DEVELOPMENT POLYPROPYLENE (PP)-MODIFIED CHICKEN EGGSHELL COMPOSITES

CHAI CHUN LEONG

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requirements for the award of the degree of
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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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I certify that this project report entitled **“DEVELOPMENT POLYPROPYLENE (PP)-MODIFIED CHICKEN EGGSHELL COMPOSITES”** was prepared by **CHAI CHUN LEONG** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons) Petrochemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ___________________________

Supervisor : Dr. Yamuna A/P Munusamy

Date : ___________________________

Specially dedicated to
my beloved parents, Chai Kok Ching and Tang Kok Fong

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ABSTRACT

Recently, eggshell powder (ESP) has raised enormous attention in polymer industry due to its high calcium carbonate content, which shows a great potential to substitute conventional mineral filler. This study was conducted to investigate the tensile and thermal properties of chicken ESP filled PP composite at different filler loading, which is 0 to 40 part per hundred resin (phr). Calcination at temperature 850 ℃ for 2 hours was done on chicken ESP before melt blending with PP at 170 ℃, mixing time of 8 minutes at 50 rpm. The thermal analysis of thermogravimetric analyser (TGA) and differential scanning calorimetry (DSC) proved that incorporation of calcinated chicken eggshell powder (CESP) in PP matrix increases the thermal stability and not much difference of melting temperatures while decreases crystallinity of composite. The tensile strength and modulus increases as the filler loading increases. Modified 40phr composite showed the highest tensile strength (66.3 MPa) and the highest modulus (3801 MPa) was observed in modified 40phr composite. On the other hand, the elongation at break of unmodified chicken ESP composites was higher than modified ESP, but both decreases at higher filler loading. The MFI values for both type of composites decreases when the filler loading increases. The PP/CESP composites have lower MFI values (more viscous) than the PP/ESP composites at all filler loadings due to better interaction formed between polymer and chicken CESP compared to with chicken ESP.

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LIST OF SYMBOLS/ABBREVIATIONS

℃	degree celcius
µ	micro
%	percentage
PP/ESP	polypropylene eggshell powder composite
$CaCO_3$	calcium carbonate
DSC	differential scanning calorimetry
ES	eggshell
ESP	eggshell powder
CESP	calcinated eggshell powder
FESEM	field emission scanning electron microscopy
FTIR	Fourier Transform Infrared Spectroscopy
T_m	melting temperature
PP	polypropylene
TGA	thermogravimetric analysis
phr	part per hundred resin
GCC	ground calcium carbonate
PCC	precipitated calcium carbonate
HDPE	high density polyethylene
PB	polybutene
CaO	calcium oxide
PVC	polyvinyl chloride
PS	polystyrene
PET	polyethylene terephthalate
LDPE	low density polyethylene

HDT	hardware detection to
M_w	molecular weight
$TiCl_3$	titanium (III) chloride
rpm	rotation per minute
kg	kilogram
g	gram
WPC	wood plastic composite
SS	sago starch
LLDPE	low density polyethylene
$Al2O_3$	aluminium oxide
$(Mg(OH)_2)$	magnesium hydroxide
FA	fly ash
MSW	municipal solid waste
GHGs	greenhouse gases
Cr	chromium
Cd	cadmium
Cu	copper
WFO	waste frying oil
NaOH	sodium hydroxide
PE-*g*-MAH	polyethylene-grafted maleic anhydride
ESP/LDPE	eggshell powder low density polyethylene composite
ESP/PP	eggshell powder polypropylene composite
$CaCO_3$/PP	calcium carbonate polypropylene composite
NBR	acrylonitrile butadiene rubber
SBR	styrene-butadiene rubber
PP/ESP10	10phr eggshell powder composite
PP/CESP10	10phr calcinated eggshell powder composite
BET	Brunauer–Emmett–Teller

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CHAPTER 1

INTRODUCTION

1.1 Background

Heterogeneous substance that consists of a combination of two or more materials to enhance its properties, whereby the characteristics and physical identities of each component are retained is known as composite material (Jose et al., 2012). Polymer requires some adjustments in its structure or physical properties in order to get an excellent range of functions. Adding fillers to a polymer is the method to produce a composite that can improve properties such as mechanical strength, thermal stability and electrical conductivity. Besides, addition of filler normally enhances the stiffness of the composites (Fuad et al., 1995). Nalwa (2000) had stated that the properties of polymer had large improvement by using nanoscale fillers such as calcium carbonate, silica and talc. Thus, in the polymer industry, focuses are given to the manufacturing of polymer composites due to the enhancement of properties such as mechanical properties and thermal stability (Mirjalili, Chuah and Salahi, 2014).

In the polymer family, polypropylene (PP) is one of the important substances which have been widely used in engineering, construction, automobile, and packaging applications. Polypropylene (PP) is a linear hydrocarbon polymer, expressed as C_nH_{2n}. PP, like polyethylene (HDPE, L/LLDPE) and polybutene (PB), is a polyolefin or saturated polymer. Polypropylene is one of those most versatile polymers available with various applications, both as a plastic and as a fibre, in virtually all of the plastics end-use markets (Colin, 2015). Figure 1.1 shows the forecasted world consumption of polypropylene in millions of tons from 1998 to 2007 by Raghavendra, Atul and Kamath (2004).

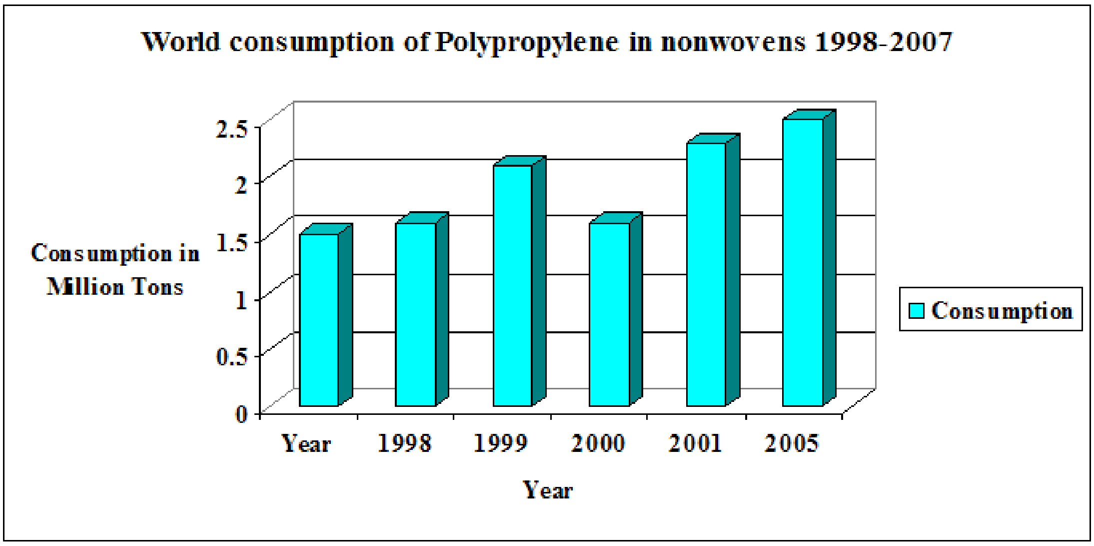


Figure 1.1: Forecasted world consumption of polypropylene in Nonwovens in millions of tons till 1996-2007 (Raghavendra, Atul and Kamath, 2004)

Figure 1.1 shows that PP consumption was generally increasing through year 1996 to 2005. There was only a slight decreased which was 0.5 million tons from year 1999 (2.5 million tons) to 2000 (1.5 million tons). After that, from 2001 to 2005, the PP usage was increased base on the forecasting research. PP is famous because it has wide engineering application due to it possesses useful properties such as transparency, dimensional stability, flame resistance, high heat distortion temperature, and high impact strength (Dey et al., 2011). PP filled with particulate fillers has continued to catch the attention of researcher due to its versatility of application and low cost (Zhao and Huang, 2008).

The pie chart in Figure 1.2 shows the composition of global solid waste reported by Thompson in 2012. From the pie chart, organic solid waste is the major contributor to the global solid waste, which is around 46%. One of the types of organic solid waste is eggshell.

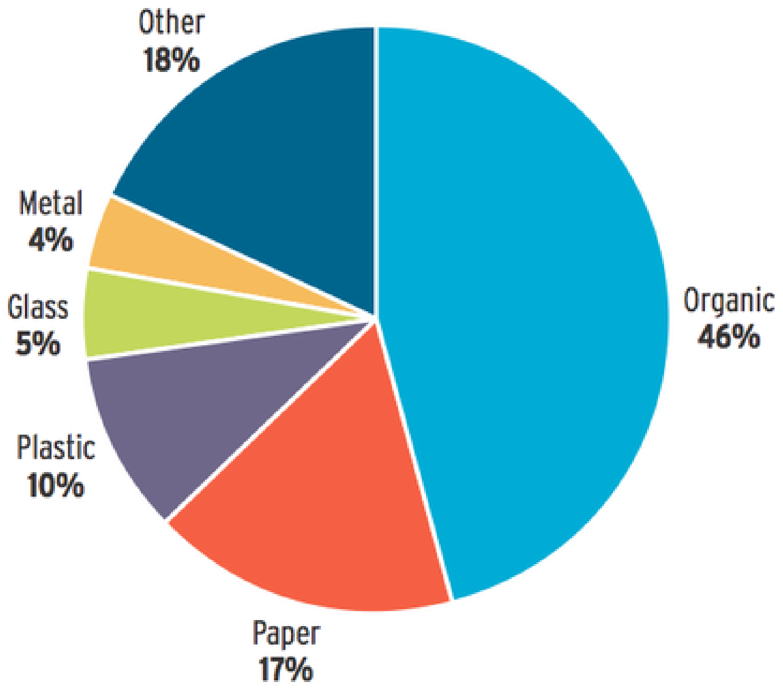


Figure 1.2: Global solid waste composition (Thompson, 2012)

Basically, eggshell is considered to be waste products from food industries, restaurants and houses. The disposal of the eggshell can cause pollution to the environment. In this work, attempt had been taken to use the calcinated eggshell as filler to reinforce PP polymer matrix. Eggshell powder could be used as alternative to replace the commercial calcium carbonate filler. This is because from our previous study, it was found that eggshell powder has physical, chemical and crystalline structure similar to commercial calcium carbonate.

1.2 Problem Statement

Due to the environment concerns on sustainability, utilization of finite sources for commercial purposes has shifted to renewable sources (Faruk et al., 2012). Nonbiodegradability of conventional filler like talc, calcium carbonate and china clay has been seeking replacement by renewable source as state by Onyeagoro (2014).

Chicken eggs represent a major ingredient in a large variety of products such as cakes, salad dressing and fast foods, whose production results in several daily tons of waste chicken eggshells (ES) and incur considerable disposal costs in Malaysia and worldwide. For example, U.S. itself disposed about 150,000 tons of the ES in landfills per year which create land availability problem (Toro et al., 2007). The disposal of the waste is a very important problem, which can cause risk to public, contamination of water resources and polluting the environment (Meski, Ziani and Khireddine, 2010).

The chicken ES constitutes by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer and contains about 95% calcium carbonate ($CaCO_3$) in the form of calcite and 5% organic materials such as type X-collagen, sulfated polysaccharides, and other proteins (Lin, Zhang and Mai, 2011). As chicken ES has high content of calcium carbonate, it can be used to substitute current commercial calcium carbonate as filler (Sutapun et al., 2013). By using chicken ES as a form of renewable resources we can reduce the reliance on calcium carbonate filler from non-renewable calcium carbonate from natural resources from the environment. Thus, the use of ES biofiller in polymer matrix will decrease the reliance on commercial $CaCO_3$ and there is a path to recycle ES waste in cost-effective way.

PP need reinforcement in order to reduce the production costs of moulded products as well as improving the mechanical properties such as strength, rigidity, durability and hardness (Khunová et al., 1999). Polypropylene composites mainly use inorganic fillers such as mineral calcium carbonate and talc (Muralisrinivasan, 2011). The chicken eggshell powder (ESP) can be calcinated to increase the calcium oxide (CaO) content through the calcination process at 850 ℃ for 2 hours (Liu et al., 2010).

1.3 Research Objectives and Aims

The objectives of this study are:

- To modify chicken eggshell powder by calcination and characterize the modified chicken eggshell powder.
- To produce new polypropylene composites with different loading of chicken eggshell powder with and without modification.
- To study the processing, tensile and thermal properties of PP/eggshell composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Thermoplastic Polymer

The types of polymers that can be melted in order to reform into a new shape or object with the application of heat is known as thermoplastic (Nurul and Mariatti, 2011). Thermoplastics pellets soften when heated and become more fluid as extra heat is applied. The melting process is completely reversible as no chemical bonding takes place. This characteristic allows thermoplastics to be remolded and recycled without undesirably affecting the material's physical properties (Industrial Strength Marketing, 2015). The type of thermoplastic polymer can be chosen according to various aspects so that it fulfils the function needed by a particular application. The considerations include the cost, mechanical properties and performance, resistance to heat and chemicals, heat stability and recyclability (Kutz, 2011).

Plastics are categorized as a cost effective material but the selling prices will vary depending to their particular performances. Plastics are still a better selection in many applications than other materials such as metals although metals tend to be cheaper. The reason is its design flexibility and lower assembly costs. Towards this era of modern technologies, the world is getting alert with the word "recycle". That is why thermoplastic polymers gained a vast popularity in world demand comparing to thermoset polymers in producing various products. A survey done by DeArmitt (2009) has predicted that thermoplastic polymer usage will increased in a 5 to 10% range per annum. Figure 2.1 illustrates the consumption of plastic in various industry sectors in Western Europe.

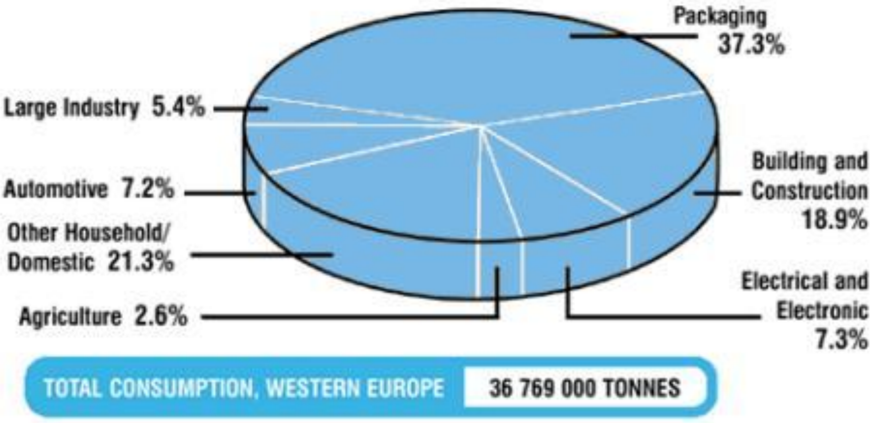


Figure 2.1: Plastic consumptions in different industry sectors in Western Europe (DeArmitt, 2009)

In the Western Europe Industries, High and Low Density Polyethylene (HDPE and LDPE), Polypropylene (PP), Polyvinyl Chloride (PVC), Polystyrene (PS) and Polyethylene Terephthalate (PET) are the main thermoplastic polymers consumed. These thermoplastics contribute estimate 75% of its total consumption in 2009 according to DeArmitt research. The details of the consumption are listed in Table 2.1.

Table 2.1: Consumption of various types of thermoplastics (DeArmitt, 2009)

Types of Thermoplastics	*Consumptions (tonnes)*
LDPE	7.6×10^6
HDPE	5.0×10^6
PP	7.0×10^6
PVC	5.8×10^6
PS	3.1×10^6
PET	3.1×10^6

2.1.1 Polypropylene (PP)

Polypropylene (PP) is a semi crystalline thermoplastic that is characterized by light weight, cheap price, high mechanical strength, easy processing, good chemical stability and electrical properties (Vladimirov et al., 2006). PP has chemical designation C_3H_6, is one of the most versatile and extensively used polymers in the world. It applies in both household and industrial applications. Its unique properties and ability to adapt to various fabrication techniques make it stand out as an invaluable material for a wide range of uses. Another special characteristic is its ability to function as both a plastic material and as a fiber. Polypropylene's unique ability to be manufactured through different methods and into different applications meant it soon started to challenge many of the old alternative materials, notably in the packaging, fiber, and injection molding industries. Its growth has been sustained over the years and it remains a major player in the plastic industry worldwide.

Polypropylene has properties that make it a very useful material for all sorts of applications. It can be referred to as the steel of the plastic industry because of the various ways in which it can be modified or customized to best serve a particular purpose. This is usually achieved by introducing special additives to it or by manufacturing it in a very particular way. This adaptability is a vital property.

Some of the most significant properties of polypropylene are (Maier and Calafut, 1998):

- High melting point: for similar plastics in the same weight category, polypropylene has a higher melting point.
- Translucent hue: polypropylene can be used for applications where some transfer of light is important or where it is of aesthetic value.
- Toughness: polypropylene is elastic without being too soft.
- Resistance to chemicals: diluted bases and acids don't react readily with polypropylene, which makes it a good choice for containers of such liquids.
- Fatigue resistance: polypropylene retains its shape after a lot of torsion, bending, and/or flexing. This property is especially valuable for making living hinges.

- Insulation: polypropylene has a very high resistance to electricity and is very useful for electronic components.

Furthermore, PP does not present stress-cracking problems and offers good electrical and chemical resistance at higher temperatures. While the properties of PP are similar to those of Polyethylene, there are specific differences which include a lower density, higher softening point (PP doesn't melt below 160 ^{o}C, Polyethylene, a more common plastic, will anneal at around 100 ^{o}C) and higher rigidity and hardness (Colin, 2015).

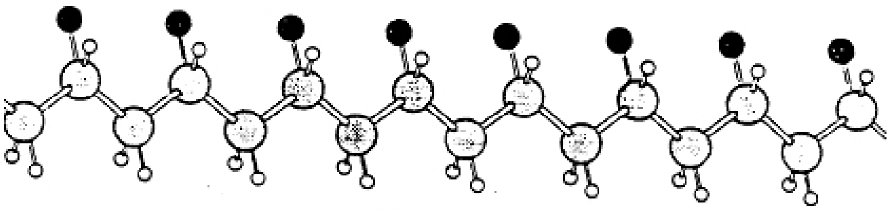
There are two main types of PP available which are homopolymers and copolymers. The copolymers are further divided into block copolymers and random copolymers (Tolinski, 2009). Each category fits certain applications better than the others but offen it doesn’t matter which one is used. Homopolymer PP can be referred as the default state of the PP material and is a general-purpose grade (Belgacem, Bataille and Sapieha, 1994). Block copolymer PP has co-monomer units arranged in blocks (mean is in a regular pattern) and contain anywhere between 5% to 15% ethylene. Ethylene improves certain properties such as impact resistance and other additives improve other properties (Banthia and Gupta, 2006). Random co-polymer PP is opposite to block copolymer PP as it has the co-monomer units arranged in irregular or random patterns along the PP molecule. They are commonly incorporated with anywhere between 1-7% ethylene and selected for applications where a more malleable, clearer product is desired (Khalid et al., 2008). Table 2.2 shows the typical properties of homopolymer and copolymer.

Table 2.2: Typical properties of homopoylmer and copolymer (Fernandes et al., 2014).

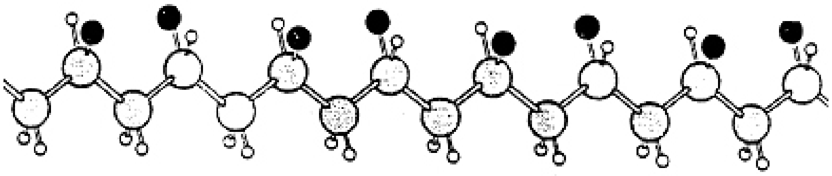
Aspects	Units	Homopolymer	Copolymer
Density	/ kgm^{-3}	905	905
Price / Tonne	/ £	680	620
Tensile Strength	/ Mpa	33	25
Tensile Modulus	/ Gpa	1.4	1
Elongation at Break	/ %	150	300
Hardness	/ Rockwell "R" Scale	90	80
Notched Izod Impact	/ kJm^{-1}	0.07	0.1
Heat Distortion Temp (HDT)	@ 0.45 MPa / ℃	105	100
Heat Distortion Temp (HDT)	@ 1.80 MPa / ℃	65	60
Volume Resistivity	/ logÙm	19	19
Oxygen Index	/ %	17	17

Homopolymer has same desity with copolymer but the price for homopolymer is higher. The mechanical properties such as tensile strength, tensile moduls, elongation at break, hardness and Notched Izod impact values are higher for homopolymer compared to copolymer. Besides, homopolymer values for the hardware detection tool (HDT) at 0.4 MPa / ℃ and 1.8 MPa / ℃ are higher than copolymer. However, the volume resistivity and oxgen index for homopolymer and copolymer are sharing the same values.

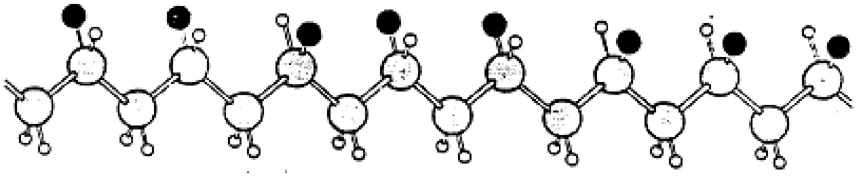
PP has three types of chemical structures which are isotatic, syndiotactic and atactic. The presence of the methyl group attached to every alternate backbone chain carbon atom can alter the properties in a number of ways such as it can cause a slight stiffening of the chain by increasing the crystalline melting point (T_m) and it can interfere with the molecular symmetry by depressing crystallinity and hence T_m (Porter, Cantow and Johnson, 1966). Figure 2.2 shows the chemical structures of PP. Commercially available isotactic polypropylene is made with two types of Ziegler-Natta catalysts. The first group of the catalysts encompasses solid (mostly supported) catalysts and certain types of soluble metallocene catalysts. Such isotactic macromolecules coil into a helical shape; these helices then line up next to one another to form the crystals that give commercial isotactic polypropylene many of its desirable properties. A ball-and-stick model of syndiotactic polypropylene. Another type of metallocene catalysts produces syndiotactic polypropylene. These macromolecules also coil into helices (of a different type) and form crystalline materials. When the methyl groups in a polypropylene chain exhibit no preferred orientation, the polymers are called atactic. Atactic polypropylene is an amorphous rubbery material. It can be produced commercially either with a special type of supported Ziegler-Natta catalyst or with some metallocene catalysts. In the case of very regular polymers, isotactic form, the net result is a melting point 30 ℃ higher than the high density polyethylene (Belgacem, Bataille and Sapieha, 1994). The isotactic character of PP allows crystallization, as a result, material can be stiffer.



Isotactic



Syndiotactic



Atactic

Figure 2.2: Chemical structures of PP (Porter, Cantow and Johnson, 1966)

First generation PP was produced through slurry polymerization. For this type of production process, an autoclave and an agitator are used in the reactor. The typical condition to fulfil the reaction effectively is 1 MPa pressure and temperature around 50 to 80 ℃ in temperature (McGreavy, 1994). Besides, the process is carried out in the present of inert hydrocarbon solvent like hexane or heptane. To obtain the polypropylene particles through the first generation process, a series of treatment units are used after polymerization starting from separation of PP, unreacted propylene recovery, deashing using alcohol to decompose and eliminate the catalyst activity, washing in water, centrifugal separation and drying for the after treatment processes. The major advantages of the simplified slurry processes are high content of solids in the slurry, good temperature control, flexibility of reactor operations, simplified overall process, high productivity of isotactic polypropylene and a very small waste from solvent recovery (Cheremisinoff, 1989). Figure 2.3 shows the liquid-phase process of polypropylene Spheripol process.

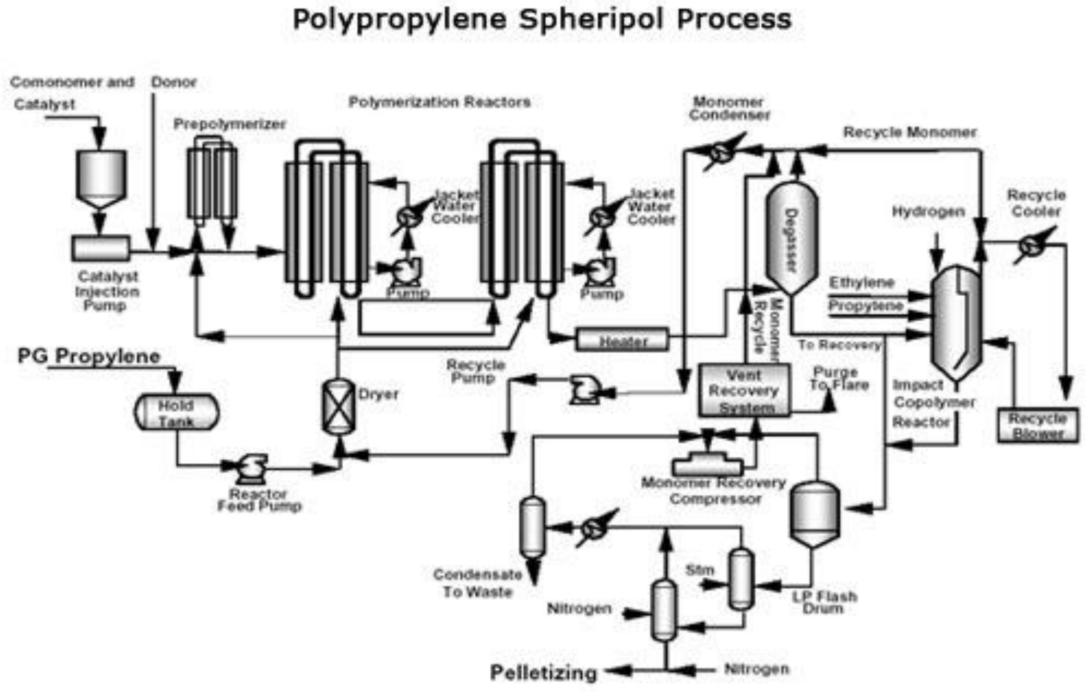


Figure 2.3: Polypropylene Spheripol process (Cheremisinoff, 1989)

Gas phase polymerization is also used for propylene polymerization. Here gaseous monomers are polymerized over solid Ziegler-type catalyst in the presence of aluminium alkly cocatalyst. In an commercial gas phase polymerization processes using different reactors, catalyst deashing and product purification steps are not required because highly efficient catalyst systems are used. Continuous stirred bed reactors, horizontal compartmented reactors, and fluidized bed reactors are used for propylene polymerization in the gas phase (Wagner, 2009). The gas phase polymerization reactor of Amoco is characterized by its unique design and operation. As shown in Figure 2.4, the reactor is a horizontal, cylindrical vessel, stirred by paddles mounted on an axial shaft with the lower section of the reactor divided into several compartments. The compartments permit variation in temperature and gas phase composition. Specially prepared high-activity unsupported or supported titanium chloride catalyst, which is temporarily inactivated by ethanol, is fed to the reactor with inert quench liquid and reactivated in the reaction zone by an aluminium alkyl cocatalyst which is sprayed onto the polymer bed. The heat of reaction is removed by evaporating liquid propylene or a quench liquid such as isobutene or isopentane. The temperature is controlled by manipulating the quench liquid flows and/or amount catalyst injected to the reactor. It has been claimed that a narrow or broad molecular weight distribution (M_w/M_n = 6-12) is obtainable by varying hydrogen concentration, temperature and catalyst composition in each compartment. An active titanium (III) chloride ($TiCl_3$) catalyst with diethylalumium chloride cocatalyst is charged to the reactor every 30 min. The reactor temperature is maintained at 71 ℃ by continuously sprayed isopentane at the appropriate rate onto the 30 rpm stirred polymer bed. The reactor pressure is controlled at 300 psig by controlling temperature in the condenser at about 50 ℃. The polymer yield obtained is 10 kg g^{-1} catalyst tacticity of 96% and the polymer is removed from the reactor as a melt. The product is the pelletized into desired size.

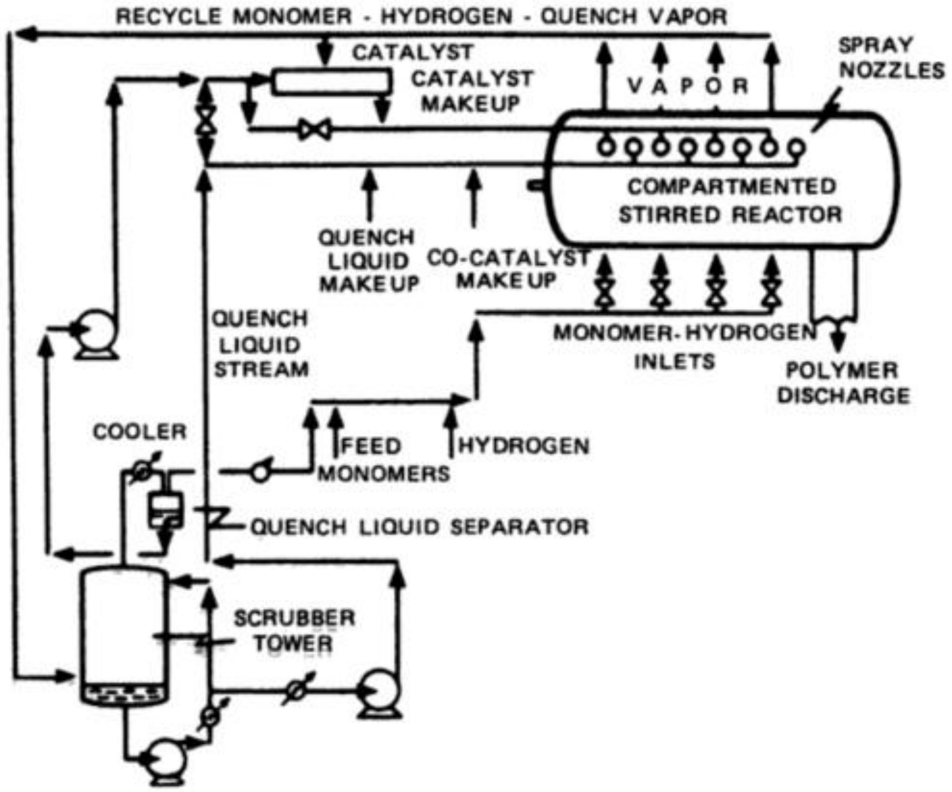


Figure 2.4: Amoco gas phase polymerization process (Cheremisinoff, 1989)

2.2 Composite Fillers

Fillers are usually rigid and it will be immiscible with the matrix of polymer. Fillers are used in different amount with the polymer based on the specification required in order to improve mechanical and physical properties of thermoplastic polymer. Fillers can be defined as materials that are irregular in shapes such as plate-like and fibrous and it is used in plastics processes of large loading volume (Xanthos, 2010).

In the starting, filler are used to reduce the cost of the expensive polymer such as polypropylene, polyvinyl chloride and polycarbonate (Mohammed, 2014). Furthermore, the thermal conductivity of polymer will increase and this will contribute to faster moulding cycles. Therefore, the rejected parts during processing are lesser (Salmah, Romisuhani and Akmal, 2011). However nowadays fillers are used mainly to improve various properties of polymers such as tensile strength, thermal stability and flame retardancy. For example, if fibrous fillers are used, the melt viscosity of the polymer will increase significantly. On the other hand, if inorganic fillers are used, the thermal expansion and mold shrinkage will eventually reduce as well (Teh et al., 2007).

Fillers can be classified as inorganic and organic fillers. They can be further divided again based on their chemical families, volume and size ratio, shapes, and their enhancements in polymers (Choi et al., 2007). For instance, calcium carbonate is likely falls in the category of inorganic fillers while rice husk falls in the category of organic fillers. Table 2.3 shows clearly some types of organic and inorganic fillers based on their chemical families while Table 2.4 shown the different kinds of filler particles shapes and their morphologies.

Table 2.3: Types of inorganic and organic fillers (Xanthos, 2010)

Chemical Families of Fillers	***Types of Fillers***
Inorganic fillers	
Oxides	Glass (fibres, spheres, hollow, spheres, flakes), MgO, SiO_2, Sb_2O_3, Al_2O_3
Hydroxides	$Al(OH)_3$, $Mg(OH)_2$
Salts	$CaCO_3$, $BaSO_4$, $CaSO_4$, phosphates
-Silicates	Talc, mica, kaolin, wollastonite, montmorillonite, nanoclays, feldspar, asbestos
Metals	Boron, steel
Organics fillers	
Graphite and carbon	Carbon fibres, graphite fibres and flakes, carbon nanotubes, carbon black
Natural polymers	Cellulose fibres, wood flour and fibres, flax, cotton, sisal, starch
Synthetic polymers	Polyamide, polyester, aramid, polyvinyl alcohol fibres

Table 2.4: Fillers particle morphology based on shapes (Xanthos, 2010)

Particle Shape	***Aspect Ratio***	***Example***
Cube	1	Feldspar, calcite
Sphere	1	Glass spheres
Block	1 - 4	Quartz, calcite, silica, barite
Plate	4 - 30	Kaolin, talc, hydrous alumina
Flake	50 – 200 ++	Mica, graphite, montmorillonite, nanoclays
Fibre	20 – 200 ++	Wollastonite, glass fibres, carbon nanotubes, asbestos fibres, carbon fibres

2.2.1 Organic Fillers

Organic fillers can be produced by recycling waste material from plants and animals. The organic fillers normally are low density, need low cost to produce and available abundantly (Kim and Burford, 1998). Thus, it is suit to replace the inorganic filler for polymeric materials in many applications. Based on research from Yam and Mak in 2014, they have successfully produced the polymer composite by using rice husk blended with PP by gas-assisted injection moulding. There is no successful case is reported in literature, as the increased shear viscosity of the non-petrochemical and natural-based polymers make it difficult for the eco-composite to flow inside the moulds. Different stages of injection pressure and delays of gas pressure were applied in order to enhance the flow characteristics. In addition, the internal wall surface of the mould must be polished to 'Mold-Tech' SPI A2, an industry standard textured finishes. The new approach uses fewer petrochemical polymers with improved moulding quality, especially for thick, moulded parts. The new method is also an environmentally-friendly approach as it uses less injection pressure and clamping force. This has created a good foundation for further research in cleaner production of different kinds of eco-composites material by gas-assisted injection moulding.

Effect of fiber length on processing and properties of extruded wood-fiber/HDPE composites were studied (Migneault et al., 2008). The production of wood plastic composite (WPC) with long fibers has been neglected, because they are difficult to handle with current production equipment. This study provides a better understanding of the effect of fiber length on WPC processing and properties. The objectives of this study were therefore to determine the role of fiber length in the formation process and property development of WPC. Composites from the three length distributions were successfully processed using extrusion. Physical and mechanical properties of the obtained composites varied with both length distribution and additive type. Mechanical properties increased with increasing fiber length, whereas performance in water immersion tests decreased.

The development of bamboo-based polymer composites and their mechanical properties were studied by Okubo, Fujii and Yamamoto (2004). Their found that bamboo fiber bundles have a potential ability to work as the reinforcement of polymer matrix. The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experimental results showed that the bamboo fibers (bundles) had a sufficient specific strength, which is equivalent to that of conventional glass fibers. The tensile strength and modulus of PP based composites using steam-exploded fibers increased about 15 and 30%, respectively, due to well impregnation and the reduction of the number of voids, compared to the composite using fibers that are mechanically extracted. The steam explosion technique is an effective method to extract bamboo fibers for reinforcing thermoplastics.

Singh et al. in 1991 had a research work about the structure and mechanical properties of corn kernels to produce a hybrid composite material. The mechanical properties of corn kernels were evaluated at three levels of kernel structure, varying in the proportions of horny endosperm, and six levels of moisture content in the range of 6 to 34% (wet basis) under a compression mode of loading. The observed values of ultimate stress, modulus of elasticity, modulus of toughness and modulus of resilience varied from 8 to 82 MPa, 20 to 480 MPa, 0.8 to 4.4 MJ m^{-3} and 0.2 to 0.8 MJ m^{-3}, respectively, within the experimental range. Each of these properties decreased in magnitude as the moisture content increased. The microscopic study revealed that the resistance of kernels to fracture was predominantly influenced by the kernel structure. The size of cracks increased with increasing strain or decreasing proportion of the horny endosperm in the kernels. The viscoelastic behaviour of the kernels was determined at two levels of kernel structure, five levels of kernel moisture (12 to 34%) with three deformation rates (1.27, 5.08 and 12.7 mm min^{-1}) by means of stress relaxation tests. The analysis of the test data suggested that the hybrid composite kernels were hydrorheologically simple materials.

Besides, mechanical properties of sago starch-filled linear low density polyethylene (LLDPE) composites were investigated (Nawang et al., 2001). Mechanical properties of composites made from sago starch (SS) and LLDPE have been investigated. Mechanical properties such as tensile strength and elongation at break decreased with increasing starch content while the modulus increased. Composite equations of Kerner, Nielsen and Halpin-Tsai were used to explain the effect of filler volume fraction on the mechanical properties of the composites. Disagreement occurs between experimental and theoretical data as filler volume fraction of the composites increases.

2.2.2 Inorganic Filler

The most widely used inorganic fillers in the polymer industry are glass, aluminium oxide (Al_2O_3), magnesium hydroxide ($Mg(OH)_2$), calcium carbonate ($CaCO_3$) particles and layered silicates. They are added to enhance the properties of polymer composites (Fu et al., 2008). One of the major classes of inorganic fillers is mineral fillers. Mineral fillers are naturally occurring materials that are mined and ground to a specified particle size. The grinding may be done dry using mechanical mills, or for finer product, the ore is ground wet. Calcium carbonate is one of the most popular mineral fillers used in the plastics industry. It is widely available around the world, easy to grind or reduce to a specific particle size, compatible with a wide range of polymer resins and economical. As an additive in plastic compounds, calcium carbonate helps decrease surface energy and provides opacity and surface gloss, which improves surface finish (Seymour, 1978). Moreover, when the particle size is carefully controlled, calcium carbonate helps increase both impact strength and flexural modulus (stiffness).

The synergetic effect of calcium carbonate (CC)-fly ash (FA) hybrid filler particles on the mechanical and physical properties of low density polyethylene (LDPE) has been investigated (Adeosun et al., 2014). Low density polyethylene is filled with varying weight percentages of FA and CC using melt casting. Composites are characterized for mechanical, thermal, microstructural and physical properties. Results show that the flexural strength increases with increases in FA content of the hybrid filler. It is evident from the study that to achieve optimum density a certain combination of both fillers need to be used. The optimum combination of CC and FA for a higher density (1.78 g/cm3) is found to be at 20 wt% FA and 30 wt% CC. An increase of 7.27% in micro-hardness over virgin polyethylene is obtained in composites with 10 wt% FA and 40 wt% CC. The presence of higher amount of CC is seen to be detrimental to the crystallinity of composites. X-ray, FTIR and DSC results show that composite with 45 wt% CC and 5 wt% FA exhibits a typical triclinic polyethylene structure indicating that the composite is amorphous in nature. There was the synergy between FA and CC fillers on flexural strength and crystallinity of composite. However, the fillers show the antagonistic effect on energy at peak and micro-hardness.

A study on evaluating the effect of nano-$CaCO_3$ particles on thermal and mechanical properties of epoxy resin cast was performed by TGA and mechanical tests **(**He et al., 2011). A silane coupling agent KH550 as an interfacial modifier was introduced into nanocomposites through preparing KH550/nano-$CaCO_3$ master batch. It is revealed that epoxy resin cast filled with nano-$CaCO_3$ particles represents higher thermal stability and mechanical strength. The improvement of thermal and mechanical properties is attributed to the surface modification of nano-particles, which can enhance the interfacial properties between nano-$CaCO_3$ fillers and epoxy resin.

The mechanical properties of nano-$CaCO_3$/epoxy/carbon fibres composites based on the modified epoxy matrix are also enhanced. Chitin whiskers (CHW) and $CaCO_3$ were reinforced with Polyacrylic acid (PAA) and mechanical and thermal properties were characterized (Ofem, Umar and Muhammed, 2015). Better mechanical properties were measured for CHW loading of 3%cw compared with neat PAA and when $CaCO_3$ was not incorporated (CHW/PAA). The failure mode was more plastic at lower filler loading of CHW. TGA indicated that the composites thermal stabilities were increased. At each stage of decomposition the weight losses were lower than those without $CaCO_3$. The final weight losses were between 20% and 37% compared with over 70% when $CaCO_3$ was not grown on the composites, a char yield of over 60% was obtained. The glass transition, T_g values increase from that of 58 ℃ for neat PAA to between 61 ℃ and 64 ℃ compared with a maximum of 60 ℃ when $CaCO_3$ was absent. The crystallization temperatures for all composites were not observed and this was attributed to the low quantity of PAA used.

A research examined the effect of a microsize/nanosize talc filler on the physicochemical and mechanical properties of filled polypropylene composite matrices (Lapcik et al., 2008). They found that increasing filler content lead to an increase in the mechanical strength of the composite material with a simultaneous decrease in the fracture toughness. The observed increase in tensile strength ranged from 15% to 25% (the maximum tensile strength at break was found to be 22 MPa). The increase in mechanical strength simultaneously led to a higher brittleness, which was reflected in a decrease in the mean impact strength from the initial 18 kJ/m^2 (for the virgin polypropylene sample) to 14 kJ/m^2 (23% decreases). A similar dependency was also obtained for the samples conditioned at −20 °C (a decrease of 12.5%). With increasing degree of filling of the talc–polypropylene composite matrix, the thermooxidative stability increased; the highest magnitude was obtained for the 20 wt% sample (decomposition temperature = 482 ℃, cf. 392 ℃ for the virgin polymer).

2.3 Food Waste

Base on John in 2011, the developing countries contribute approximately 3.8 million ton of solid waste in a total out of 5.2 million solid wastes generation worldwide. As waste generation increases significantly, it results in greater demand for both waste collection and innovative treatment options. The goal of municipal solid waste (MSW) management which deals principally with household waste but includes commercial waste generated in municipal areas is to treat the waste in an environmentally and socially acceptable manner, with appropriate clean technologies. Serious local, regional, and global public and environmental health problems may happen including air pollution, soil and groundwater contamination, and emissions of greenhouse gases (GHGs) if the goal is not achieve. Besides, according to Mohamed (2015) from Global Environment Centre, there is over 23,000 tonnes of solid waste being produced each day in Malaysia and the amount will increase to 30,000 tonnes by the year 2020. Out of the 30,000 tonnes of solid waste that are being discarded daily by Malaysian homes, 47% is food waste. The waste composition in percentages was tabulated in Table 2.5. The food waste produced is the main root cause to most issues associated to landfills such as foul odor, toxic leachate and emission of greenhouse gases (Sankoh, Yan and Tran, 2013). Proper solid waste management have to be undertaken to ensure that it does not affect the environment and not cause health hazards to the people living there (Dummer, Dickinson and Parker, 2003). One of the biggest fractions of food waste comes from eggshell. Eggshell is the waste mainly from the food industry and incur considerable disposal fees in Malaysia and worldwide. The disposal of the waste is a very important problem, which can cause risk to public, contamination of water resources and polluting the environment. One way to reduce the waste from eggshell is to recycle it to useful products.

Table 2.5: Solid waste composition in Malaysia (Mohamed, 2015)

Type of Solid Waste	Percentage (%)
Food Waste	47
Plastics	14
Paper	15
Metal	4
Glass	3
Others	17

2.4 Eggshell

Chicken egg consists of 60% albumen, 30% yolk and another 10% of eggshell and membrane as reported by by Ummartyotin and Tangnorawich (2015). The different parts of chicken egg are presented in Figure 2.5. The eggshell consists of eggshell membrane and calcified eggshell matrix. Besides, it is stated that chicken eggshell (ES) containing more than 95% of calcite form mineral and 1-3.5% of organic matrix (Intharapat, Kongnoo and Kateungngan, 2012).

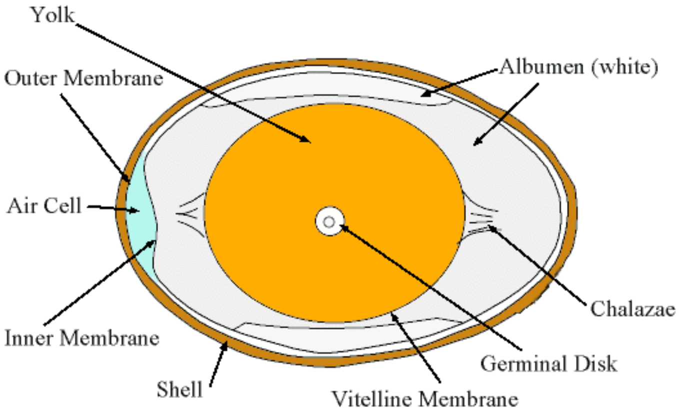


Figure 2.5: Schematic of different parts of egg structure (Ummartyotin and Tangnorawich, 2015)

ES is a combination of both inorganic and organic components. The main component of ES is calcium carbonate in the form of calcite which has a density of 2.710 g cm^{-1} (M.M. Cordeiro). The other components that exist are 1 wt.% magnesium carbonate, 1 wt.% calcium phosphate, and organic materials such as type X collagen, sulfated polysaccharides, and other proteins about 4 wt.% (Hassan, Aigbodion and Patrick, 2012).

The ES calcite is in vertical crystal layer, palisade layer and mammilary knob layer as presented in Figure 2.6. The inner most layer of calcite – mammilary layer (~100 µm thickness) grows on the outer egg membrane and creates the base for palisade layer which is the thickest part (~200 µm) of the eggshell. The top layer is the vertical layer (~5-8 µm thickness) covered by the organic cuticle (Izumi et al., 1994). Furthermore, the numerous pore canals are distributed at the outer eggshell surface about 7,000-17,000 pores per egg, but these are unevenly over the shell surface (Nys, Bain and Van Immerseel, 2011). However, if the source or place of the chicken ES obtained is different, the composition might vary slightly.

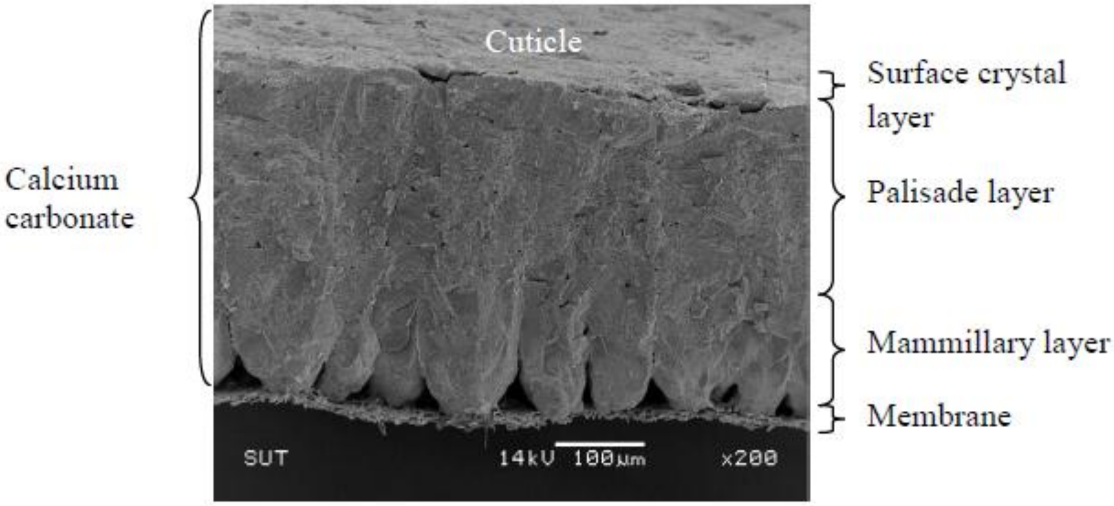


Figure 2.6: SEM micrograph of a cross-fractured chicken eggshell structure (Dennis et al., 1996)

2.5 Applications of Eggshell

Chicken eggshell are used in various applications in order to minimize their effect on environmental pollution. ES might probably is the best natural source of calcium. The ES usually employed in form of powder. Chicken ES is inexpensive, abundant and good characteristic for many potential applications such as medical and cosmetic applications. It can use as soil conditioner or an additive for animal feed (Yoo et al., 2009). Furthermore, ES can be used as fertilizer as it has high contents of calcium, magnesium and phosphorous. ES is also utilized as raw material for synthesis of hydroxyapatite which studied by Ummartyotin and Tangnorawich (2015). The hydroxyapatite from ES can be used for bone repairing. Furthermore, it also can be used for skin permeation as well as bio-based implant for organ and any tissue engineering (Mohammadi, Lahijani and Mohamed, 2014).

In addition, Chojnacka (2005) used the calcinated ES powder for the biosorption of heavy metal such as chromium (Cr), cadmium (Cd) or copper (Cu). The paper presents results of studies carried out on sorption of Cr (III) ions from aqueous solutions by eggshells as a low-cost sorbent. It was found that crushed eggshells possess relatively high sorption capacity, when comparing with other sorbents. Eggshells were able to remove the concentration of Cr (III) ions below the acceptable level, i.e. at 40 ℃, at the initial concentration of metal ions 100 mg/kg, at sorbent concentration 15 g/l. Egg shells were subjected to calcination–hydration–dehydration treatment to obtain calcium oxide (CaO) with high activity (Niju et al., 2014). The performance of CaO obtained from the calcination–hydration–dehydration treatment of egg shell and commercial CaO was tested for its catalytic activity via transesterification of waste frying oil (WFO). The results showed that the methyl ester conversion was 67.57% for commercial CaO and it was 94.52% for CaO obtained from the calcination–hydration–dehydration treatment of egg shell at a 5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65 ℃ and a reaction time of 1 hour. The biodiesel conversion was determined by ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). In the research of Wei, Xu and Li (2009), they applied waste chicken eggshell as low-cost solid catalyst for biodiesel production. It was found that high active, reusable solid catalyst was obtained by just calcining eggshell. Utilization of eggshell as a catalyst for biodiesel production not only provides a cost-effective and environmental friendly way of recycling this solid eggshell waste, significantly reducing its environmental effects, but also reduces the price of biodiesel to make biodiesel competitive with petroleum diesel. Hydrogen sulphide (H_2S) is fatal to benthic aquatic lives as depletes the dissolved oxygen in their ecosystem. The present work evaluated on characterization and the application of chicken eggshell as green and economical adsorbents for the treatment of hydrogen sulfide from wastewaters (Omar, Faizah and Umar, 2014). The grounded chicken eggshells were characterized into calcinate waste eggshell, activate carbon derived from wastes of eggshell (modified adsorbents) and eggshell without treatments (unmodified adsorbent). It is concluded that the chickens' eggshell are very useful green and economic adsorbents due to their availability and absence of any toxic and hazardous constituent's elements from all adsorbents. The calcinate modified been the most suitable followed by the activate carbon modified adsorbent. The grounded chicken eggshell without treatments was the least suitable for the removal of H_2S from wasters. The use of hen's eggshell as a possible bone substitute has reported (Dupoirieux, Pourquier and Souyris, 1995). In the first part of the study, particles ranging from 400 μm to 600 μm in diameter were bioassayed in an intramuscular pouch in rodents. This material was found to be biocompatible, but appeared not to have osteoinductive capacities. In the second and third part of the study, this material was used as an interpositional graft material in critical-size defects of rat mandibles and rabbit skulls. At 2 months, a morphologic restoration was obtained using the graft, but the healing was only achieved by fibrous union. In the fourth part of the study, the material was experimented on as an onlay bone graft on rabbit mandibles. A 6-month follow-up of the implant confirmed its stability. In conclusion, the use of this safe and inexpensive material is suggested for filling limited bone defects in non-weight-bearing areas. The use of eggshell powder for bone augmentation may also be considered, after further studies, to assess its long-term stability.

2.6 Eggshell-Filled Composites

Shuhadah and Supri (2009) studied the effect of chemical modification by isophthalic acid and ESP content at 5%-25% on the mechanical properties of ESP/LDPE composites. The ESP after deproteinizing with 10% sodium hydroxide (NaOH) was chemically modified with 6% of isophthalic acid and ethanol. They found that the tensile strength of the composites decreased with increasing ESP content. This was due to the poor adhesion between ESP and LDPE matrix and the agglomeration of filler particles. The tensile strength of ESP/LDPE composites with chemical modification was higher than that of ESP/LDPE composites without chemical modification. This was probably due to the better interfacial adhesion between filler and matrix after chemical modification. The stronger the interfacial adhesion, the better the stress transfer from the matrix to the filler. Young's modulus of the composites with and without chemical modification increased with increasing filler content. This was due to the filler exhibiting high stiffness compared to LDPE matrix. In addition, the Young's modulus of the composites with chemical modification was lower than that of the composites without modification. This was attributed to isophtahlic acid toughening the composites and reduction in Young's modulus of the composites. In addition, it was reported that the elongation at break of the unmodified composites and modified composites was decreased as the filler content was increased. This was because the increasing in filler content resulted in the stiffening of the composites. It was also reported that the elongation at break of the unmodified LDPE composites was higher than that of the modified LDPE composites.

Supri, Ismail and Shuhadah (2010) investigated effect of polyethylene-grafted maleic anhydride (PE-*g*-MAH) on properties of low density polyethylene/eggshell powder (LDPE/ESP) composites. The ESP/LDPE composites were prepared from different ESP content and the addition of PE-g-MAH. The tensile strength, elongation at break and thermal stability of ESP/LDPE composites with PE-g-MAH were greater than ESP/LDPE composites, and their differences became more pronounced at higher filler content. The interfacial adhesion between ESP and LDPE was improved with the addition of PE-g-MAH.

Toro et al. (2007) investigated the Young's modulus of ESP/PP composites compared to that of $CaCO_3$/PP composites. It was reported that ESP with particle size of 8.4 μm led to higher Young's modulus of composites than $CaCO_3$ with particle sizes of 17.1, 2.0, and 0.7 μm. This was due to ESP/PP composites having better phase continuity than $CaCO_3$/PP composites.

Ji et al. (2009) examined the possibility of ESP used as filler for epoxy composites. The epoxy composites were prepared from ESP at content of 1-10 wt%. They found that the strongly improvement of impact strength of epoxy composites at ESP content of 5 wt% were 16.7 kJ/m_2 compared with 9.7 kJ/m_2 of neat epoxy resin. When increasing ESP content to 10 wt%, the impact strength of the composites decreased from 16.7 kJ/m_2 to 12.3 kJ/m_2. They concluded that ESP had a potential source of filler for epoxy composites.

The effect of particle size and dispersion of nano ESP and nano $CaCO_3$ on thermomechanical properties and curing characteristics of the ESP or $CaCO_3$ particles filled elastomers such as acrylonitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR) and natural rubber (NR) was studied (Saeb et al., 2012). The average particle size of ESP and $CaCO_3$ was 50 and 349 nm, respectively. The fillers content were 5, 10 and 15 phr. It was observed that the ultimate tensile properties of SBR and NR nanocomposites were improved to some extent when 5 phr of ESP nanofiller was added to the rubber compound compared to $CaCO_3$. In the case of NBR nanocompounds, the mechanical properties were seemingly comparable, irrespective of the type of nanofiller. This contradictive behavior could be attributed to the alteration of crosslink density due to particular filler–matrix interaction while using mineral and natural fillers. The results of the rheometric study revealed that using ESP rather than $CaCO_3$ slightly increases the scorch time of all types of prepared nanocomposites, whereas a significant drop in the optimum curing time was seen for NBR nanocomposites containing ESP biofiller. Moreover, TGA curves showed similar thermal stability for SBR nanocomposites containing ESP and $CaCO_3$ fillers. Finer particle size of $CaCO_3$ and higher porosity of

ESP at high and low loading levels was respectively the main reasons for improvement of ultimate properties.

In the study of Hussein, Salim and Sultan (2011) on the work of water absorption and mechanical properties of high – density polyethylene/eggshell composite had result of that the addition of eggshell powder to the polymer leads to decrease in the tensile strength and modulus of elasticity. However on other hand it increases the elongation at break, and impact strength. The decreases in tensile strength are due to the poor adhesion of the filler-matrix and the agglomeration of filler particles. The decrement in tensile modulus can refer to increase the resistance of material to deformation. The elongation at break for the composites increasing with increasing filler content because the addition of eggshell powder causes an increase in the elasticity which leads to reduce the strength of the material. The composites with higher filler content show more water absorption. This is due to the higher contents of filler content in the composites that can absorb more water. As the filler content increases, the formation of agglomerations increases due to the difficulties of achieving a homogeneous dispersion of filler in composites.

2.7 Calcination of Eggshell

The purpose of calcination of eggshell is to increase the calcium oxide (CaO) content (Liu et al., 2010). Naemchan, Meejoo, Onreabroy, and Limsuwan (2007) used eggshell without eggshell membrane and its particle size of less than 200 μm to prepare eggshell at 200-900 ℃ for 1 hour and identify its crystal structure by X-ray diffraction (XRD). They found that the crystal structure of calcined eggshell was identified as calcite ($CaCO_3$) only at the treatment temperature from 200 ℃ up to 600 ℃ corresponded to the previous report from Engin, Demirtaş, and Eken (2006). However, the calcium carbonate phase decreased and CaO appeared as the eggshell was treated above 700 ℃. In addition, it was reported that the treatment of eggshell at 900 ℃ for 1 hour led to the complete phase transformation from $CaCO_3$ to CaO as reported from Engin et al. (2006). On the other hand, Lee and Oh (2003) reported that $CaCO_3$ was completely transformed into CaO at

800 ℃ for 1 hour. Wei et al. (2009) reported that the calcination of eggshell below 600 ℃ for 2 hour did not cause to the formation of CaO. However, the eggshell was calcined at 700 ℃ for 2 hour obtained $CaCO_3$ as a major component and CaO as a minor component.

The calcined eggshell was prepared in several temperatures. For example, Lee and Oh (2003) washed and uncrushed raw eggshell was calcined in an air atmosphere at various temperatures up to 1000 ℃, for 1 hour at each temperature. Another technique for calcined eggshell preparation was reported by Park et al. (2007). The eggshells were rinsed several times with deionized water to remove impurity and interference materials for instance organics and salts. Then, the sample was dried at 100 ℃ for 24 h in the dry oven. Calcinations were performed in the furnace at 800 ℃ for 2 hour after crushing the dried sample. Finally, samples having 40-100 mesh separated with a vibration selector were used.

2.8 Calcium Carbonate ($CaCO_3$)

Three crystalline forms of calcium carbonate ($CaCO_3$) presence in nature are calcite, aragonite and vaterite (Kitamura et al., 2002). Aragonite and vaterite are less stable than calcite under ambient temperature and atmospheric pressure (Krithiga and Sastry, 2011) and vaterite is least stable (Tai and Chen, 2008). Calcite has a specific gravity of 2.60-2.75 and a hardness of 3.0 on the Mohs' scale with rhombohedral form as the most widespread crystal system. Aragonite is orthorhombic crystal system having a specific gravity of 2.92-2.94 and a hardness of 3.5-4.0 on the Mohs'scale (Carr and Frederick, 2004). Figure 2.7 shows the crystal form of calcite and aragonite.

Figure 2.7: Crystal form of (a) calcite and (b) aragonite (Carr, Frederick and Staff, 2014)

Calcium carbonate is the most common deposit formed in sedimentary rocks, which compose primarily of calcite crystal (Ash and Ash, 2007). The sedimentary rocks are, for instance, chalk and limestone. There are two types of $CaCO_3$ used as filler for polymeric material which are ground $CaCO_3$ (GCC) and precipitated $CaCO_3$ (PCC).

The commercial grades of GCC are usually produced from chalk, limestone or metamorphic rocks (Piringer and Baner, 2008). More than 90% of the $CaCO_3$ used in plastics industry is GCC (Xanthos, 2010). Calcite is the most common crystal system for GCC. Chemical composition of commercial GCC grades comprises $CaCO_3$ as the major composition (94-99%), magnesium carbonate ($MgCO_3$) as major impurity and alumina, iron oxide, silica and manganese oxide as the minor impurity (Kirk, 2007). GCC has a density of 2.7 g/cm^3 with a hardness of 3 mohs which means less abrasive to processing equipments (Bruhn and Burlini, 2005). GCC with a particle size (D50) range of 0.8-5 μm and whiteness of 85-95% is normally used as filler in plastic industry (Senthil and Madan, 2015).

PCC can be produced in three crystal forms, calcite, aragonite, and vaterite (Lazzeri et al., 2005). In most PCC, aragonite is the crystal system predominantly produced (Carr and Frederick, 2004). However, the calcite crystal form is most commonly used in plastic industry (Lazzeri et al., 2005). Chemical composition of PCC is roughly the same as of GCC. However, PCC has $CaCO_3$ content of 98-99%, is purer than GCC and is lower in silica and lead content (Xanthos, 2010). Its other properties are very similar to GCC. The particle size of PCC is in a range of 1-10 µm for using in plastics industry. The PCC has high purity, very fine particles, regular in shape, a narrow particle size distribution, and high surface area (Shi et al., 2015). The PCC is widely used as functional fillers in the polymer composites.

CHAPTER 3

METHODOLOGY

3.1 Materials

PP (density = 0.946g/ml) is obtained by from Zarm Scientific company and the chicken eggshells were collected from restaurants in Kampar, Perak.

3.2 Preparation of Eggshell Powder

The procedures to produce the chicken eggshell powder (ESP) are summarized in Figure 3.1. First, chicken eggshells (ES) are washed for several times and membranes were removed manually. Chicken ES was smashed into small pieces using a stone mortar and were crushed using Waring HGB550 Blender. Then, the eggshell is further grinded into powder using Retsch ZM200 Grinder at 6000 rpm. Three teaspoon of chicken ES was added into the grinder for each session. Grinding of eggshell took about 25 seconds for each session using 1mm trapezoid hole ring sieves and followed by 0.12 mm round hole sieve.

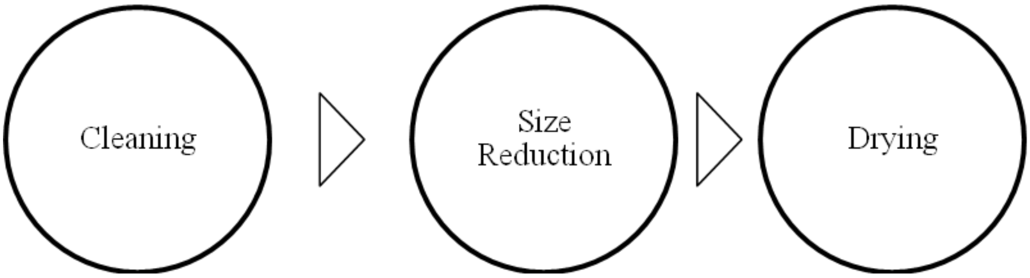


Figure 3.1: Flow diagram of eggshell powder production

The chicken ESP was sieved using 125 µm, 90 µm and 45 µm sieve plate. The chicken ESP was poured into 125 µm sieve plate and the remaining plates are stacked together in descending sequence. The powder at the last tray was collected in order to obtain particles with size lesser 45 µm. Eggshells powder were dried using Tuff TVAC-53 vacuum oven at 80 ℃ for 24 hours to remove moisture before it is blended with PP.

3.2.1 Calcination of Eggshell Powder

The eggshell powder was calcinated in normal furnace at 850 ℃ for 2 hours (Shan et al., 2016). The product was in black colour and it was in solid pieces. The solid pieces were put in the grinder model Retsch ZM200 Grinde at 6000 rpm to regrind it into powder form again. Then, it was sieved using 125 µm, 90 µm and 45 µm sieve plate. The particles when go through the 45 µm sieve were collected.

3.3 Characterization of ESP and Modified ESP

3.3.1 Particle Size Distribution

Particle size distribution (PSD) is an indication of different sizes of particle which are presented as proportions. Measurement was carried out by referring relative particle amount as a percentage where the total amount of particles is 100% in the sample particle group. In PSD test, various kinds of standards such as volume, area length and quantity are normally used to determine particle amount (Shimadsu Corporation, 2013). The cumulative distribution of particles passing the sieve expresses the percentage of the particles amount from specific particles sizes or below. In this study, Mastersizer 2000, Hydro2000 MU (A) was used to determine the particle size distribution of calcinated chicken ESP using refactive index of 1.334.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

ESP and calcinated ESP were subjected to FTIR analysis. The IR spectrum of raw materials was recorded using Spectrum RX1 Perkin Elmer analyzer. The spectra were recorded from 4000-400 cm^{-1} wavelength with 32 scan. The powder samples were prepared using KBR standard.

3.3.3 Thermal Decomposition of Filler

ESP and calcinated ESP were subjected to Thermal Gravimetric Analysis (TGA) test using Mettler Toledo TGA. During the test, the raw materials were heated up from room temperature to 800 ℃, with heating rate of 20 ℃/min under nitrogen flow.

3.3.4 Morphological Study

FESEM-JEOL 6701-Field emission scanning electron microscope was used to investigate the surface morphology of ESP and calcinated ESP. The raw materials were sputter coated with titanium particles prior to scan. The acceleration voltage used was 20 kV. In the scan, the raw materials were magnified at 10,000X.

3.4 Melt Blending of Composite

The composite were produced using melt blending technique in Brabender Plastograph EC 815652 internal mixer. The formulation of the composite was tabulated in Table 3.1. Three set of each formulation was prepared.

Table 3.1: Formulation of composite

PP (phr)	100	100	100	100	100
ESP* (phr)	0	10	20	30	40

*With and without modification of calcination

The temperature of internal mixer was set to 170 °C and the processing torque was set at 50 rpm. The PP resins were added into mixing chamber after the system was stabilized. The torque of the mixer rose rapidly and after the torque reached its peak; it will decrease rapidly until it is stabilized. The ESP was added quickly to the mixer chamber at this point. The total mixing time was 8 minutes.

3.5 Hot and Cold Press

The samples from the internal mixer were compressed with the aid of Gotech Hydraulic hot and cold press machine at 175.5 °C. The preheating, pressing and cooling time is 6, 2 and 2 minutes respectively.

3.6 Tensile Testing on Composite

PP composite undergoes tensile test using Universal Testing Machine (WDW-5Y Single Column). The test was conducted in accordance to ASTM-D638 standard. Three dumbbell shape sample for each set of PP composites with different loadings and compositions of fillers were cut using hydraulic cutter. The width and thickness at the bridge of dumbbell samples was measured with the aid of micrometer screw gauge. The test was carried out at pulling rate 50 mm/min. Tensile strength, modulus, and elongation at break were recorded from the software after the sample was fractured. The tensile fracture surface was observed under FESEM in order to understand the nature of the fracture.

3.7 Characterization of Composite

3.7.1 Thermal Decomposition of Composites

PP composites were subjected to thermal decomposition test using Mettler Toledo TGA. During the test, the composites materials were heated up from 30-800 ℃, with heating rate of 20 ℃/min under nitrogen flow.

3.7.2 Thermal Properties Analysis

PP composites were subjected to differential scanning calorimetry (DSC) test using Mettler Toledo DSC1/500 analyzer. The composites were heated up from 0-250 ℃ and then cooled from 250-0 ℃, under nitrogen flow at rate of 10 ml per minute. The samples were cut and weighted before it was placed into aluminum sealed pan. The melting and crystallization temperature was determined through the graph produced by DSC. The amount of crystallinity of PP was also calculated based on Equation (1):

$$x_c^m = \frac{\Delta H_m}{W_p \times \Delta H_{100}} \times 100\% \qquad \text{Eq. (1)}$$

Where

x_c^m = crytallinity, %

ΔH_m = melting heat, J/g

ΔH_{100} = melting heat for 100% crystalline PP, 207.10 J/g

W_p = weight fraction of polymer in the sample

3.7.3 Melt Flow Index (MFI)

MFI was done with the purpose of measuring the ease of flow or melt flow rate (MFR) for the PP-chicken ESP composites and the PP-calcinated chicken ESP composites in molten state. In the testing, Procedure A of ASTM D1238 was applied using 230 ℃. The melt flow apparatus used was Tinius Olsen Extrusion Plastometer model MP600. The total mass of material that was extruded from the die was weighted and calculated in g/10 min.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Characterization of ESP and CESP

4.1.1 Particle Size Distribution

Figure 4.1 (a) and (b) demonstrate the particle size distributions curve of chicken ESP and chicken CESP. From Figure 4.1(a), the particle size of chicken ESP at peaks $d_{0.5}$ is obtained as 0.199 µm. The particle size distribution of commercial calcium carbonate is 7.102 µm at peaks $d_{0.5}$ as shown in Figure 4.1 (c).

Figure 4.1(b) is the particle size distributions curve of chicken CESP. The particle size of chicken CESP at peaks $d_{0.5}$ is obtained as 0.135 µm which is finer than the chicken ESP. Previous studies by many researchers had proven that fillers with smaller particle size will have more surfaces for interaction with polymer matrix. Thus it is expected that CESP has larger surface area compared to chicken ESP. However this assumption need to verified with Field Emission Scanning Electron Microscope (FESEM) images and Brunauer–Emmett–Teller (BET) surface analysis (Cree and Rutter, 2015).

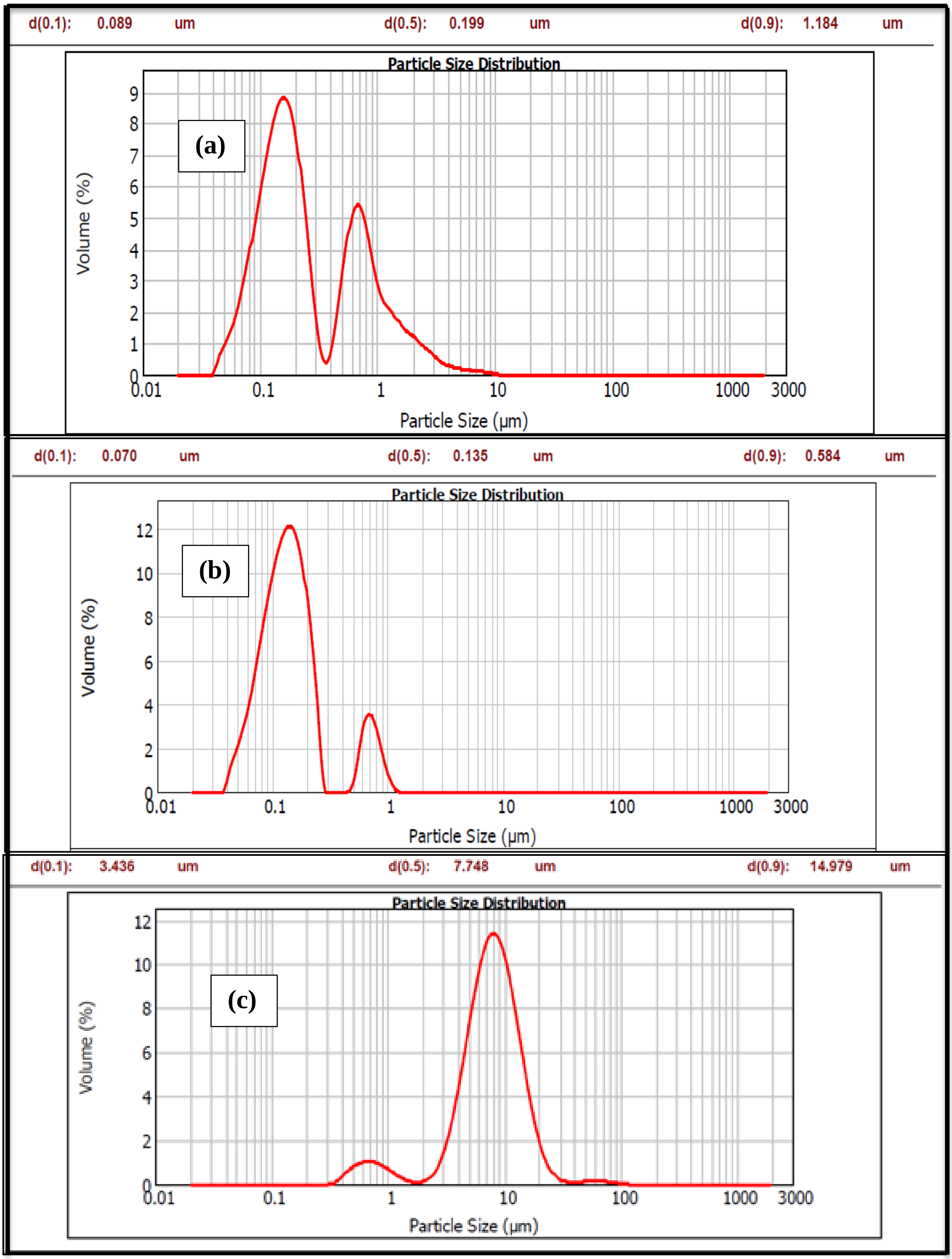
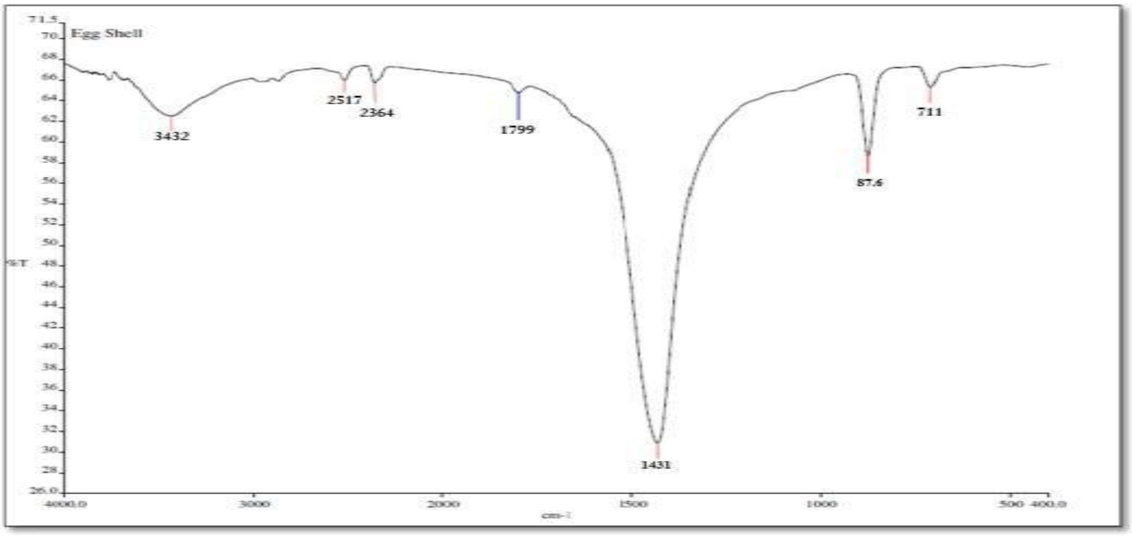


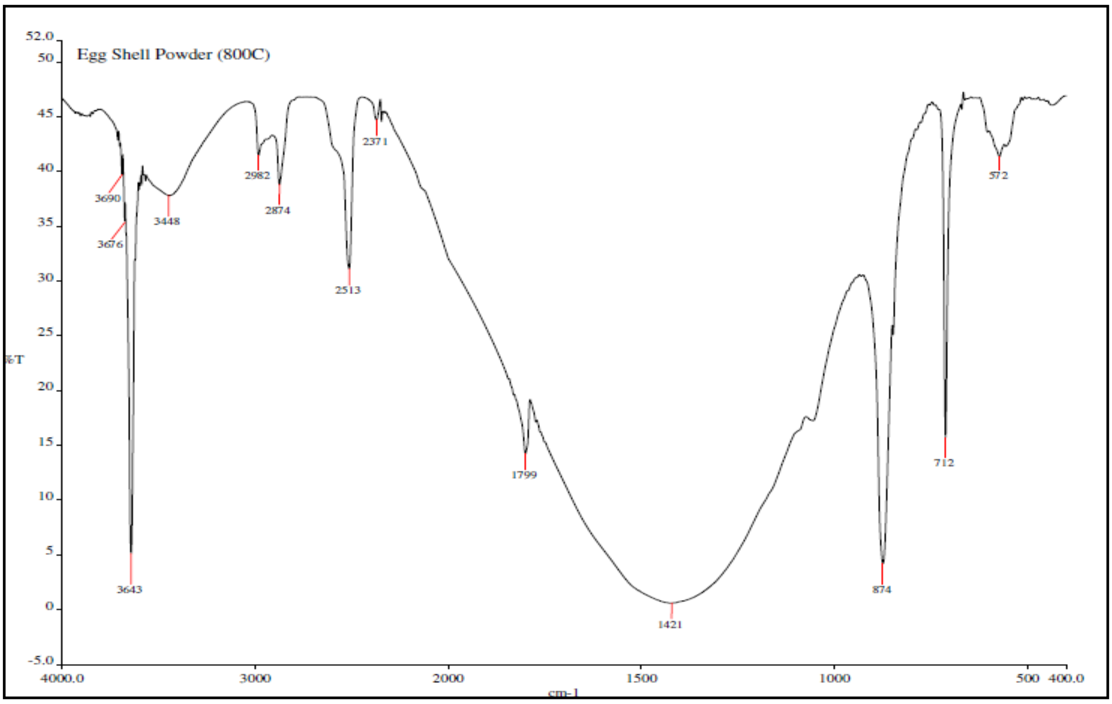
Figure 4.1: Particle size distribution of (a) chicken ESP (b) chicken CESP and (c) commercial calcium carbonate

4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4.2 (a) and (b) illustrates the FTIR analysis for chicken ESP and chicken CESP through numerous bands from 4000 to 400 cm^{-1}. From Figure 4.2 it can be distinguished that in both spectra appears a prominent peak of carbonate CO_3^{2-} at 874 cm^{-1}. According to Hariharan et al., (2014) similar absorption peak for ESP is reported at 875 cm^{-1}. The presence of these bands justifies the carbonate content in ESP. The strong band at 3643 cm^{-1} in Figure 4.2 (b) corresponds to the O-H bonds from the remaining hyrdroxide (Park et al., 2007). Whereas the band at 1421 cm^{-1} is much sharper compare to 1431 cm^{-1} in Figure 4.2 (a). This band corresponds to medium doublet centered of C-O bond. The sharp and strong band at 572 cm^{-1} corresponds to the Ca-O bonds where it does not appear in Figure 4.2 (a) for pure ESP. The peak 712 cm^{-1} is referred to the vibration bands of the carbonate CO_3^{2-} molecular ion for C-O symmetric stretching (Cree and Rutter, 2015). Shan et al., (2015) reported that calcium oxide has a strong broad band between 250 cm^{-1} and 600 cm^{-1} corresponding to a stretching vibration of the Ca-O group. A peak at 3643 cm^{-1} is due to the OH^- group which corresponded to calcium hydroxide ($Ca(OH)_2$) from absorption of moisture in the sample by calcium oxide (CaO) (Cree and Rutter, 2015). Therefore from the analysis it can be proven that the pure ESP had successfully undergone calcinations process.



(a)



(b)

Figure 4.2: FTIR analysis of (a) chicken ESP (b) chicken CESP

4.1.3 Thermal Gravimetric Analysis (TGA)

The thermal stability of the chicken ESP and CESP was analyzed by TGA test. Figure 4.3 (a) illustrates the TGA result for chicken ESP. The chicken ESP was thermally stable until 545 ℃. The results show the presence of three thermal events (region) for chicken ESP with two step decomposition. The first region at (~65 ℃) is attributed to the removal of physically adsorbed water on the particles of the waste powder. The second region 300 ℃ is related to decomposition of organic compositions of shell membrane and matrix protein of eggshell (Sutapun et al., 2013). For the third region ~699.14 ℃ is caused by decomposition of calcium (Freire and Holanda, 2006). Calcium oxide (CaO) can absorb more water than carbonate (O'Neil, 2013). Figure 4.3 (b) shown the TGA result for chicken CESP. There is two steps decomposition for this process. The first step decomposition is caused by the dehydration of calcium hydroxide (Sutapun et al., 2013). At the second step, the chicken CESP started to degrade at ~534.38 ℃ for the decarbonation of calcium carbonate which is not much difference compare with the chicken ESP (Sutapun et al., 2013)..

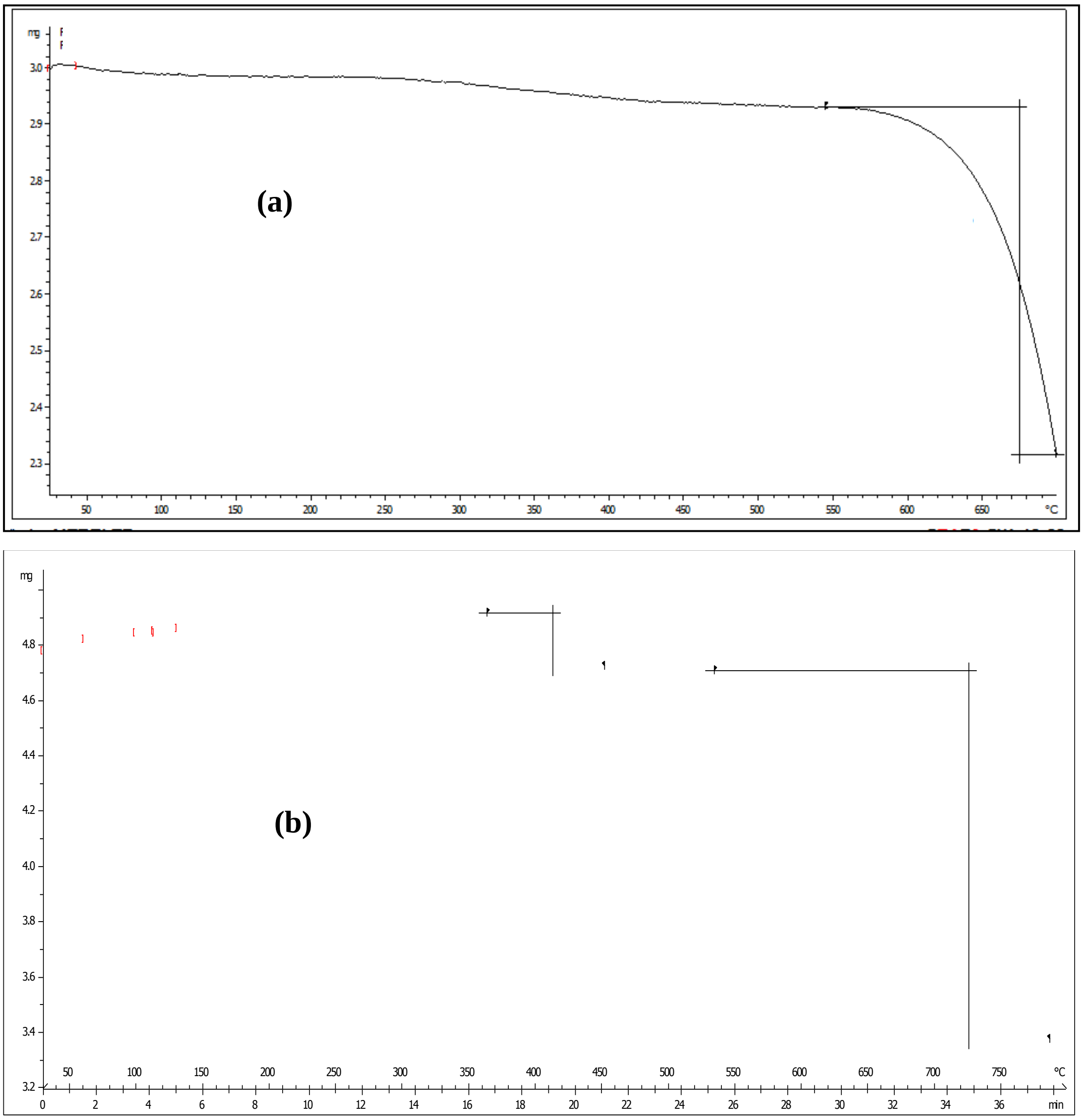
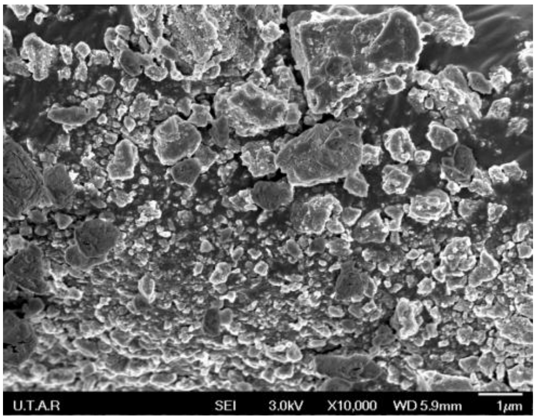


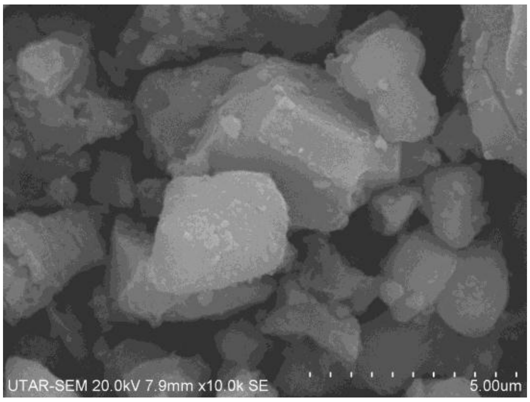
Figure 4.3: TGA of (a) chicken ESP and (b) chicken CESP

4.1.4 Morphology Study

The morphology of chicken ESP and CESP is examined using Field Emission Scanning Electron Microscope (FESEM). The apparent morphologies are shown in Figure 4.4. The chicken ESP was irregularly in shape (Witoon, 2011). The ESP powder heated to 850 ℃ is shown in Figure 4.4 (b). The morphology of the particles was depicted to be rounder in shape, smoother on their surface and more regularly as compared to chicken ESP without calcination. This change may have been due to the particles transforming from calcium carbonate to calcium oxide and releasing of carbon dioxide (Cree and Rutter, 2015).



(a)



(b)

Figure 4.4: FESEM image of (a) chicken ESP and (b) chicken CESP at 10,000X magnification

4.2 Processing Characteristics of Composite

Figure 4.5 shows the stabilization torque of composites at different loading of fillers. It is observed that when the filler loading increases the stabilization torque also increases. The result indicated that the dispersed chicken ESP and CESP particles in the melted PP hindered the polymer chain mobility (Koay, Husseinsyah and Osman, 2013). However, PP/ESP composites have higher stabilization torque than PP/CESP composites at all filler loading. For example, comparing filler loading of 40% for

PP/ESP40 and PP/CESP40 composites, PP/CESP40 composite has lower stabilization torque (11.3 Nm) than the PP/ESP40 (14.2 Nm). This means that the process ability is better for PP/CESP40 compared to PP/ESP40. When the torque is lower, the production cost can be saved because less energy is required for rotation of rotor/screw (Balakrishna, Ismail and Othman, 2013).

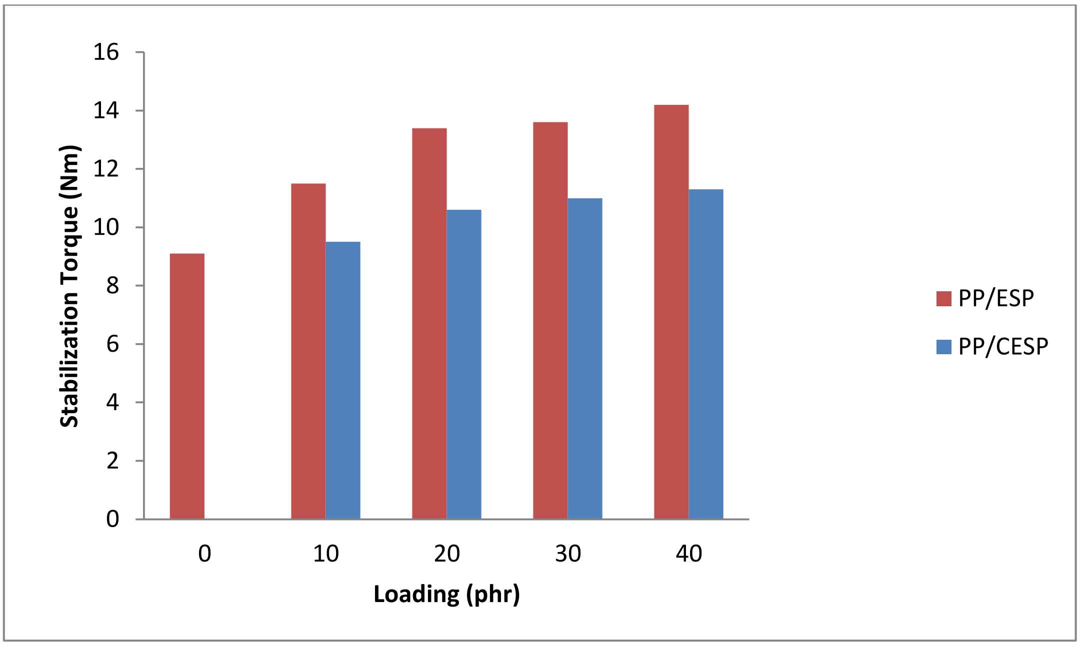


Figure 4.5: Stabilization torque of composites at different loading

4.3 Tensile Properties of Composite

The mechanical properties of the composites are studied by tensile test. Tensile strength is the maximum stress that a material can bear before breaking. Figure 4.6 show that both composites exhibits higher tensile strength than the neat PP at all filler loading. This is a good reinforcing effect because most fillers reinforced composites' tensile strength will drop due to low aspect ratio of filler, agglomeration of filler, less interfacial interaction between filler and matrix which leads to its poor ability to transfer stress from the matrix (Salmah, Koay and Hakimah, 2012; Chun, Husseinsyah and Azizi, 2013). When the filler's loading increases, the tensile strength for both types of the composites also increases. In comparison with PP/ESP composites, PP/CESP composites exhibit higher tensile strength at all filler loading.

This is because the finer particles size and more regularly shape of the chicken CESP which could promote a maximal interface contact between filler and polymer matrix due to larger specific surface area of the CESP (Bart, 2006). Besides, the increase in strength of the composite is due to good filler-matrix interactions, which also enable more stress to be transferred from the matrix to the fillers during external loading (Katz and Milewski, 1987).

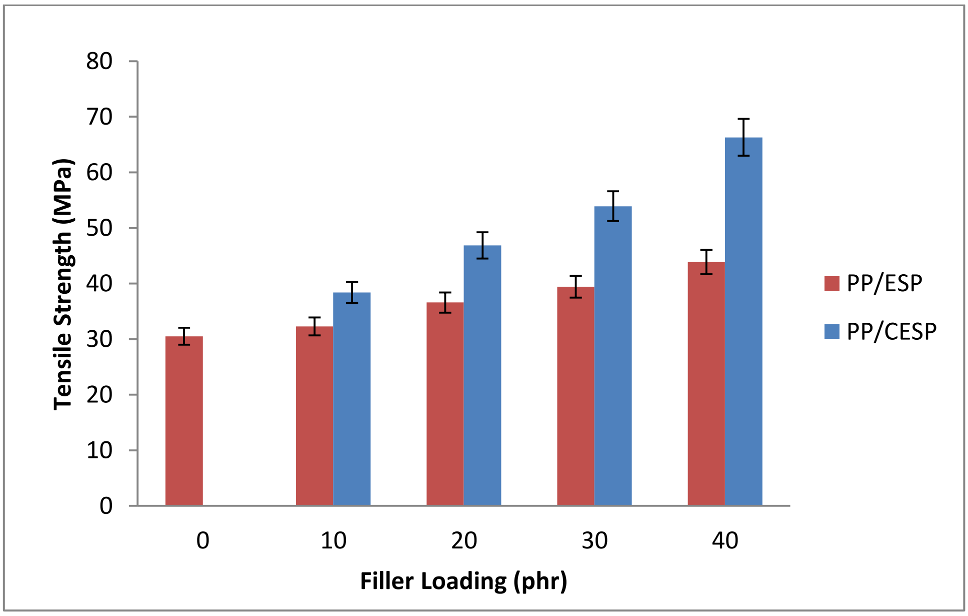


Figure 4.6: Tensile strength comparison of different composites

High stiffness of a material can be indicated by increment of tensile modulus. Figure 4.7 show that the tensile modulus of PP composites is higher than the original PP. The higher the filler loading, the higher the tensile modulus of the composites. The reason is the eggshell powder is stiffer than PP matrix (Fu et al., 2008). It observed that the composites filled with chicken CESP fillers have much higher tensile modulus than the composites filled with chicken ESP. This is because the better dispersion and distribution of the chicken CESP fillers in the polymeric matrix (Thio et al., 2002). When the dispersion and distribution of the filler is more homogenous and the surface area of the filler is larger, there will be more adsorption of polymer matrix on the surface of the filler. This will reduce the segmental mobility of polymeric chain and increases its stiffness. The similar result was also reported by

Amri, Husseinsyah and Hussin (2013). The smaller particle size of CESP and its good dispersion in the matrix has led to high increment in PP modulus.

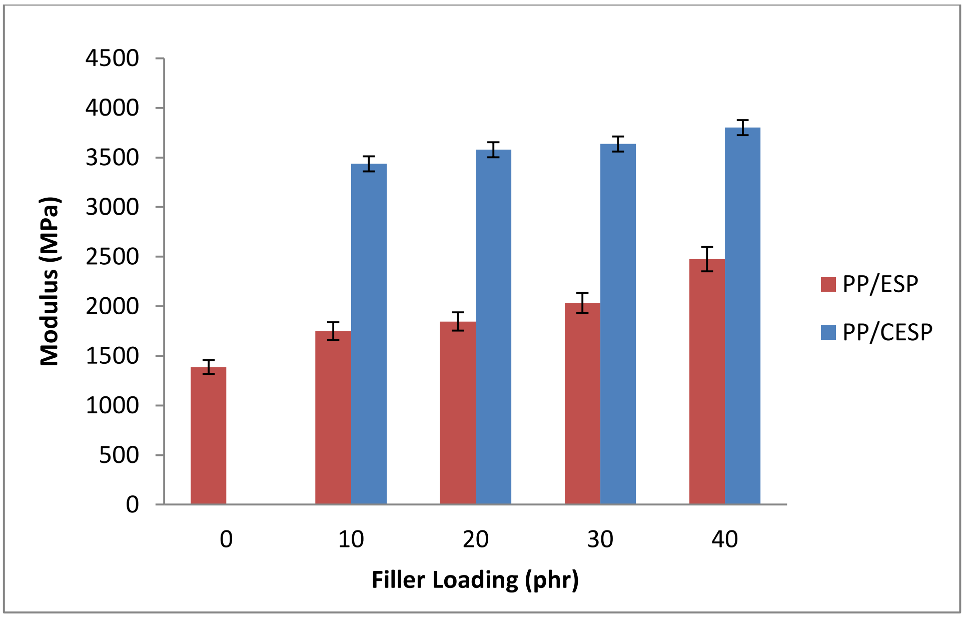


Figure 4.7: Modulus comparison at different filler loading

Elongation at break is a measure of ductility of a material. It can be observed from Figure 4.8 that the elongation at break of the composites decreases when the filler loading increases. The decrease in elongation at break is probably caused by the presence of the rigid chicken ESP and CESP particles and led to lower elongation property. The high filler loading restrain PP chains movement and results in the presence of highly localized strain which cause dewetting between matrix and filler. Therefore, the PP matrix becomes stiffer and less ductile (Zuiderduin et al., 2003).

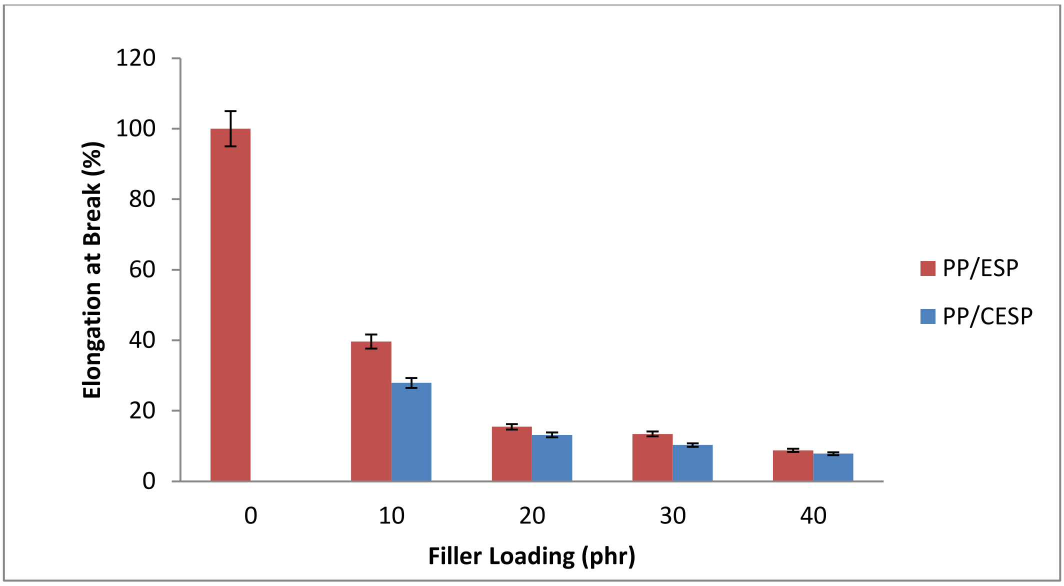


Figure 4.8: Percentage of elongation at break with different composites

Figure 4.9 illustrates the tensile fracture micrograph for pure PP, PP filled with chicken ESP and CESP under different filler loading by FESEM at magnification of X500. Figure 4.9 (a) illustrates the tensile fracture micrograph of the pure PP. As can be seen from the Figure 4.9 (a), the surface morphology for PP is smooth. Figure 4.9 (b) illustrates the tensile fracture micrograph of PP filled with 10phr loading ESP (PP/ESP10) and Figure 4.9 (c) illustrates the tensile fracture micrograph of PP filled with 10phr loading CESP (PP/CESP10) composites. It can be observed that Figure 4.9 (b) shows rougher surface with more matrix tearing compared to Figure 4.9 (c). In addition, both micrographs show that at lower filler loading, less filler is intact within the matrix throughout the polymer. Hence these indicate insufficient filler loading throughout the polymer matrix. This justifies lower mechanical properties at lower filler loading compared to higher filler loading. No propagation of crack growth was observed. Figure 4.9 (d) illustrate the tensile fracture micrograph of PP filled with 40phr loading ESP (PP/ESP40) and Figure 4.9 (e) illustrate the tensile fracture micrograph of PP filled with 40phr loading CESP (PP/CESP40) composites. As can be seen from both the sample more filler are dispersed homogenously throughout the matrix. This indicates sufficient filler loading. Moreover, Figure 4.9 (e) shows less voids with more fillers remain intact within the matrix compared to Figure 4.9 (d). This indicates good bonding between the CESP fillers and PP matrix. PP/CESP40 sample also shows lesser plastic deformation than PP/ESP40 composites. This justified the higher modulus strength for composite from PP/CESP40. In both all samples agglomeration of filler could not be observed.

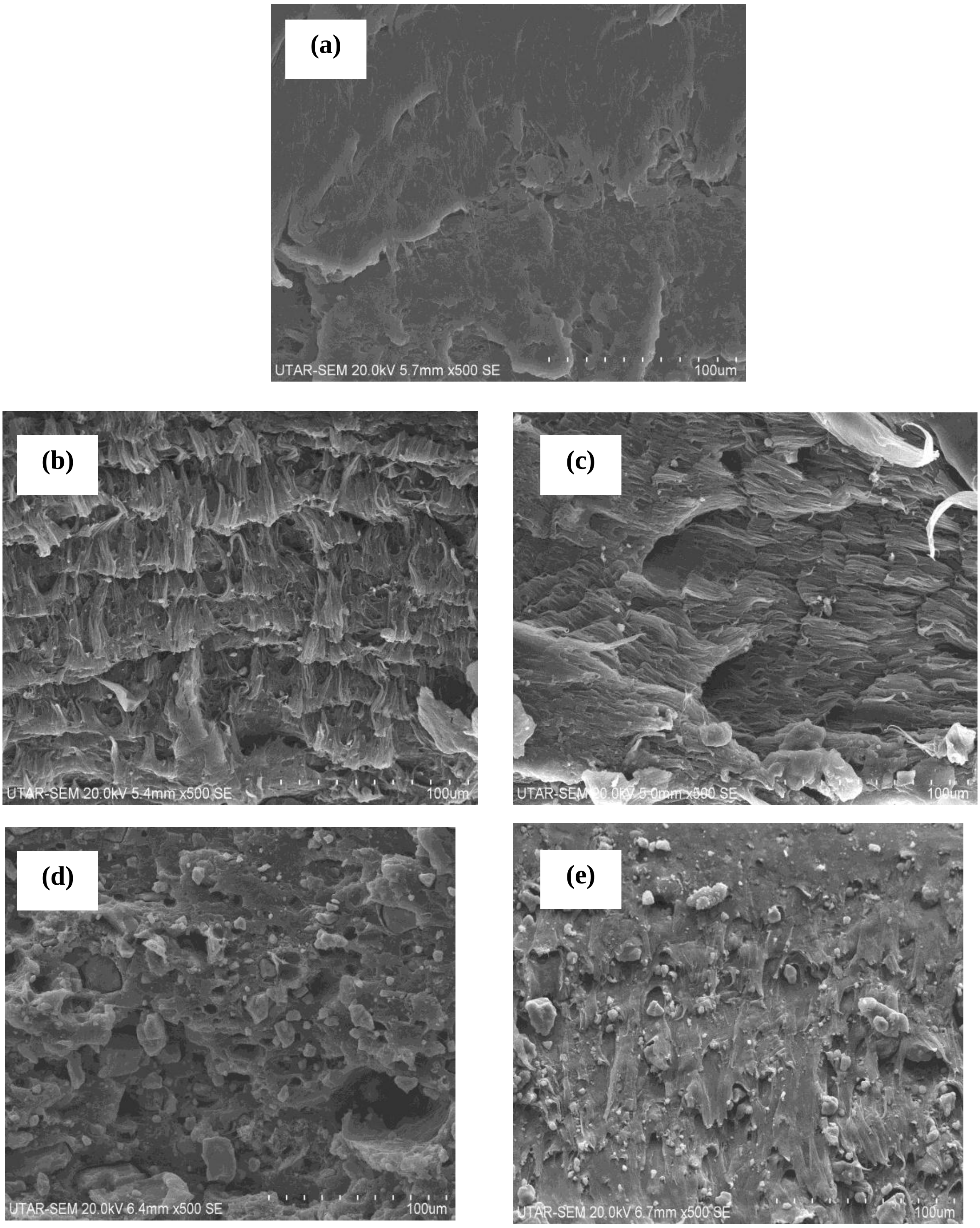


Figure 4.9: FESEM micrograph at 500X magnification of (a) PP (b) PP/ESP10 (c) PP/CESP10 (d) PP/ESP40 and (e) PP/CESP40

4.4 Characterization of Composite

4.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

From Table 4.1, the bands at frequency 3000 cm^{-1}-2800 cm^{-1}, 1457 cm^{-1}, 1376 cm^{-1}, 1163 cm^{-1}, 996 cm^{-1} and 975 cm^{-1} represent the characterization bands of polypropylene. The band at 1420 cm^{-1}, 872 cm^{-1} and 713 cm^{-1} represents CO_3^{2-} vibration which show the occurrence of carbonate group in the compostie. The composites which exhibit a transmission band at frequency 572 cm^{-1}, represent the Ca-O content in the calcinated filler. Similary published data for this peak occurred between the frequencies of 500 cm^{-1} to 670 cm^{-1} (Witoon, 2011).

Table 4.1: Assignment of functional groups to peaks in FTIP spectra

Frequency (cm^{-1})	Functional Group
3000-2800	C-H stretching vibration
1457	CH_2 bending vibration
1376	CH_3 bending vibration
1163	CH_3 symmetric deformation vibration
996	CH_3 rocking vibration
975	CH_2 rocking vibration
1420 ,872 and 713	CO_3^{2-} vibration
572	Ca-O bonding

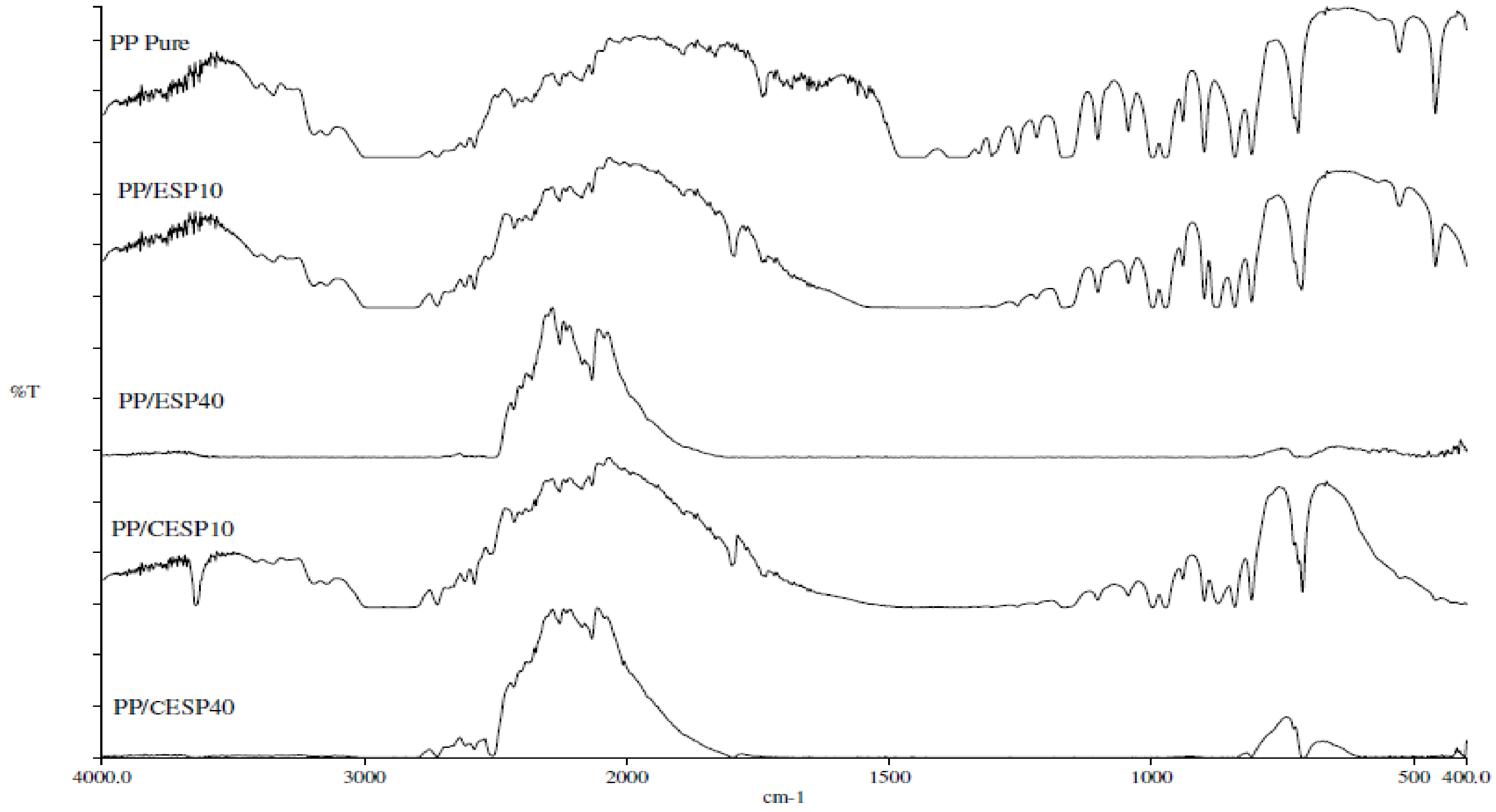


Figure 4.10: FTIR spectra of different composites

4.4.2 Thermal Gravimetric Analysis (TGA)

From Table 4.2, it is observed that all the composites have higher thermal stability than the PP itself. Figure 4.11 show that PP has only one decomposition step while all the composites have two decomposition steps. In this case, the filler had changed the decomposition pathway of PP which means the second decomposition step is due to the presence of filler and it is very obvious for PP/ESP40 and PP/CESP40 composites. Besides, the filler loading increases, the higher the thermal stability for the composites. This is mainly because filler increases thermal stability by three ways; act as insulator, reduce the emission of volatile decomposition product during exposure to heat due to formation of torturous path in the polymer matrix because of good dispersion and it form stable char on the top of the composite (Shih and Huang, 2011; Jang et al., 2013). From the results it can be seen that PP filled with CESP shows better thermal stability which indicates better dispersion of the CESP in PP compared to ESP.

Table 4.2: Temperature of samples at 50% weight loss

Samples	Temperature at 50% weight loss (℃)
PP	462
PP/ESP10	470
PP/ESP40	479
PP/CESP10	472
PP/CESP40	484

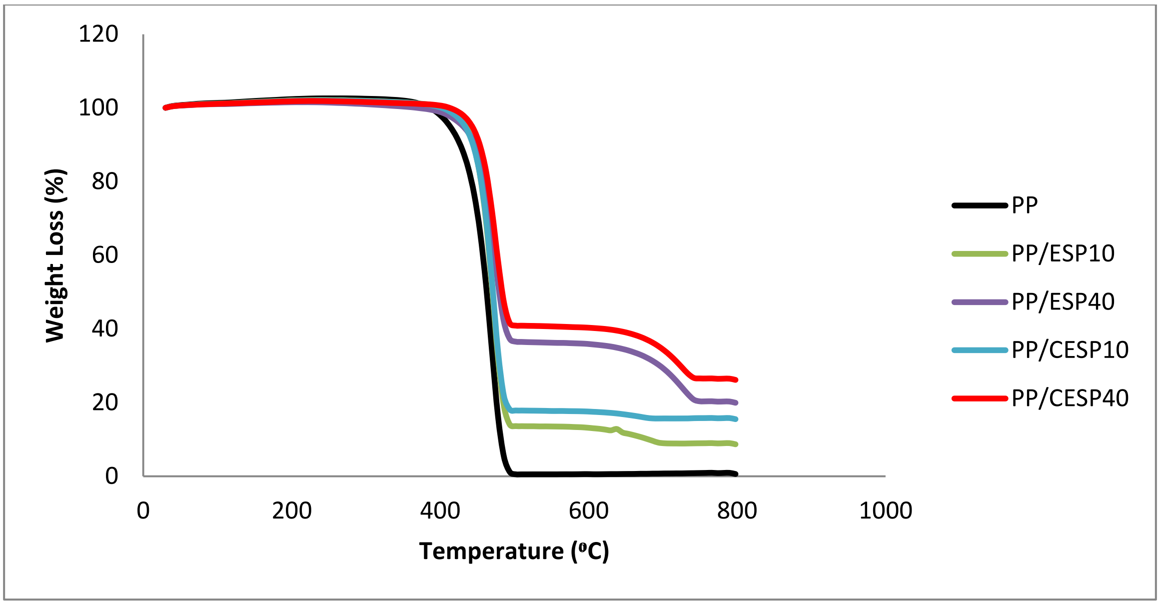


Figure 4.11: TGA analysis of composites

4.4.3 Differential Scanning Calorimetry (DSC)

Table 4.3 summarized the thermal properties of different composites and Figure 4.12 shows the comparison of heating and cooling curve of different composites. The melting temperature and crystallization temperature of PP are not much affected by both types of the filler loading. This indicates that the processing temperature is not affected with the presence of the fillers. All the composites had higher crystallinity compared to virgin PP and as the loading of the filler increases from 10 to 40 wt% the crystallinity is further increased. Previous research also proves that some filler can increase the crystalinility of the polymer composites by acting as nucleating agents for crystalline phase growth. The examples of fillers that can increase crystallinity are talc, oyster shell powder and rice husk powder (Menard, 2008). However from the results it can also be concluded that polymer composites filled with CESP exhibit slightly lower crystallinity compared to ESP filled composites.

Table 4.3: Thermal properties of different composites

Composite	**Melting Temperature (℃)**	**Crystallization Temperature (℃)**	**ΔHm (J/g)**	**Crystallinity, X_c^m (%)**
PP	164.29	127.42	72.43	34.97
PP/ESP10	167.35	127.24	68.40	36.69
PP/ESP40	168.91	126.67	54.24	43.65
PP/CESP10	168.07	125.65	64.79	34.76
PP/CESP40	168.09	126.48	51.84	41.72

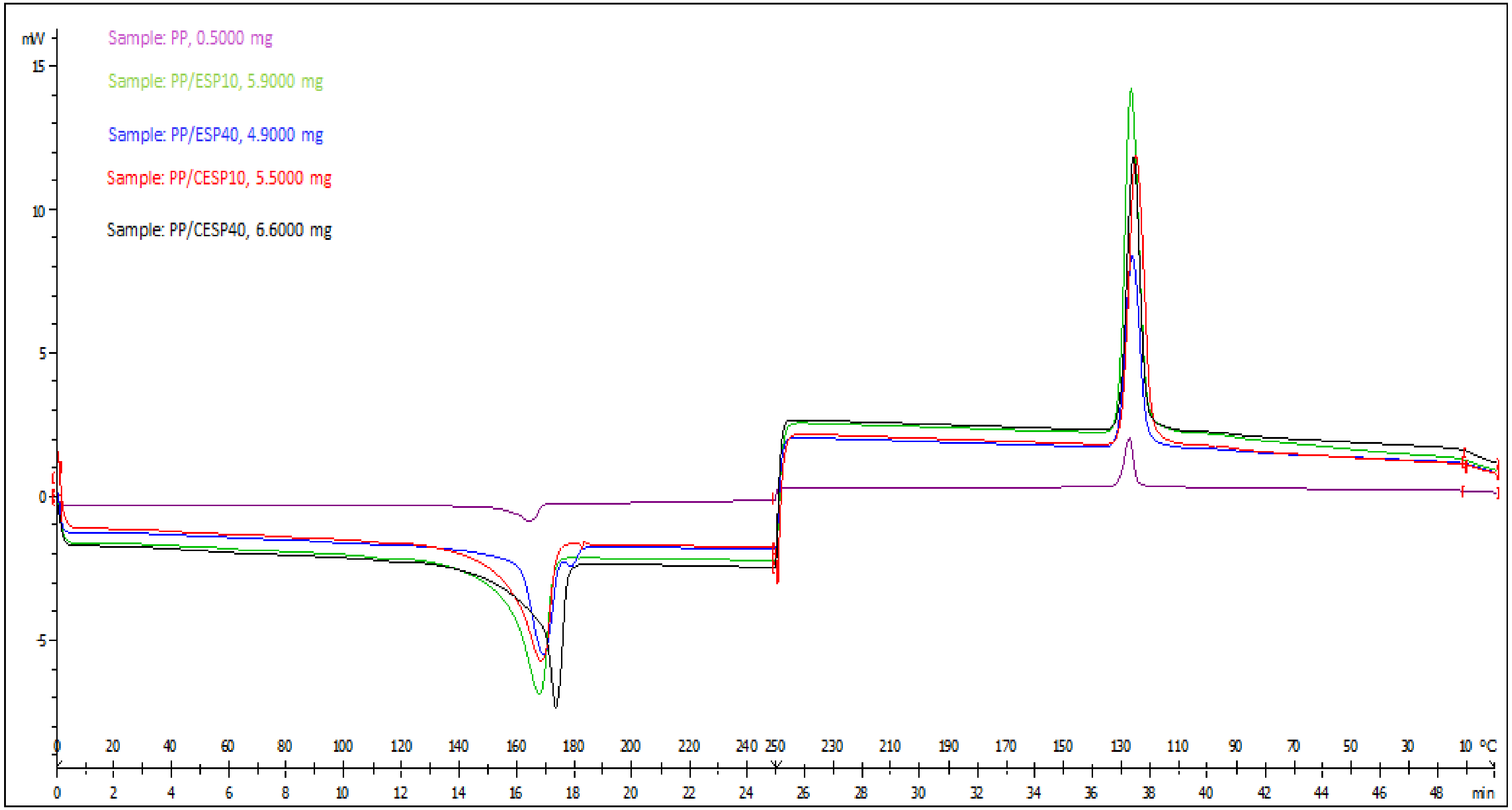


Figure 4.12: Comparison of heating and cooling curve of different composites

4.4.4 Melt Flow Index (MFI)

Table 4.4 records the MFI values of the sample. The viscosities of the sample are measured by their respective MFI values. As the results from the Table 4.4, the MFI values for both type of composites decreases when the filler loading increases. This means that the viscosities of the both composites increase as the filler loading increases. The PP/CESP composites have lower MFI values (more viscous) than the PP/ESP composites at all filler loadings due to better interaction formed between polymer and chicken CESP compared to with chicken ESP. The presence of these interactions makes the segmental motion of the polymer chains more difficult, causing greater flow activation energy (Barus et al., 2010). As the polymer chain moves slower, the viscosity of the PP/CESP composites are higher than the PP/ESP composites. By looking at bigger picture, the MFI values did not show significant difference among the 5 samples where the difference between any 2 values does not exceed 0.25g/10min which mean 4.69 Pa s (46.90 poise) viscosity with shear stress 2.814 psi and shear rate 0.60 s^{-1}.

Table 4.4: MFI values of different composites

Loading (%)	MFI PP/ESP composite (g/10min)	MFI PP/CESP composite(g/10min)
0	5.4	5.4
10	4.96	3.76
20	4.82	3.73
30	4.16	3.69
40	3.66	3.3

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, the chicken eggshell powder (ESP) was modified by calcination and the eggshell powder was characterized using the particle size analyser, FESEM, FTIR and TGA. New polypropylene (PP) composites with different loading of chicken ESP with and without modification were produced. The processing, tensile and thermal properties of PP/eggshell composites were determined.

Incorporation of filler enhances the process ability and reduces the processing torque. PP filled with calcinated eggshell powder (CESP) composites has lower stabilization torque at all loading compared to PP/ESP composites which mean PP/CESP composites has better process ability. Dispersion of filler in polymer matrix increases the tensile strength and modulus of composites while decreases elongation at break. PP/CESP composites exhibit higher tensile strength at all filler loading compared to PP/ESP composite. Better reinforcement effect is achieved when using CESP compared to ESP. This is because the finer particles and more regularly shape of the chicken CESP could produce a maximal interface contact with polymer chains due to larger specific surface area. The composites filled with chicken CESP fillers have much higher tensile modulus than the composites filled with chicken ESP. This is because the better dispersion and distribution of the chicken CESP fillers in the polymeric matrix. The decrease in elongation at break is probably caused by the presence of the rigid chicken ESP and CESP particles and led to lower elongation property. Besides, the filler loading increases, the higher the thermal stability for the composites. The chicken CESP is more stable because it provides better dispersion. The melting temperature and crystallization temperature of PP are not much affected by both types of the filler loading. This meaning that the processing temperature is not affected with the presence of the fillers. The viscosities of the both composites increase as the filler loading increases. The PP/CESP composites have lower MFI values (more viscous) than the PP/ESP composites at all filler loadings due to better interaction formed between polymer and chicken CESP compared to with chicken ESP.

5.2 Recommendation

Several recommendations that could be done in future studies:

- Overall mechanical properties testing can be done such as impact test, hardness test and fatigue test.
- Size of filler which will affects the dispersion and the properties of composites should be investigated. Nano-scale filler is recommended for the next study.
- Try to increase the elasticity of the composites by adding other type of impact modifier such as rubber.

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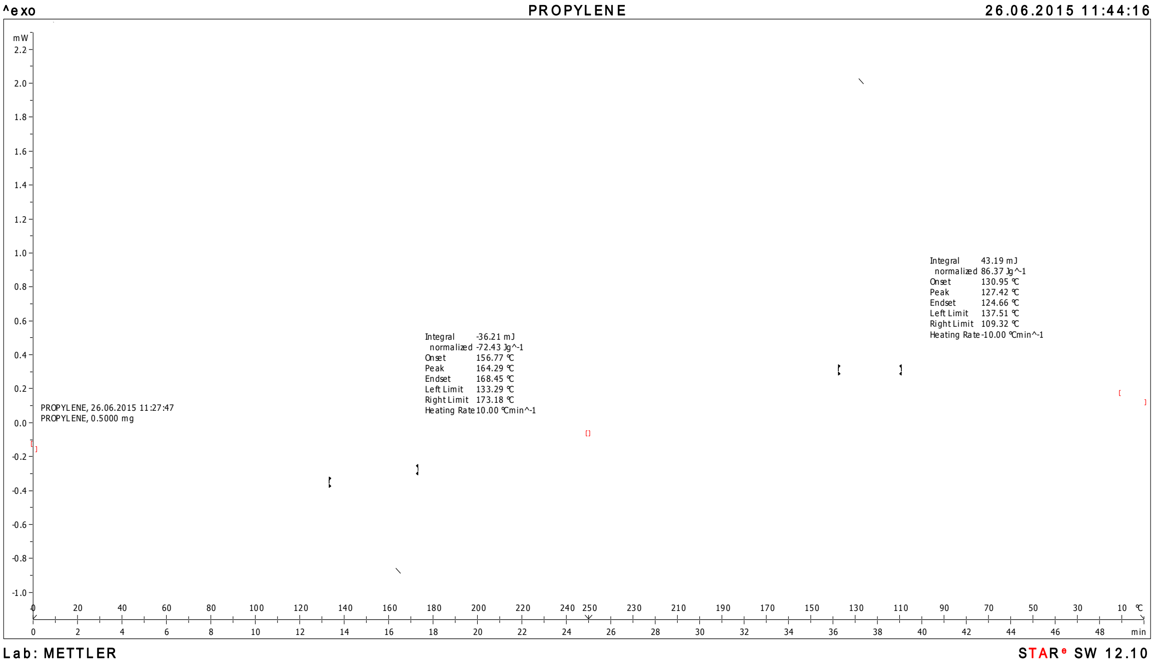
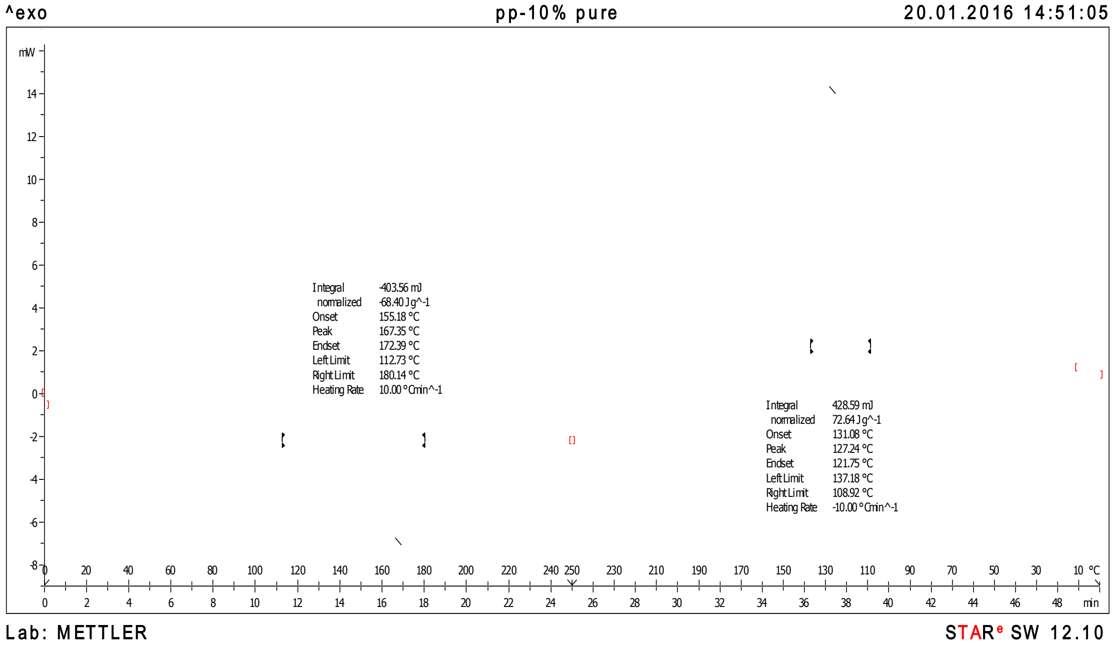
APPENDICES

APPENDIX A: DSC Results

(a) PP



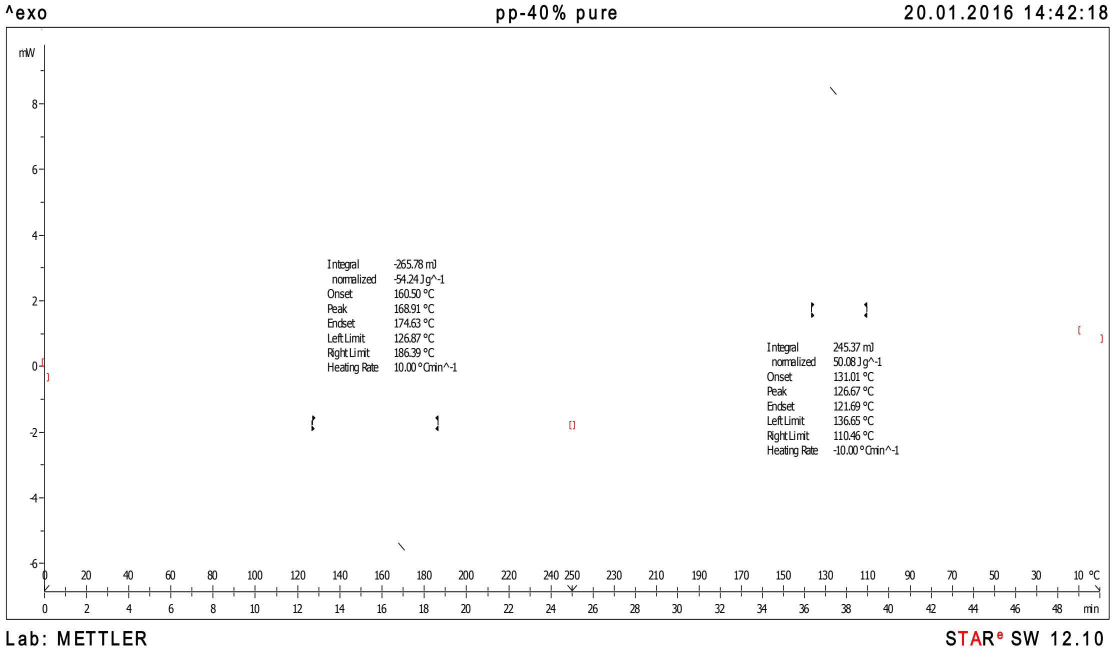
(b) PP/ESP10



Integral	-403.56 mJ
normalized	-68.40 Jg^-1
Onset	155.18 °C
Peak	167.35 °C
Endset	172.39 °C
Left Limit	112.73 °C
Right Limit	180.14 °C
Heating Rate	10.00 °Cmin^-1

Integral	428.59 mJ
normalized	72.64 Jg^-1
Onset	131.08 °C
Peak	127.24 °C
Endset	121.75 °C
Left Limit	137.18 °C
Right Limit	108.92 °C
Heating Rate	-10.00 °Cmin^-1

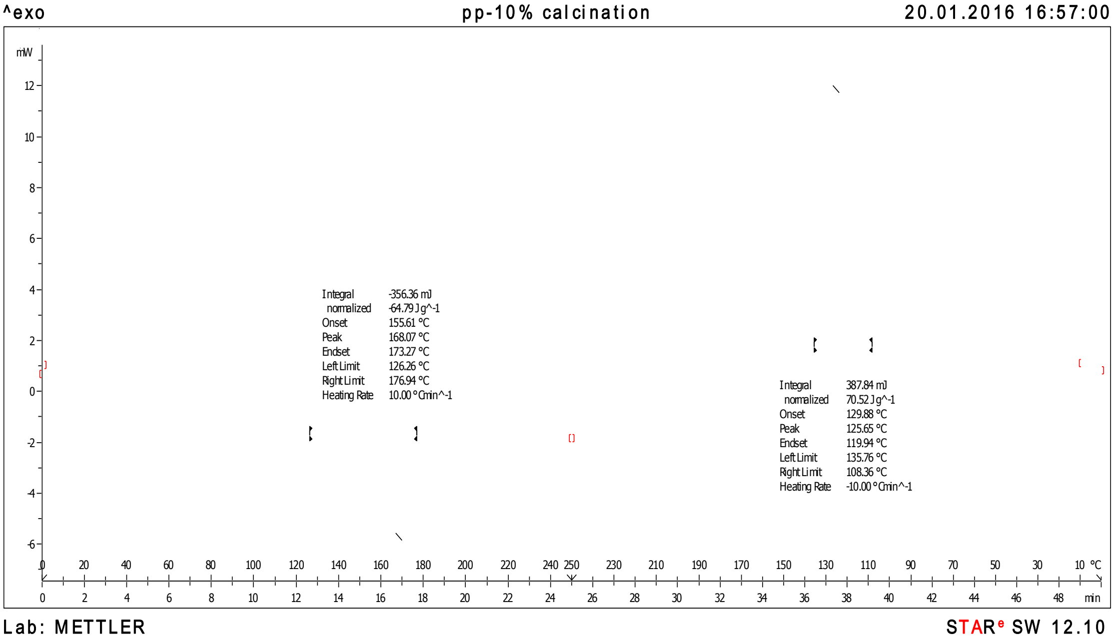
(c) PP/ESP40



Integral	-265.78 mJ
normalized	-54.24 Jg^-1
Onset	160.50 °C
Peak	168.91 °C
Endset	174.63 °C
Left Limit	126.87 °C
Right Limit	186.39 °C
Heating Rate	10.00 °Cmin^-1

Integral	245.37 mJ
normalized	50.08 Jg^-1
Onset	131.01 °C
Peak	126.67 °C
Endset	121.69 °C
Left Limit	136.65 °C
Right Limit	110.46 °C
Heating Rate	-10.00 °Cmin^-1

(d) PP/CESP10


^exo

pp-10% calcination

20.01.2016 16:57:00

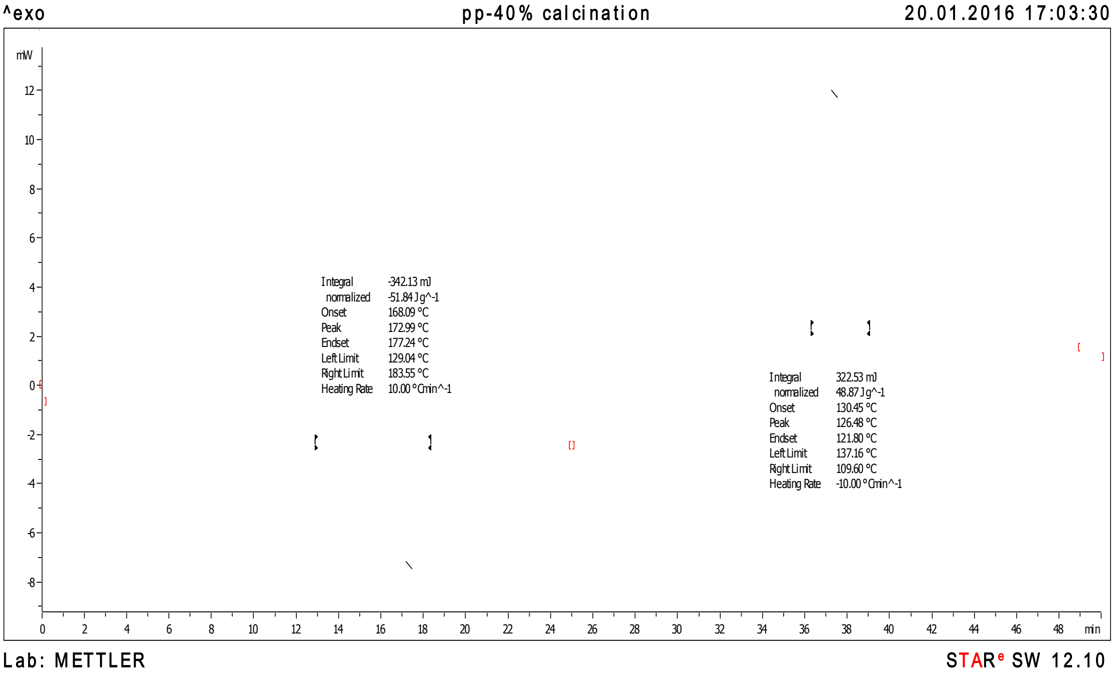
Integral -356.36 mJ
normalized -64.79 Jg^-1
Onset 155.61 °C
Peak 168.07 °C
Endset 173.27 °C
Left Limit 126.26 °C
Right Limit 176.94 °C
Heating Rate 10.00 °Cmin^-1

Integral 387.84 mJ
normalized 70.52 Jg^-1
Onset 129.88 °C
Peak 125.65 °C
Endset 119.94 °C
Left Limit 135.76 °C
Right Limit 108.36 °C
Heating Rate -10.00 °Cmin^-1

Lab: METTLER

STARe SW 12.10

(e) PP/CESP40


^exo

pp-40% calcination

20.01.2016 17:03:30

Integral -342.13 mJ
normalized -51.84 Jg^-1
Onset 168.09 °C
Peak 172.99 °C
Endset 177.24 °C
Left Limit 129.04 °C
Right Limit 183.55 °C
Heating Rate 10.00 °Cmin^-1

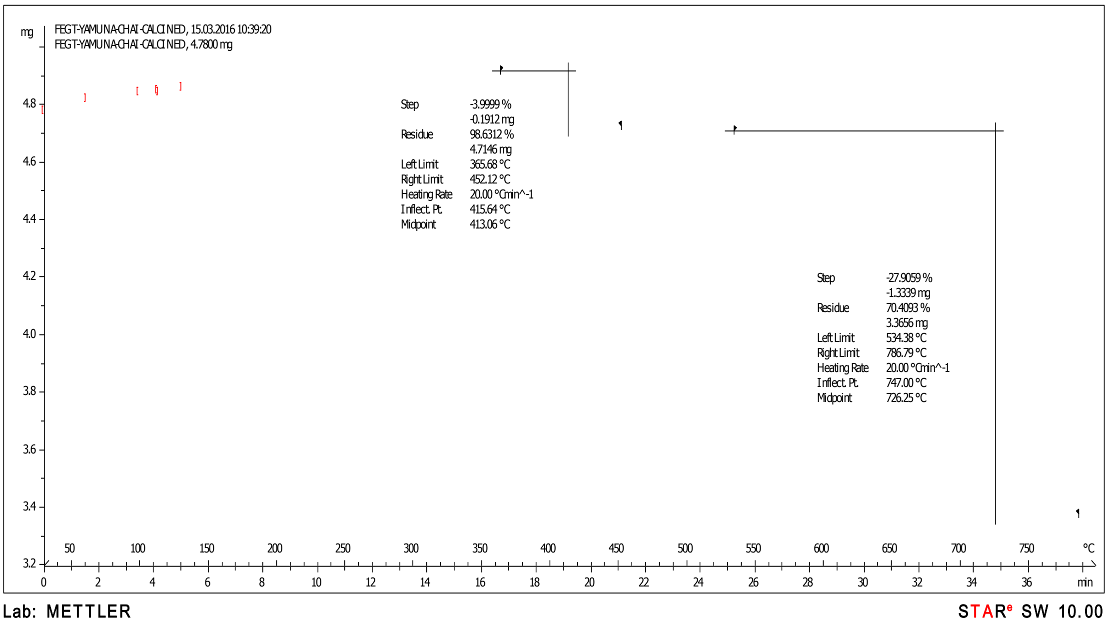
Integral 322.53 mJ
normalized 48.87 Jg^-1
Onset 130.45 °C
Peak 126.48 °C
Endset 121.80 °C
Left Limit 137.16 °C
Right Limit 109.60 °C
Heating Rate -10.00 °Cmin^-1

Lab: METTLER

STARe SW 12.10

APPENDIX B: TGA Results

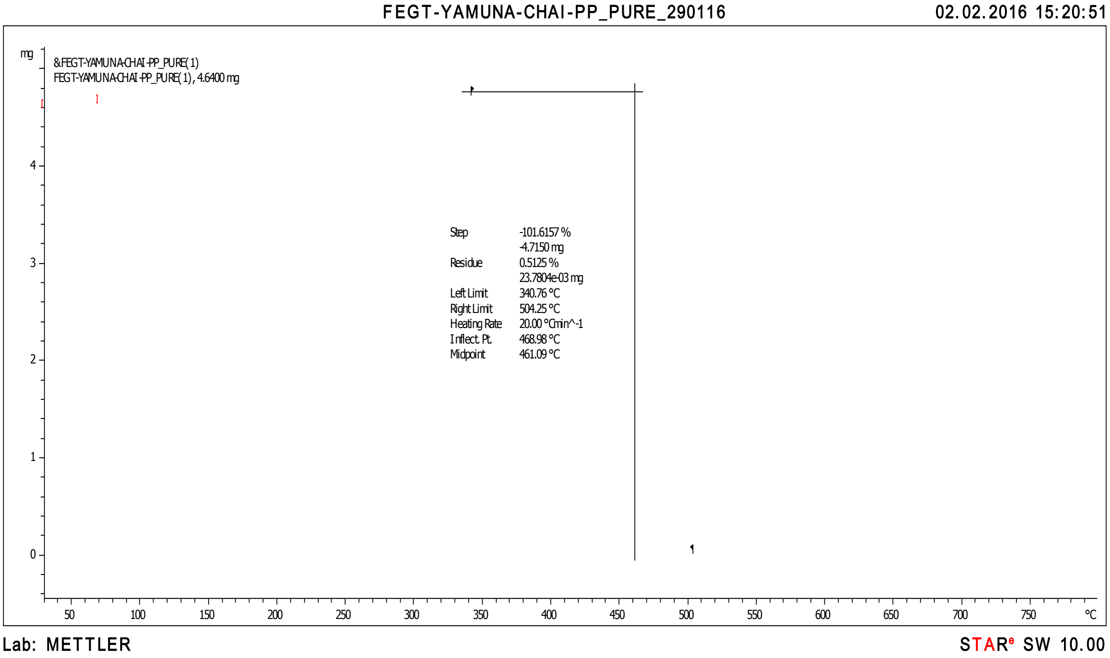
(a) Calcinated ESP



Step -3.9999 %
-0.1912 mg
Residue 98.6312 %
4.7146 mg
Left Limit 365.68 °C
Right Limit 452.12 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 415.64 °C
Midpoint 413.06 °C

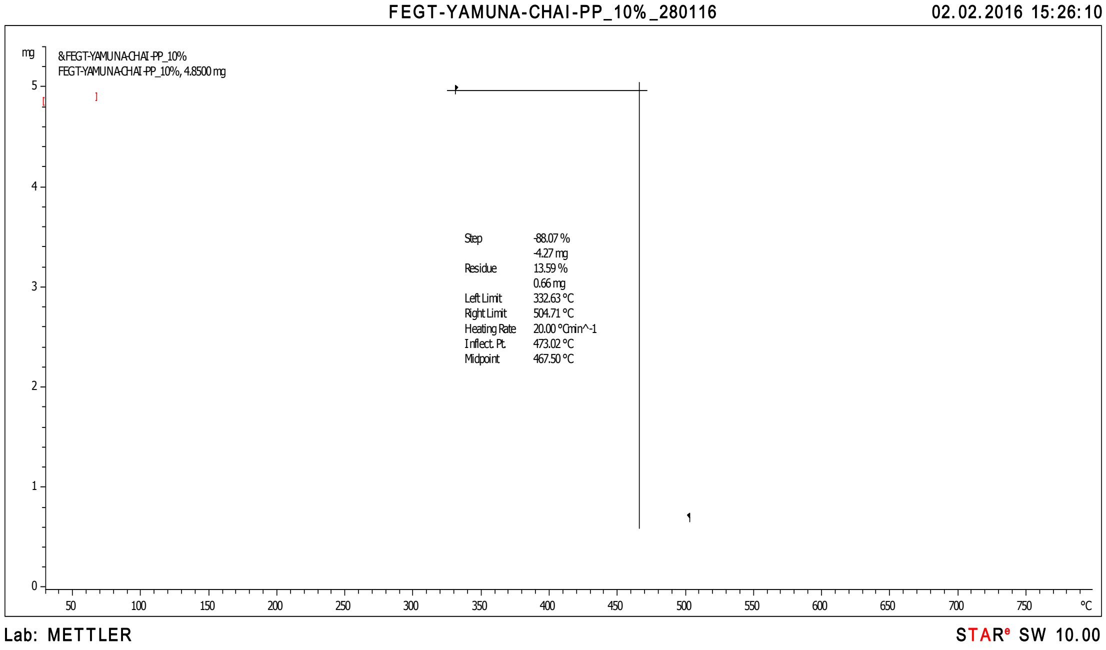
Step -27.9059 %
-1.3339 mg
Residue 70.4093 %
3.3656 mg
Left Limit 534.38 °C
Right Limit 786.79 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 747.00 °C
Midpoint 726.25 °C

(b) PP Pure



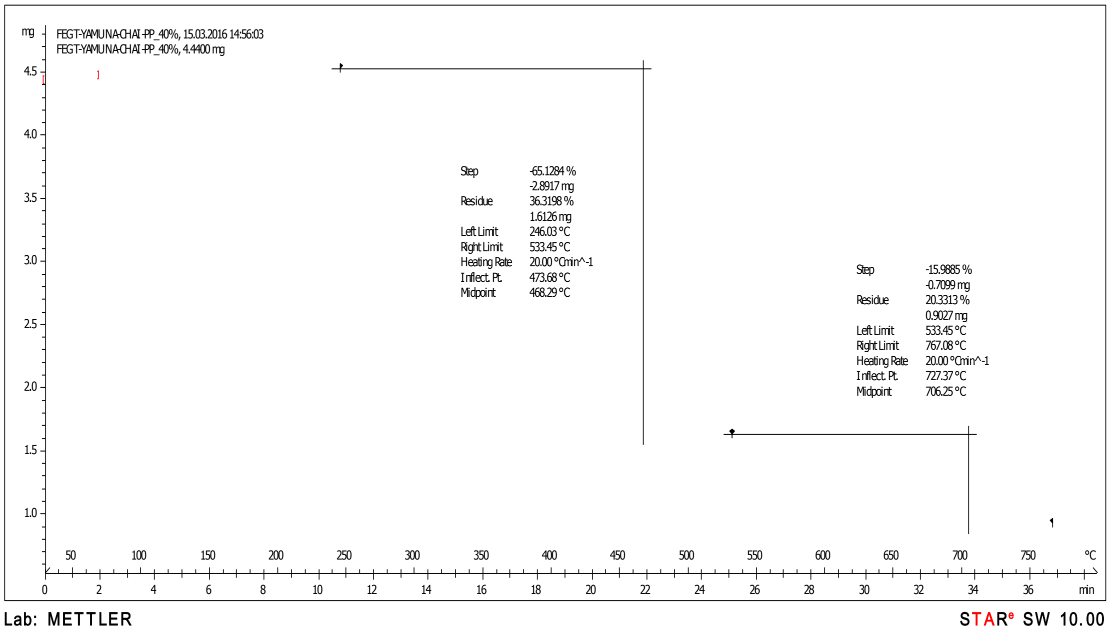
Step -101.6157 %
-4.7150 mg
Residue 0.5125 %
23.7804e-03 mg
Left Limit 340.76 °C
Right Limit 504.25 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 468.98 °C
Midpoint 461.09 °C

(c) PP/ESP10



Step	-88.07 %
	-4.27 mg
Residue	13.59 %
	0.66 mg
Left Limit	332.63 °C
Right Limit	504.71 °C
Heating Rate	20.00 °Cmin^-1
Inflect. Pt.	473.02 °C
Midpoint	467.50 °C

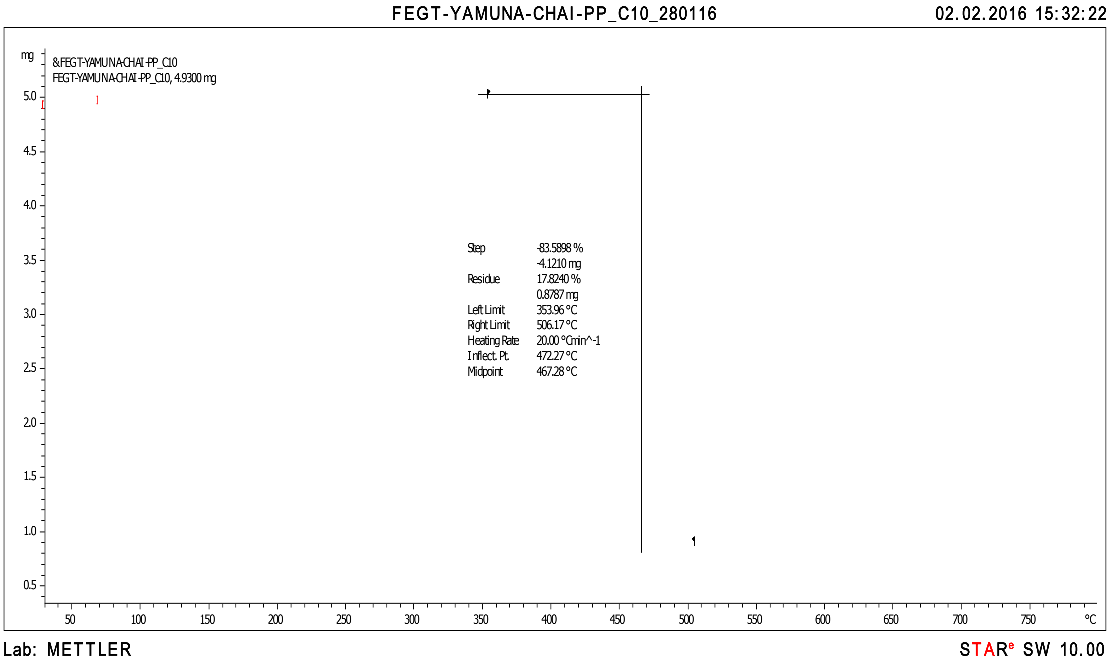
(d) PP/ESP40



Step	-65.1284 %
	-2.8917 mg
Residue	36.3198 %
	1.6126 mg
Left Limit	246.03 °C
Right Limit	533.45 °C
Heating Rate	20.00 °Cmin^-1
Inflect. Pt.	473.68 °C
Midpoint	468.29 °C

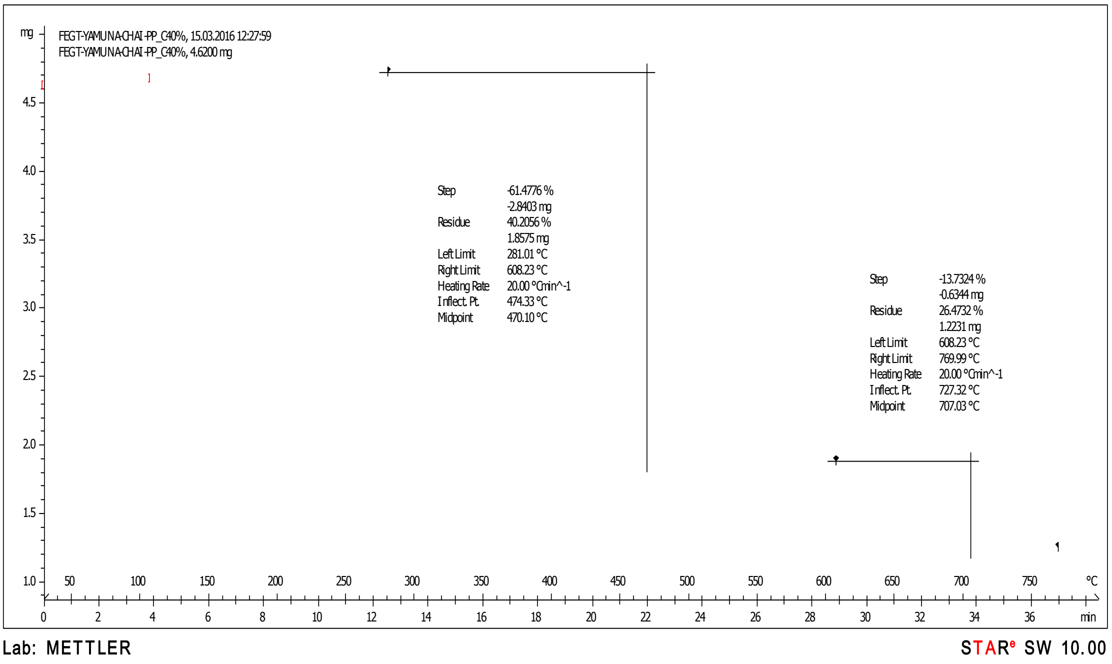
Step	-15.9885 %
	-0.7099 mg
Residue	20.3313 %
	0.9027 mg
Left Limit	533.45 °C
Right Limit	767.08 °C
Heating Rate	20.00 °Cmin^-1
Inflect. Pt.	727.37 °C
Midpoint	706.25 °C

(e) PP/CESP10



Step -83.5898 %
-4.1210 mg
Residue 17.8240 %
0.8787 mg
Left Limit 353.96 °C
Right Limit 506.17 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 472.27 °C
Midpoint 467.28 °C

(f) PP/CESP40

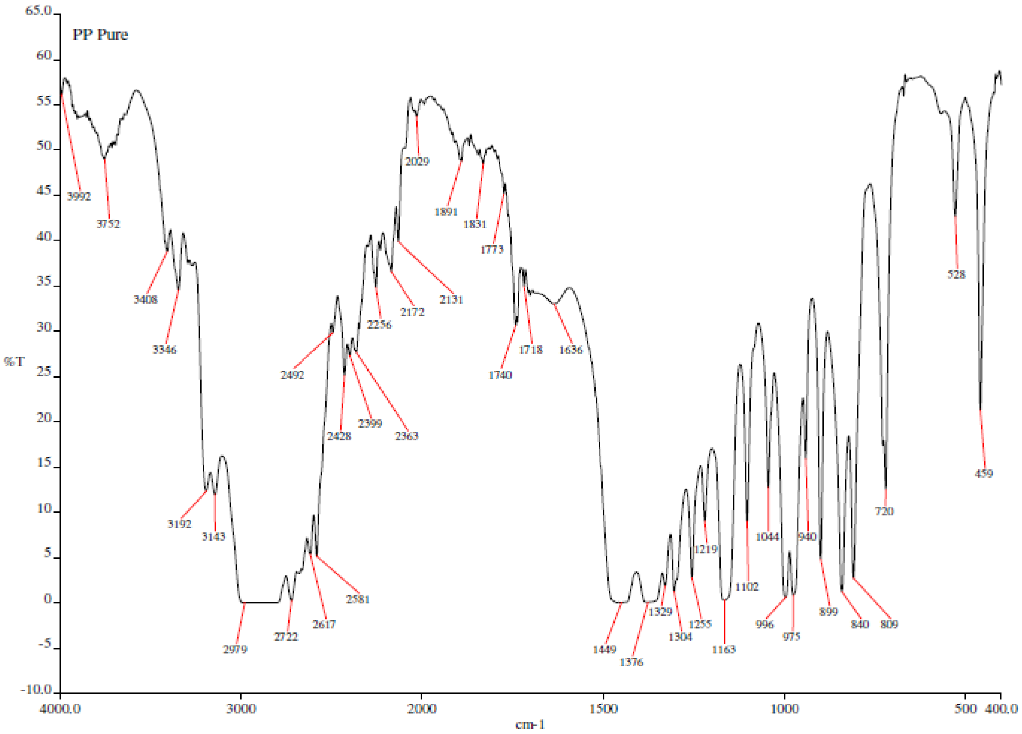


Step -61.4776 %
-2.8403 mg
Residue 40.2056 %
1.8575 mg
Left Limit 281.01 °C
Right Limit 608.23 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 474.33 °C
Midpoint 470.10 °C

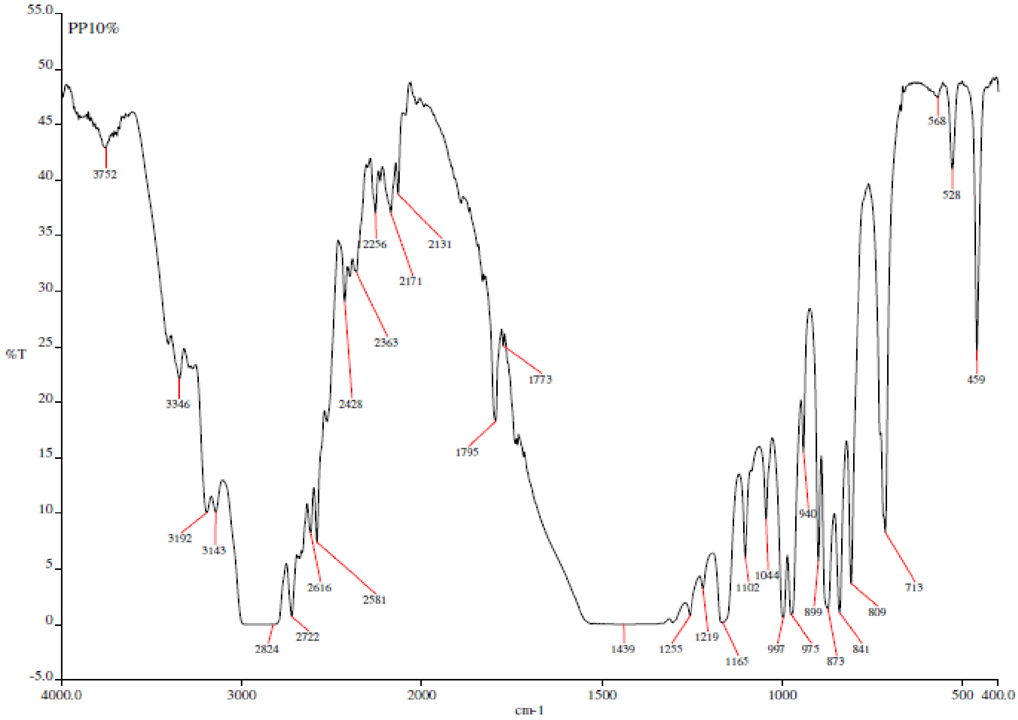
Step -13.7324 %
-0.6344 mg
Residue 26.4732 %
1.2231 mg
Left Limit 608.23 °C
Right Limit 769.99 °C
Heating Rate 20.00 °Cmin^-1
Inflect. Pt. 727.32 °C
Midpoint 707.03 °C

APPENDIX C: FTIR Results

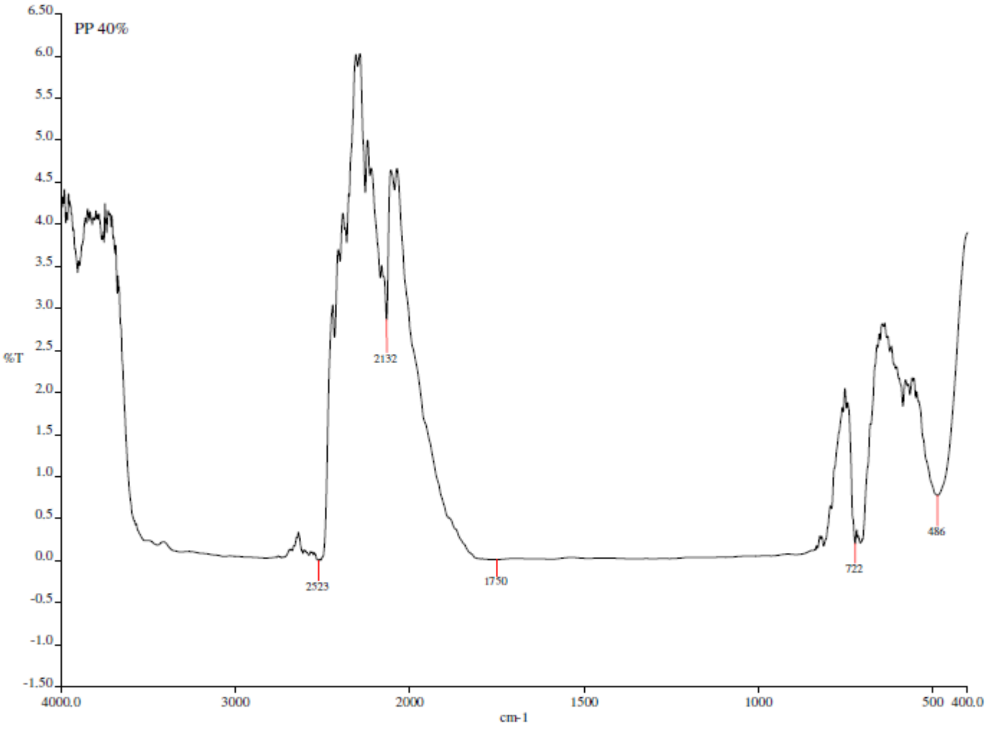
(a) PP Pure



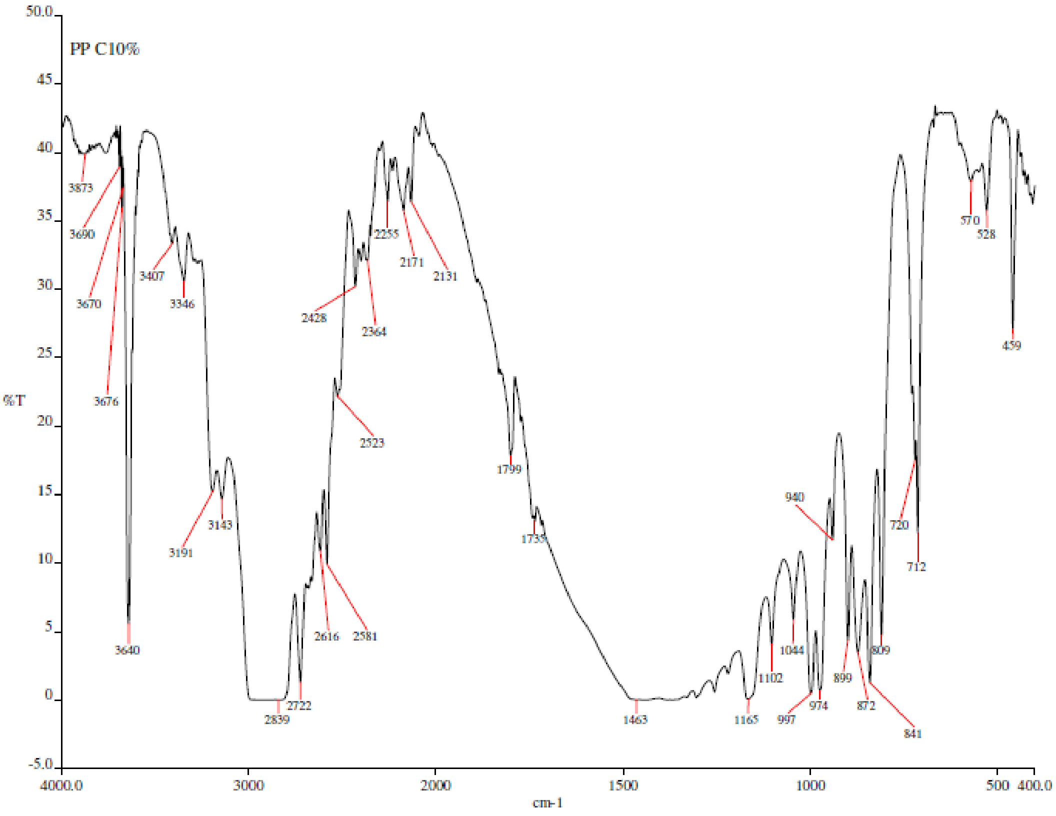
(b) PP/ESP10



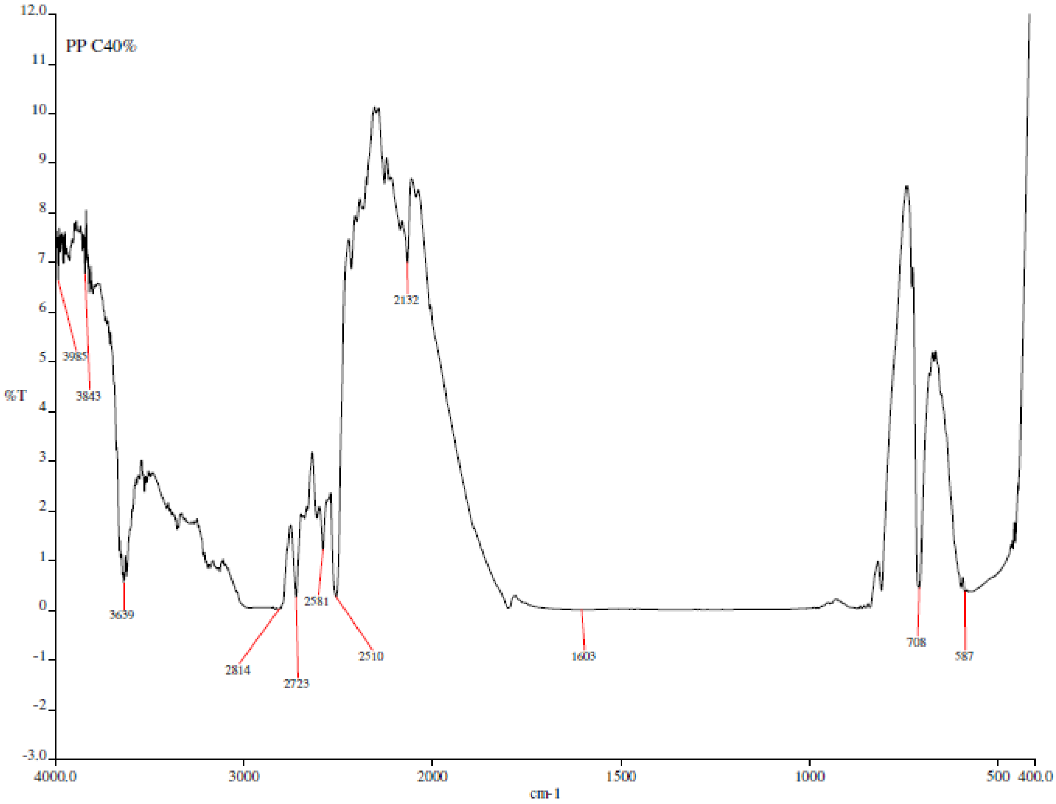
(c) PP/ESP40



(d) PP/CESP10



(e) PP/CESP40


PP C40%
12.0
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3.0
%T
3985
3843
3639
2814
2723
2581
2510
2132
1603
708
587
4000.0
3000
2000
1500
1000
500
400.0
cm-1