stability*, *108*, 330–338. doi:10.1016/j.polymdegradstab.2014.01.002

Gregorová, A., et al,.(2005). Stabilization effect of lignin in polypropylene and recycled polypropylene. *Polymer Degradation and Stability*, *89*(3), 553–558. doi:10.1016/j.polymdegradstab.2005.02.007

Hilburg, S. L., et al,. (2014). A universal route towards thermoplastic lignin composites with improved mechanical properties. *Polymer*, *55*(4), 995–1003. doi:10.1016/j.polymer.2013.12.070

Hull, D. and Clyne, T.W. (1996). An introduction to composite materials. Cambridge University Press, Cambridge

Ibrahim, M. N. M., et al,.(2004). Characterization of lignin precipitated from the soda black liquor of oil palm empty fruit bunch fibers by various mineral acids, *21*, 57–67.

Joffres, B., et al,. (2014). Applied Catalysis B : Environmental Catalytic hydroconversion of a wheat straw soda lignin : Characterization of the products and the lignin residue, *145*, 167–176.

Kadla, J. F., and Kubo, S. (2004). Lignin-based polymer blends: analysis of intermolecular interactions in lignin–synthetic polymer blends. *Composites Part A: Applied Science and Manufacturing*, *35*(3), 395–400. doi:10.1016/j.compositesa.2003.09.019

Kaxiras, E. (2001). Materials Science. *Computing in Science and Engineering*, *3*(6). doi:10.1109/MCISE.2001.963423

Kharade, A. Y., and Kale, D. D. (1999). Lignin-Filled Polyolefins, *72*(November 1997), 1321–1326.

Košíková, B., et al,.(1995). The effect of adding lignin on modification of surface properties of polypropylene. *European Polymer Journal*, *31*(10), 953–956. doi:http://dx.doi.org/10.1016/0014-3057(95)00052-6

Kraslawski, A. V. and A. (2011). Challenges in industrial applications of technical lignins, *6*(Sjöström 1982), 3547–3568.

Laurichesse, S., and Avérous, L. (2014). Chemical modification of lignins: Towards biobased polymers. *Progress in Polymer Science*, *39*(7), 1266–1290. doi:10.1016/j.progpolymsci.2013.11.004

Laurichesse, S., and Avérous, L. (2013). Synthesis , thermal properties , rheological and mechanical behaviors of lignins- grafted -poly (ε -caprolactone), *54*, 3882–

3890.

Li, J., et al,. (2011). Preparation of a lignin-based composite and its properties. *BioResources; Vol 6, No 2 (2011).*

Li, Y. A. N., and Mlyna, J. (2004). The First 85 % Kraft Lignin-Based Thermoplastics *, (February 1997), 1899–1910.

Li, Y., and Sarkanen, S. (2002). Alkylated Kraft Lignin-Based Thermoplastic Blends with Aliphatic Polyesters. *Macromolecules*, *35*(26), 9707–9715. doi:10.1021/ma021124u

Lora, J. (2008). Monomers, Polymers and Composites from Renewable Resources. *Elsevier*. doi:10.1016/B978-0-08-045316-3.00010-7

Luong, N. D., et al,.(2011). An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis. *Polymer Bulletin*, *68*(3), 879–890. doi:10.1007/s00289-011-0658-x

Mariotti, N., et al,. (2013). Combination of Esterified Kraft Lignin and MAPE as Coupling Agent for Bark/HDPE Composites. *Journal of Materials Science Research*, *3*(2), 8–22. doi:10.5539/jmsr.v3n2p8

Mousavioun, P., et al,. (2010). Thermal stability and miscibility of poly(hydroxybutyrate) and soda lignin blends. *Industrial Crops and Products*. doi:10.1016/j.indcrop.2010.08.001

Olsson, S., et al,.(2011). The use of esterified lignin for synthesis of durable composites. In: Proceedings of the 7th meeting of the Nordic-Baltic Network in Wood Material Science and Engin. (n.d.), 173–179.

Ouyang, X., et al,. (2010). Oxidative Degradation of Soda Lignin Assisted by Microwave Irradiation. *Chinese Journal of Chemical Engineering*, *18*(4), 695–702. doi:10.1016/S1004-9541(10)60277-7

Pe, A. A., Rodrigue, D., & Gonza, R. (2015). Self-hybridization and Coupling Agent Effect on the Properties of Natural Fiber / HDPE Composites. doi:10.1007/s10924-014-0706-3

Peng, Y., et al,.(2014). Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin, and cellulose. Applied Surface Science, 317, 385–392. doi:10.1016/j.apsusc.2014.08.140

Pouteau, C., et al,.(2004). Lignin–polymer blends: evaluation of compatibility by image analysis. *Comptes Rendus Biologies*, *327*(9-10), 935–943. doi:10.1016/j.crvi.2004.08.008

Pouteau, C., et al,. (2003). Antioxidant properties of lignin in polypropylene. *Polymer Degradation and Stability*, *81*(1), 9–18. doi:10.1016/S0141-3910(03)00057-0

Pucciariello, R., et al,. (2004). Physical properties of straw lignin-based polymer blends. *Polymer*, *45*, 4159–4169. doi:10.1016/j.polymer.2004.03.098

Republic, S. (1995). The effect of adding lignin on modification, *31*(95), 953–956.

Sahoo, S., et al,. (2011). Characterization of industrial lignins for their utilization in future value added applications. *Biomass and Bioenergy*. doi:10.1016/j.biombioe.2011.07.009

Sahoo, S., et al,.(2011). Enhanced properties of lignin-based biodegradable polymer composites using injection moulding process. *Composites Part A: Applied Science and Manufacturing*, *42*(11), 1710–1718. doi:10.1016/j.compositesa.2011.07.025

Sailaja, R. R. N., and Deepthi, M. V. (2010a). Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin. *Materials and Design*, *31*(9), 4369–4379. doi:10.1016/j.matdes.2010.03.046

Sailaja, R. R. N., and Deepthi, M. V. (2010b). Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin. *Materials and Design*, *31*(9), 4369–4379. doi:10.1016/j.matdes.2010.03.046

Seydibeyoğlu, M. Ö. (2012). A novel partially biobased PAN-lignin blend as a potential carbon fiber precursor. *Journal of Biomedicine and Biotechnology*, *2012*, 598324. doi:10.1155/2012/598324

Soygun, K., et al,.(2013). Investigation of Mechanical and Structural Properties of Blend Lignin-PMMA. *Advances in Materials Science and Engineering*, *2013*, 1–6. doi:10.1155/2013/435260

Sun, R., and Tomkinson, J. (2001). Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping. *Separation and Purification Technology*, *24*(3), 529–539. doi:10.1016/S1383-5866(01)00153-8

Thakur, V. K., et al,. (2014). Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. *ACS Sustainable Chemistry and Engineering*, *2*(5), 1072–1092. doi:10.1021/sc500087z

Yeo, J.-S., et al,.(2015). Chemical surface modification of lignin particle and its application as filler in the polypropylene composites. *Journal of Industrial and Engineering Chemistry*. doi:10.1016/j.jiec.2015.06.010

Youngavb, R. A. (2002). Lignin-Polypropylene Composites. Part 1 : Composites From Unmodified Lignin and Polypropylene, *23*(5), 1–8.

Zhong, M., et al,. (2011). Strong , flexible high-lignin polypropylene blends, *12*, 2–4.

APPENDIX

Appendix A.1Matrix material, lignin type, coupling agents used or modification applied, process type, characterization and related reference works.

MATRIX	LIGNIN TYPE	COUPLING AGENT/MODIFICATION	PROCESS TYPE	CHARACTERIZATION	REFERENCE
Polyethylene terephthalate (PET)	Solid lignin (from industrial waste black liquor)	-	Blending	DSC and TGA	(Hilburg et al., 2014)
PP	Alkali lignin (extracted from pulping black liquor)	-	Co-rotating twin-screw extruder	QUV accelerated weathering test, Colorimetric analysis, SEM, surface gloss measurement, contact angle measurement, Flexural Properties, ATR-FTIR	(Peng et al., 2014)
Poly(Lactic Acid) (PLA)	Commercial alkali lignin (CL) and lignin extracted from almond shells by organosolv process (OL)	Acetylation reaction	Extrusion with double screw	HPLC, FT-IR, GPC, DSC and TGA, mechanical testing, contact angle hydrolytic degradation, optical microscope	(Gordobil, Egüés, Llano-Ponte, and Labidi, 2014)
Polyethylene Glycol-PEG 400	The soda lignin (Protobind 1075)	4,4’-diphenyl methane diisocyante (MDI)	Blending	Rheological tests, Contact angle measurement,DMA, Tensile Test, FTIR, FESEM–EDAX and DSC	(Chauhan et al., 2014)
Polyurethane	Kraft pine lignin	-	Foam formation	TGA, DMTA, compression force deflection (CFDV), SEM, FTIR	(Cinelli, Anguillesi, and Lazzeri, 2013)
Polymethyl metacrylate (PMMA) resin	Kraft Lignin	-	Polymerization in mold	The transverse and impact strength tests, SEM, FTIR, eTMA	(Soygun, Şimşek, Yılmaz, and Bolayır, 2013)

Appendix A.2 (continued)

MATRIX	LIGNIN TYPE	COUPLING AGENT/MODIFICATION	PROCESS TYPE	CHARACTERIZATION	REFERENCE
High density polyethylene	Lignin (by LignoBoost process)	polyethylenegraftedwithmaleic anhydride (MAPE) and/or esterified lignin	Blend	TGA, SEM-EDS, Physical and Mechanical Testing , Statistical Analyses	(Mariotti, Wang, Rodrigue, and Stevanovic, 2013)
PAN (polyacrylonitrile)	Protobind 1000, Protobind 5000, and Protobind 2400	-	Solution casting	Optical microscopy, SEM, FTIR, TGA, DMA	(Seydibeyoğlu, 2012)
Polybutylene succinate (PBS)	Lignin 'Arboform® F 45'	Polymeric methylene diphenyl diisocyanate (PMDI)	Microextruder (DSM Xplore, Netherland)	C, N, S analysis Mechanical testing, FTIR, DSC, DMA, TGA, SEM, density measurement	(Sahoo et al., 2011)
LDPE	Kraft softwood lignin	Esterification	Compounding (micro extruder) and film extrusion	ATR-FTIR, DSC,TGA, Tensile Test, optical microscopic images	(Olsson et al., 2011)
Phenol formaldehyde resin	Enzymatic hydrolysis (EH) lignin	formaldehyde	Atomizing resin blender	TG-DSC, PY-GC-MS	(J. Li, Li, Wang, Yang, and Guo, 2011)
PBS	Alkaline lignin	Methylenediphenyldiisocyanate (MDI) 0.5 to 2%.	Blend	FTIR, XRD, SEM, DSC, Swelling test, mechanical test, the water absorption,	(Fan et al., 2011)
PP	Alkylated lignin	Bromododecane	Blended by melt-mixing	Tensile and flexural tests, SEM, TG tests, LOI measurement,	(Zhong et al., 2011)

Appendix A.3 (continued)

MATRIX	LIGNIN TYPE	COUPLING AGENT/MODIFICATION	PROCESS TYPE	CHARACTERIZATION	REFERENCE
Bacterial PHB was obtained from Sigma Aldrich	Soda lignin was extracted from bagasse by the soda Process	-	Blended with mini lab twin screw	TGA, DSC, SEM, FTIR	(Mousavioun et al., 2010)
LDPE	Lignin (Sigma Aldrich, USA) up to 40 wt. %)	Esterification (using phthalic anhydride)	Blending (melt mixing)	Mechanical properties, TGA, SEM, FTIR, RIS, DSC	(Sailaja and Deepthi, 2010a)
LDPE	Lignin (Sigma Aldrich, USA)	Blends of LDPE, lignin phthalate, LDPE-g-maleic anhydride	Blend	FTIR, Relative impact strength (RIS), SEM, DSC	(Sailaja and Deepthi, 2010b)
Chitosan powder (deacetylation degree of 90%)	Lignin (from paper industry)	-	Blending	SEM, FTIR, Mechanical properties, TGA, The water vapor permeability (WVP)	(Chen et al., 2009)
PET (Caripack P82, Shell)	Hydrolytic lignin (0, 2.5, 5, 10, 20 % weight)	-	mechanical mixingfollowed by thermal extrusion (single-screw)	polarizing optical microscope, WAXD, SAXS, DSC	(Canetti and Bertini, 2007)
(PP) and recycled PP	The sulphur-free lignin (beech wood pre-hydrolysis) 0.5 to 10 wt%	-	compounding in a laboratory size Brabender	DSC, heat resistance (Vicat softening temperature)	(Gregorová, Cibulková, Košíková, and Šimon, 2005)
PP, PEBD, POE, PS, PAN, PVC, PVAc, PHBV,PEA, PBSA	Kraft lignin	-	The blend (with three zone micro-extruders)	Microscope, UV micro spectrophotometry, Light microscopy	(Charlyse Pouteau et al., 2004)

Appendix A.4 (continued)

MATRIX	LIGNIN TYPE	COUPLING AGENT/MODIFICATION	PROCESS TYPE	CHARACTERIZATION	REFERENCE
PVA, PP, PET, PEO	Hardwood kraft lignin (0, 25,50,75, 87.5, 95,100 % weight)	-	mechanical mixing followed by thermal extrusion (single-screw)	DSC, FT-IR, Functional group analyses, GPC	(Kadla and Kubo, 2004)
Poly(vinyl acetate)	85% (w/w) underivatized industrial kraft lignin	-	Solution Casting	Tensile Test, DSC	(Y. A. N. Li and Mlyna, 2004)
polyolefin blend (70 PP/30 PE)	The lignin from sulphite process (lignosulfonates)	compatibilizing agent Exxelor 805	the open roll mixer/press method	physico-mechanical indices determination, TG/DTG, FTIR, ESRand contact angle measurements, the soil burial and terrestrial plant growth tests, tensile test	(Cazacu et al., 2004)
PP	Lignins (extracted from: bran, wheat straw), Kraft lignins (extracted using different solvents)	-	Blend extruded with a micro-extruder	High Performance Size Exclusion Chromatography, FTIR, DSC, TGA, UV-Spectrometry	(C. Pouteau et al., 2003)
lsotactic polypropylene	Indulin AT 10-60% wt. (purified from kraft lignin)	Two maleic anhydride modified polypropylene (MAPP)	Blend (melt mixing)	Tensile, flexural and unnotched Izod impact strength	(Youngavb, 2002)
Miscible aliphatic polyesters	The alkylated kraft lignin	-	Solvent Casting	Tensile Test, DSC, XRD	(Y. Li and Sarkanen, 2002)
LDPE and non-stabilized PP in powder form	Lignin PLE by prehydrolysis of beech wood (up to 30% by wt.)	-	Blending (single screw extruder)	melt flow index (MFI), The tensile test, the light stability (LS) and the long-term heat stability (LTHS)	(Alexy et al., 2000)

Appendix A.5 (continued)

MATRIX	LIGNIN TYPE	COUPLING AGENT/MODIFICATION	PROCESS TYPE	CHARACTERIZATION	REFERENCE
Two PPs with different molecular weights	Kraft lignin (10 to 55% wt.)	-	melt blending in a thermokinetic mixer	tensile testing	(Gonza, 1999)
LDPE, HDPE, PP	Dry lignin powder (up to 30% wt.)	EAA or titanate coupling agent	melt-blended	The Izod impact, Rheological measurement (rotational parallel plate viscometer), The color strength and color analysis, DSC	(Kharade and Kale, 1999)
PP powder	Organocell Lignin, Pre-hydrolysis Lignin, Alcelllignin	-	Blending	Zetapotential and Contact angle measurement	(Košíková, Revajová, and Demianová, 1995)
The isotactic polypropylene (iPP)	Pristine lignin	Hydrolysis condensation reaction using (3-aminopropyl) triethoxysilane and then was treated with PP-graft-maleic anhydride (to give MAPP anchored Lignin)	melt-blending	FT-IR, SEM-EDX and XPS	(Yeo et al., 2015)

Curriculum Vitae

PERSONAL INFORMATION

Name: Tuğçe

Surname: UYSALMAN

Education Status : MSc. Student

Marital Status : Single

Nationality : Turkish

Date/Place of Birth : 23.04.1990/İZMİR

Driver's License : B (2010)

Cell Phone: +90 553 342 30 52

E-mail: tugceuysalman@gmail.com

Address: Zeytinpark Evleri, 119/4 Sokak, No:1, Daire:1, D Blok, Bornova/İzmir, TURKEY

EDUCATION INFORMATION

University (Master's Degree) **İzmir Katip Çelebi University**

Engineering and Architecture Faculty

10.2013- 06.2015 (predicted) Materials Sciences and Engineering (English)

University (Bachelor's Degree) **Ege University**- (Formal Education)

09.2008- 06.2013 Engineering Faculty, ChemicalEngineering (English)

University(Bachelor's Degree) Erasmus Exchange Program **Alicante University** - (Formal Education)-

09.2011- 06.2012 Engineering Faculty, ChemicalEngineering (Spanish)

High School **Manisa Fatih Anatolian High School**

06.2008

PROJECTS/ORGANIZATIONS

Organizing committee member of **IV. Polymeric Composites International Symposium and Exhibition** which is organized by Chamber of Chemical Engineers- **May 2014-May 2015**

TEYDEB 1505 project writing to a company located in İzmir - **February 2015-April 2015**

TÜBİTAK scholarship student in the ongoing SAN-TEZ project entitled **"Application and Development of Environmentally Friendly, Light, Natural Fiber Filled Polypropylene Composites in Automotive Industry" - November 2013-2015**

I have worked about **"Polymeric Restoration Dental Composites"** as Diploma Project student in Ege University -**September 2012-2013**

WORK EXPERIENCE

- **Project Student** 11.2013-11.2015 (2 years) İzmir

İzmir Kâtip Çelebi University-Farplas Oto Yedek Parçaları İmalatı, İthalatı ve İhracatı A.Ş

In the scope of SAN-TEZ Project:

- Manufacturing of natural fiber reinforced polypropylene composites by using twin screw extruder,
- Production of composite plates in hot press,
- Characterization and optimization studies,
- Project work plan tracking,
- Reporting of studies,
- Monitoring and documentation of the tender process.

- **Project Engineer** 07.2013-09.2013 (2 months) İzmir

Tecno Electro Market Endüstriyel Otom. Müh. Elektrik Elektronik İletişim San. ve Tic. LTD. ŞTİ.

- **Interpreter** 07.2013 – 09.2013(2 months) İzmir Part Time

Ekoloji Journal

- **Internship** 01.2013 - 02.2013 (1 month) İzmir- TURKEY

Polibak Plastik Film Sanayi

- **Internship** 06.2012 - 08.2012 (2 months) Alicante – Spain

CEMEX España S.A.B/Alicante

PUBLICATIONS/PAPERS

- Uysalman, T., Atagür, M., Kara, H., Yıldırım, A.,Girginer, B., Seydibeyoğlu, M.Ö., Sever, K.," The Effect of Two Different Coupling Agents on Thermal and Mechanical Properties of Lignin Reinforced Polypropylene Composites", May 2015
- Atagür, M., Uysalman, T., Kara, H., Seydibeyoğlu, M.Ö., Malayoğlu, U., "Production and Characterization Of TPU Nanocomposites Reinforced with Clay Minerals Which Have Different Microstructures", May 2015
- Ulutan, S., Uysalman, T., Şengiz, C.B., Kurt-Çömlekçi, G., "Polimerik Diş Restorasyon Kompoundlarının Işınlama ile Kürlenmesi", Plastik Ambalaj Teknol., Eylül 2014, sayfa 54-58

KEY TECHNICAL SKILLS

- **Foreign Languages** English(Advance), German (Beginner) ,Spanish (Good)
- **Computer Skills** Microsoft Office, MATLAB, IntelliCAD, Aspen-Plus, Archimate, Prezi

CERTIFICATE INFORMATION

- **TEYDEB 1505 Project Writing Workshop**, Ebiltem TTO, 2015 (2 days)
- **Advanced Composite Materials Workshop,** Turkish Composites Manufacturers Association and Aerospace Clustering Association, 2015 (1 day)
- **IV. Polymeric Composites International Symposium and Exhibition,** Chamber of Chemical Engineers, 2015 (3 days)
- **Rheology Seminar**, Anton Paar, 2014 (1 day)
- **TGA Operator Education,** PerkinElmer, Inc. 2014 (1 day)
- **Dynamic Mechanic Analysis (DMA) Q800 Operator Education**, TA Instruments, 2014 (1 day)
- **Atomic Force Microscopes (AFM) Education**, Redoks, 2013 (1 day)
- **II. National Aegean Composite Materials Symposium**, Ege University, 2013 (3 days)
- **Effective communication and diction**, Rodos Group, 2013 (1 day)
- **ISO 14001, 18001, 22000, 9001:2008, 19011**, BEMAR Group - 03.2013
- **III. National Chemical Engineering Students Platform**, Kocaeli University - 10.2012
- **Spanish Course**, Alicante University - 02.2012, B1 Level
- **Expoquimica 2011**, Alicante University - 11.2011
- **Spanish Course**, OBEM DANIŞMANLIK ORG. TURZ. ÖZEL EĞİTİM HİZ. TİC. LTD. ŞTİ - 02.2011

I have completed 108-hour training program (from 6 October 2010 to February 19, 2011) as A2 (pre-intermediate) level.

- **Quality Information in Basic Level**, TMMOB Engineers Chamber - 12.2010
- **Persuasion Techniques**, BEMAR Career School - 10.2010
- **Career Planning and Improving Vision**, EGAM Group - 10.2010

EK BİLGİLER

Interests: Latin dances, Photography, wood art, travel to new places

Community member: Chamber of Chemical Engineers
İzmir Katip Çelebi Üniversity Ballroom Dancing

Smoking: Not smoking

PERSONAL TRAITS

Leadership, Good at interpersonal skills and team player, Successful at planning and take action dutifully, Ability of adaptability to change, Goal-oriented and aim for achievement, Energetic and empathic

REFERENCES

Bülent Çelik	bulent.celik@polibak.com.tr
Prof. Dr. Sevgi Ulutan	sevgi.ulutan@gmail.com
M. Özgür Seydibeyoğlu	seydibey@gmail.com
Dr. Altan Yıldırım	a.yildirim@farplas.com