SILICON BASED PRECERAMIC POLYMERS AND THEIR USES IN POLYMER COMPOSITES: SYNTHESIS, CHARACTERIZATION AND PROCESSING

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ABSTRACT

SILICON-BASED PRECERAMIC POLYMERS AND THEIR USES IN POLYMER COMPOSITES: SYNTHESIS, CHARACTERIZATION AND PROCESSING

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The objectives of this study are to synthesize poly(dimethylsilane) (PDMS) preceramic polymer and to investigate its effect on morphology, flame retardant and mechanical properties of polypropylene (PP) based composites.

There are mainly two parts in this thesis. In the first part, PDMS was synthesized by electrochemical polymerization of dichlorodimethylsilane, which was dissolved in 1,2 dimethoxyethane (DME) solvent consisting of tetrabutyl ammonium perchlorate (TBAP), as supporting electrolyte. PDMS was obtained in powder form and characterized with Fourier transform infrared, ultraviolet-visible and proton nuclear magnetic resonance spectroscopic analyses, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

Since PDMS has some impurities coming from TBAP and DME, alternatively, the PDMS synthesis was done by electrochemical reduction of dichlorodimethylsilane without using solvent and/or supporting electrolyte for seven days. PDMS was produced as pure and characterized with the same methods used for previous synthesis.

In the second part of this thesis, PP based composites with additives were prepared by using a twin-screw extruder and injection molding machine and were characterized with limiting oxygen index (LOI), horizontal burning, TGA, differential scanning calorimetry (DSC), tensile and impact tests and SEM analysis.

Triphenyl phosphate, boron phosphate, magnesium hydroxide, intumescent flame retardants (IFR) (melamine phosphate (MP) and pentaerythritol (PER)), antimony trioxide and poly(methylsilsesquioxane) were additives used in this study other than PDMS. According to LOI test results, the highest LOI value among the PDMS composites was obtained in 1% PDMS, 14.25% MP and 4.75% PER (w/w) containing composite as 24%, whereas the LOI value of neat PP was measured as 17.5%. It was determined that elastic moduli of all the composites studied were higher than neat PP.

Keywords: Poly(dimethylsilane), preceramic polymers, flame retardancy, poly(propylene), limiting oxygen index, mechanical properties

ÖZ

SİLİKON BAZLI PRESERAMİK POLİMERLER VE ONLARIN POLİMER KOMPOZİTLERİNDE KULLANIMLARI: POLİMER SENTEZİ, KARAKTERİZASYONU VE PROSESİ

Dönmez Karadal, Sibel
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Bu çalışmanın amaçları, poli(dimetilsilan) (PDMS) preseramik polimerini sentezlemek ve onun polipropilen (PP) bazlı kompozitlerin morfolojisi, alev geciktiricilik ve mekanik özellikleri üzerindeki etkisini incelemektir.

Bu tezde esas olarak iki kısım bulunmaktadır. İlk kısmında, PDMS, destek elektrolit olarak tetrabütilamonyum perklorat (TBAP) bileşeni içeren 1,2 dimetoksietan (DME) çözücüsünde çözünmüş diklorodimetil silan monomerinin elektrokimyasal polimerizasyonu ile sentezlenmiştir. PDMS pudra şeklinde elde edilmiş ve Fourier Dönüşümlü Kızılötesi, Ultraviyole-Görünür Bölge ve Nükleer Manyetik Resonans spektroskopik analizleri, termogravimetrik analiz (TGA) ve taramalı electron mikroskopisi (SEM) ile karakterize edilmiştir.

PDMS'in TBAP'tan ve DME'dan kaynaklanan safsızlıklar içermesinden dolayı, alternatif olarak, PDMS sentezi, solvent ve destek elektrolit olmadan diklorodimetilsilanın 7 gün süreyle elektrokimyasal indirgenmesiyle gerçekleştirilmiştir. PDMS saf halde üretilmiştir ve önceki sentezde kullanılan aynı metotlarla karakterize edilmiştir.

Bu tezin ikinci kısmında, PP bazlı kompozitler, katkı maddeleri ile, çift-vidalı ekstrüder ve enjeksiyonlu kalıplama cihazı kullanarak hazırlanmış ve sınırlayıcı oksijen indeksi (LOI), yatay yanma, TGA, diferansiyel taramalı kalorimetre (DSC), çekme ve darbe testleri, ve SEM ile karakterize edilmiştir.

Trifenil fosfat, bor fosfat, magnezyum hidroksit, kabaran ve kül oluşturan alev geciktiriciler (melamin fosfat (MP), pentaeritritol (PER)), antimon trioksit ve poli(metilsilseskuoksan), PDMS dışında kullanılan katkı maddeleridir. PDMS kompozitleri arasında, LOI test sonuçlarına göre en yüksek LOI değeri, ağırlıkça %1 PDMS, %14.25 MP, %4.75 PER içeren kompozitte, %24 olarak elde edilmiştir. Saf PP'nin LOI değeri ise %17.5 olarak ölçülmüştür. Çalışılan bütün kompozitlerin elastik modüllerinin saf PP'den daha yüksek olduğu belirlenmiştir.

Anahtar kelimeler: Poli(dimetilsilan), preseramik polimerler, alev geciktiricilik, polipropilen, sınırlayıcı oksijen indeksi, mekanik özellikler

To my family and my soul mate

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NOMENCLATURE

ΔL	Total elongation distance
A	Absorbance
AO	Antimony trioxide
APP	Ammonium polyphosphate
ASTM	American Society for Testing and Materials
ATH	Aluminum hydroxide
BP	Boron phosphate
BSi	Silicon containing preceramic oligomer
c	Concentration of particles in solution
$CDCl_3$	Deuterated chloroform
DB	Decabromodiphenyl oxide
DME	Dimethoxyethane
DSC	Differential scanning calorimetry
e	Molar absorbance coefficient
E	Elastic modulus
F	Applied force to the material
FT-IR	Fourier transform infrared
FT-IR/ATR	Fourier transform infrared/attenuated total reflectance
FR	Flame retardant
HCl	Hydrogen chloride
HMPA	Hexamethylphosphoric triamide
I	Intensity of transmitted light by the specimen
I_o	Intensity of incidental light at a certain wavelength
IFR	Intumescent flame retardant
IR	Infrared

l	Distance of the light transmission through the sample
L	Length of material before failure
L_o	Initial length of material
LOI	Limiting oxygen index
MP	Melamine phosphate
MH	Magnesium hydroxide
NIR	Near infrared
NMR	Nuclear magnetic resonance
PBDE	Polybrominated diphenylether
PCB	Polychlorinated biphenyl
PCS	Polycarbosilane
PDMS	Poly(dimethylsilane)
PDMS(p)	Poly(dimethylsilane) in powder form
PER	Pentaerythritol
PET	Poly(ethylene terephthalate)
PMMA	Poly(methyl methacrylate)
PMSQ	Poly(methylsilsesquioxane)
PP	Polypropylene
PP-g-MA	Polypropylene-grafted-maleic anhydride
S	Cross-sectional area
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SiBCN	Silicon boron carbon nitride
SiC	Silicon carbide
SiCN	Silicon carbon nitride
T	Transmittance
TBAP	Tetrabutyl ammonium perchlorate
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane

TPA-1	Tris(3,6-dioxaheptyl)amine
TPP	Triphenylphosphate
UV-VIS	Ultraviolet-Visible
ZnB	Zinc borate
ε	Elongation at break
λ	Wavelength
σ	Tensile strength
ύ	Wavenumber

CHAPTER 1

INTRODUCTION

Polypropylene is a widely used thermoplastic polymer in various applications, such as piping, packaging, bags, house ware, membranes, medical devices, etc. It offers a combination of lightness, rigidity, toughness, heat resistance, chemical resistance, etc. Of late years, it has been gained recognition both in industrial and domestic products. Furthermore due to its fiber property, polypropylene is a major raw material of textile industry: used in carpets, curtains, beddings, etc. In other words polypropylene based products are a part of human beings' lives.

Due to the wholly aliphatic chemical structure of polypropylene it burns very rapidly and easily under ambient conditions. Fire caused by plastics is considered as a serious threat and a problem which should be solved. Here, flame retardancy is a scientific area which includes several approaches and mechanisms against the flammable materials.

The scientific studies on flame retardancy of polypropylene are focused on the usage of flame retardant additives. First, Blatz and coworkers published flame retardant additive formulations of polypropylene in 1964 [1]. They offered a combination with halogenated flame retardants in order to achieve a reasonable level for flame retardancy of polypropylene. Although the halogenated additives are known as the most effective flame retardants, they are considered to be harmful to environment, since they cause smoke and toxic gases during combustion such as HCl, HBr, etc. [2]. Recently, the flame retardancy researches and studies have mainly focused on halogen-free systems for this purpose. In polypropylene composites, the metal hydroxides, borates, phosphorous, nitrogen and silicon based flame retardants are mostly used as halogen-free additives. In industrial scale, mostly used flame retardant for polypropylene is the metal hydroxides because of having considerably lower costs and also being environmentally-friendly additives. However, metal hydroxides should be used at high loadings, such as 60% (w/w), in polypropylene composites, in order to obtain flame retardancy, also that decrease the mechanical properties of polypropylene [3]. Borates, phosphorous and nitrogen containing systems are also effective, when used together in certain formulations [3]. On the other hand, it has been shown that addition of small amount of silicon based flame retardants can significantly decrease flammability of various polymers [4]. The recent studies in flame retardant materials concentrate on the usage of Silicon (Si)-based materials like silicones, silicas, organosilanes, silsesquioxanes and silicates [3].

Poly(dimethylsilane) (PDMS), which belongs to the class of polysilanes, also organosilanes, is a linear preceramic polymer with silicon atoms in its backbone. Due to the presence of Si atoms in the chemical structure, it not only improves the flame retardant property of polypropylene but also provides good mechanical properties. Poly(dimethylsilane) has also been used widely for the synthesis of polycarbosilane (PCS), which is one of the most important ceramic material precursor for making silicon carbide [5].

Poly(dimethylsilane) is prepared from the dichlorodimethylsilane monomer through several polymerization methods. It has been first synthesized by Wurtz-type alkali metal coupling method [6]. However, the rigorous reaction conditions (due to the presence of highly reactive metals) and difficulties in controlling the molecular weight can be attributed as disadvantages. Furthermore, it is claimed that the yield of Wurtz-type reaction is generally low and large-scale synthesis is challenging because of involving very reactive alkali metals and high temperatures [7].

Other alternative methods of synthesis are transition-metal catalyzed polymerization of silanes (dehydrogenative coupling) [6], anionic polymerization of masked disilenes [8], ring-opening polymerization [9] and electroreduction of organosilanes [10]. Recently it has been shown that synthesizing polysilanes through electrochemical reduction of organohalosilanes provides reasonable reaction yields [10], mild reaction conditions and uniform molecular weight distribution [11].

The present study includes two main parts: electrochemical synthesis and characterization of poly(dimethylsilane), and preparation and characterization of polypropylene composites with poly(dimethylsilane) for flame retardancy purposes.

To the best of our knowledge, this is the first time that poly(dimethylsilane) has been synthesized by electro-reduction of dichlorodimethylsilane alone. The monomer, dichlorodimethylsilane, is put in an electrolytic cell which is equipped with copper electrodes, and constant potential energy (32 V) is applied in an inert atmosphere. After the polymerization, poly(dimethylsilane) is characterized by Fourier transform infrared (FTIR), Ultraviolet-visible (UV-VIS), Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopies and thermogravimetric analysis (TGA).

In the second part, polypropylene composites with poly(dimethylsilane) are prepared by using a twin-screw extruder. In order to test and compare the efficiency of PDMS additive in polypropylene another synthesized preceramic polymer, poly(methylsilsesquioxane), is also used. Beside Si-based additives, various commercial flame retardants, such as magnesium hydroxide, boron phosphate, melamine phosphate, pentaerythritol are used with preceramic polymers in polypropylene in order to achieve a contribution. Furthermore, the total amount of additives in polypropylene composites does not exceed 20% by weight, since it is also aimed to preserve the mechanical properties of polypropylene. The flammability, thermal and mechanical properties and morphologies of composites are characterized as well.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Preceramic Polymers

Preceramic polymer is determined as an oligomer or polymer that converts into ceramic by heating above its decomposition temperature [12]. Mostly, they are used as precursors in silicon carbide (SiC) production. Since ceramics are thermally resistive materials and preceramics are converted by heating to ceramics, they are also used as flame retardant additives by improving the thermal stability of base polymer.

By using preceramic polymers, there occur new opportunities for producing ceramics. Beside SiC, the other ceramics are produced with preceramic polymers such as silicon carbon nitride (SiCN), silicon boron carbon nitride (SiBCN), etc. [13]. The preceramics, have gained a great attention by researchers, which are used in several industries such as automobile, astronomy, electronics, etc. [5]. Polysiloxanes, polysilazanes, polysilanes, metallopolysiloxanes and metallopolysilanes are known as preceramic polymers [14]. In the next section, polysilanes are described.

2.1.1 Polysilanes

The materials which have silicon atoms in their molecular structure have attracted great attention, since they can be used as precursors for ceramics [15, 16], or as materials for microlithography [17-19]. Also due to the unique chemical structure of polysilanes, there are opportunities to produce conducting, photo-conducting, or nonlinear optical new materials [20].

Polysilanes have silicon atoms in their backbone. Their general formula is $(RSi)_n$ and R may be an alkyl, aryl, alkaryl or aralkyl group and n should be at least 8. If the value of “R” in a polysilane is stearically hindered or large group, it is soluble in a liquid organic medium [21].

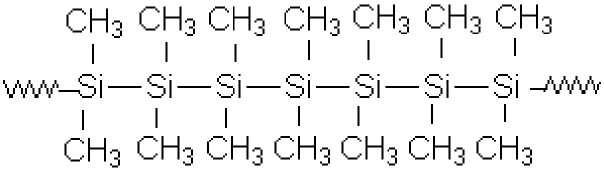
Lots of studies have been done by several researchers on the synthesis of polysilanes [6]. There are also many studies of their characterization and thermal behaviors [5, 10, 20, 22-24]. The polysilanes have a large usage for the synthesis of polycarbosilane (PCS) which is a ceramic material and used for preparing ceramic Si-C fibers, composites, whiskers, etc. [5].

Polysilanes have α-conjugated electrons, which provide unique properties rather than π-conjugated conductive polymers. For instance, even the polysilanes have saturated bones; so they can have optical and electrical activities [25-27]. This special electronic property implements photoreactivity and photoconductivity [25].

There are various types of polysilanes in literature such as linear permethylated polysilanes, cyclic permethylated polysilanes, branched polysilanes, cyclic permethylated polysilanes, branched polysilanes and cage permethyl polysilanes [7]. Some kinds of polysilanes with substituents of phenyl and isobutyl groups and also polysilanes having a mixture of methyl and other substituents, for example hydrogen, halogen or phenyl substituents are also known. The sizes of polysilanes vary. For example, linear polysilanes have generally less than 10 silicon atoms in the chain, whereas cyclic and polycyclic polysilanes have often more than 10 silicon atoms [21].

2.1.2 Poly(dimethylsilane)

Poly(dimethylsilane) (PDMS) is the simplest member of polysilanes and it is convenient to investigate the basic properties of polysilanes. PDMS is the first polymer in dialkyl substituted Si backbone polymer class. The chemical formula of poly(dimethylsilane) is $[-Si(CH_3)_2-]_n$ as given in Figure 2.1 [28]. Poly(dimethylsilane), also known as dimethylpolysilane, has a linear structure and it is white solid powder at ambient temperature.



$$\sim\!\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}\!\sim$$

Figure 2.1 Chemical structure of poly(dimethylsilane)

It shows all-trans rigid conformation at room temperature. Furthermore it has crystal and electronic structures [29].

Poly(dimethylsilane) is mainly used to synthesize polycarbosilane (PCS) which is precursor of SiC, like most polysilanes [30-33]. PDMS is also well-known with the σ-conjugation in their backbone which leads to some very interesting electronic properties [6]. As well as they are used as precursor of PCS, they also find application areas in light emitting diodes, opto-electronic devices, flat-screens, full color displays, color-based chemical sensors, etc. [10].

2.1.3 Electrochemical synthesis of poly(dimethylsilane)

Poly(dimethylsilane) (PDMS) has been first synthesized by Wurtz-type alkali metal coupling method from the monomer of dichlorodimethylsilane. Wurtz-type reaction has some disadvantages, such as difficulties in controlling the molecular weight or intensive reaction conditions because of alkali metals. Furthermore, in general the yield of Wurtz-type reaction is low and large-scale synthesis is challenging because of involving very reactive alkali metals and high temperatures [11]. The researches have been focused on the alternative methods for this synthesis. For instance, sonochemical coupling of dichlorosilane promoted by alkali metal [34] is a good alternative synthesis, under milder conditions. Other alternative methods are the transition metal catalyzed reaction of hydrosilane [35], the anionic polymerization of masked disilenes [36], and ring-opening polymerization [37]. Recently, electrochemical reaction gains attention as an alternative method for synthesizing polysilanes. This method bases on the reduction of organosilanes electrochemically. Furthermore it provides reasonable reaction efficiency [10], monomodal molecular weight distribution and moderate reaction conditions [11].

Elangovan et al. [10] have electrochemically synthesized poly(dimethylsilane) (Figure 2.2) from the dichlorodimethylsilane monomer in a single compartment cell with aluminum electrodes. They have used tetrabutylammonium tetrafluoroborate as supporting electrolyte, and 1,2 dimethoxyethane as solvent. In another study of Bordeau et al. [22], aluminum electrodes have been used. They have not introduced any solvent into the system and have produced PDMS from the same monomer which consists of a small amount of so-called complexing agent, hexamethylphosphoric triamide (HMPA) or tris(3,6-dioxaheptyl)amine (TPA-1) [22]. In literature several sacrificial electrodes have been used such as mercury, aluminum, magnesium, silver, copper, hydrogen electrodes, etc. [23, 38, 39].

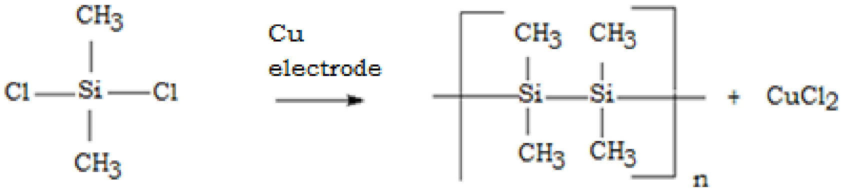


Figure 2.2 Electrochemical synthesis of poly(dimethylsilane) [34]

Since polysilanes are used as precursors of silicon carbide materials and have excellent thermochromic and photoresist properties [40], the researchers have focused on the alternatives for synthesis with alkali metals. The electrochemical polymerizations of polysilanes, which can be described as a good alternative to alkali metal reduction, have been discovered in 1976 [41, 42]. In electrochemical polymerization of polysilanes, various type of electrodes have been used such as aluminum, magnesium, mercury, or copper. Jammegg et al. [23] have used for sacrificial anode, a silicon carbide rod and a modified hydrogen anode. By using these anodes, they have observed chlorinated organic products and formation of HCl gas, as a result of electrochemical reduction of silane monomer according to the reaction given below in Figure 2.3:

$$R_3SiCl + H_2 \xrightarrow{\text{2 faradays}} R_3SiSiR_3 + 2HCl$$

Figure 2.3 Electroreduction of silane monomer

Hengge and Litscher [41] have done the first electrochemical synthesis by using an divided electrolytic cell and mercury anodes. The solvent was, 1,2 dimethoxyethane (DME) and the electrolyte was tetra butyl ammonium perchlorate (Bu_4NClO_4). They synthesized hexamethyldisilane from the trimethylchlorosilane monomer as given in Figure 2.4:

cathode: $2Me_3SiCl + 2e^- \rightarrow Me_3Si\text{-}SiMe_3 + 2Cl^-$
anode: $2\,Cl^- + 2Hg \rightarrow Hg_2Cl_2 + 2e^-$

Figure 2.4 Reactions on the cathode and anode

Several researchers also examined several types of chlorosilane monomers. Bordeau et al. [22] carried out the electrolysis in a simple, undivided cell. They used stainless steel cathode and an aluminum or magnesium anode.

Jammegg et al. [23] synthesized also polysilanes by electrochemical reaction. They used an undivided cell in which there was a mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA)-or HMPA alone-as the solvent and tetraethylammonium tetrafluoroborate (Et_4NBF_4) as the supporting electrolyte with a concentration of 0.02 mol/l. They have obtained poly(dimethylsilane) (PDMS) through the electro-reduction of dichlorodimethylsilane with a ratio of monomer to solvent as 5 mol/l. They also found out that, when the ratio of monomer to solvent is 0.5-0.8 mol/l, decamethylcyclopentasilane and/or dodecamethylcyclohexasilane are produced instead of PDMS. However in the synthesis of octaphenylcyclotetrasilane, the polymer was formed only in negligible amounts. Also the monomer/solvent ratio did not have any effect on this reaction.

In electrolysis of polysilanes, several solvent/electrolyte systems, such as dimethoxyethane/tetrabutylammonium tetrafluoroborate (DME/Bu_4NBF_4) and tetrahydrofuran/lithium perchlorate ($THF/LiClO_4$) and the anode materials made from Cu, Ag, or Pt, were used. For instance, Nonaka et al. [43] carried out the synthesis of poly(dimethylsilane) in a divided cell with Pt electrodes (both cathode and anode). They made electrochemical reduction of dimethyldichlorosilane monomer with the addition of trimethylsilylchloride or triphenylsilyl chloride. They used DME/Bu_4NBF_4 as solvent/electrolyte system. When Nonaka et al. [43] used aluminum electrodes instead of Pt electrodes in an undivided cell, they synthesized poly(dimethylsilane) at high efficiency without addition of monochlorosilanes. In addition to dichlorodimethylsilane, the monomers: dichloro(methyl)phenylsilane ($MePhSiCl_2$), diphenyldichlorosilane (Ph_2SiCl_2) and mixtures of various mono- and dichlorosilanes led to the formation of oligo- and polysilanes, depending on the silane concentration and the electrode/solvent/electrolyte system [23].

2.1.4 Experimental techniques for the characterization of poly(dimethylsilane)

Several characterization methods, such as Fourier Transform Infrared (FTIR), Ultraviolet-visible (UV-VIS), Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopies are used to investigate the formation of poly(dimethylsilane) in literature [10, 23]. The methodology and theories of these tests are explained in the following section.

2.1.4.1 Fourier transform infrared spectroscopy, FT-IR

Infrared (IR) electromagnetic radiation takes part of the electromagnetic spectrum (Figure 2.5) having wavenumbers from 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. It is between the red end of visible region and the beginning of the microwave region [44].

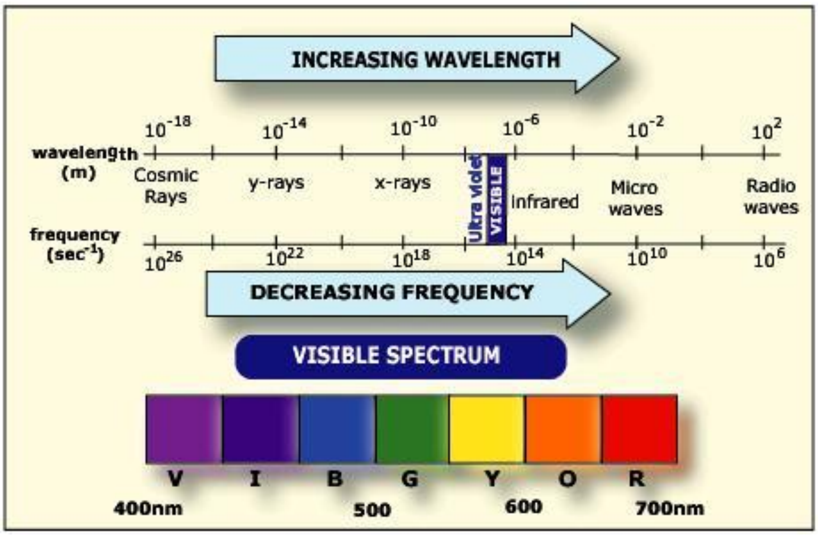


Figure 2.5 Electromagnetic spectrum [45]

The term wavenumber ($\dot{\upsilon}$) or wavelength (λ) is used in the spectrum to identify radiation absorption points. Wavenumber is the number of waves per unit length. Thus, wavenumbers are proportional to frequency, as well as the energy of the IR absorption, whereas the wavelengths are inversely proportional to frequencies and their associated energy. The relation between wavenumber $\dot{\upsilon}$ (cm^{-1}) and wavelength λ (μm) can be seen in the following equation (2.1):

$$\dot{\upsilon}(cm^{-1})=\frac{1}{\lambda(\mu m)}x10^{4} \qquad (2.1)$$

The IR absorption spectrum is shown in a graphical form, which has wavelength or wavenumber in the x-axis and absorption intensity or percent transmittance in the y-axis.

Another term used to describe IR absorption is the transmittance, T. Transmittance is the radiant power transmitted by the specimen (I) per unit the radiant power incident on the specimen (I_0). Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T) (2.2) [44].

$$A = \log_{10}\left(\frac{1}{T}\right) = -\log_{10} T = -\log_{10}\left(\frac{I}{I_0}\right) \tag{2.2}$$

In the infrared spectrum, there are three parts: the near-, mid- and far- infrared, which is stated according to the distance to visible region. The near-IR is at approximately 14000–4000 cm^{-1}, the mid-infrared is approximately 4000–400 cm^{-1} and the far-infrared, approximately 400–10 cm^{-1} by wavelengths [46].

The principle of the infrared spectrum depends on the absorption of the IR light beams by the sample. The light is transmitted through the sample and it shows the absorbed energy by specimen at certain wavelengths. The absorption occurs, when the IR light frequency is equal to the vibration frequency of a chemical bond (Figure 2.6), which gives information about molecular structure of material [46].

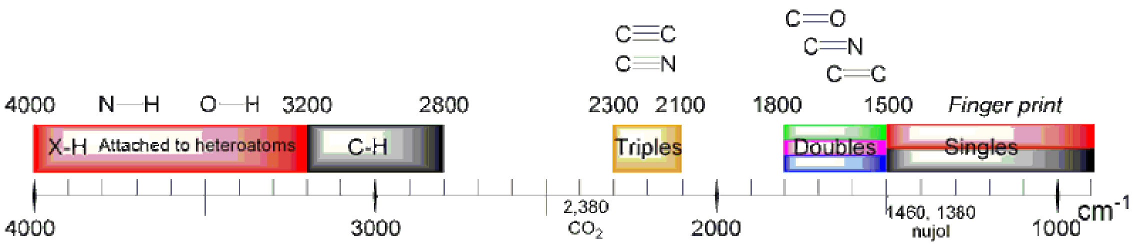


Figure 2.6 The main chemical bond vibrations in the IR region of electromagnetic spectrum

The samples in all phases can be analyzed by different sample preparation techniques. For gaseous samples, the sample glass tubes are used. For liquid samples, the plates from salts, such as potassium bromide or calcium fluoride, in order to state the liquid sample between two salt plates. These salts do not absorb the infrared light. For materials in powder form the same method is also useful. The powder sample is mixed with a certain amount of salt and pressed with high pressure to obtain a pellet formed sample. The solid samples, especially polymers, can be cut as a film by using a microtome. The solid samples are also crushed with an oily mulling agent with a pestle. Additionally, air is mostly used as reference material in order to compare the IR spectrum of material [46].

In the instrument of Fourier transform infrared (FT-IR) spectroscopic analysis; there is a IR light source which sends IR light through the sample. In order to focus the IR light which is passing through the specimen, a moving mirror exists in the instrument. Due to the position of mirror and light output, the signals are saved. This data-processing technique is called as Fourier transform which represents the spectra of sample [46].

2.1.4.2 UV-Visible spectroscopy, UV-VIS

The absorption or reflectance of ultraviolet-visible light by materials is measured by ultraviolet-visible spectrometry (UV-VIS). The light is in the visible and adjacent (near-UV and near-infrared (NIR)) ranges [47].

The UV-VIS spectroscopy obeys the Beer-Lambert law given below (Equation 2.3). A, I_0, I, l and c indicate absorbance, the intensity of the incidental light at a certain wavelength, transmitted intensity, the distance of the light transmission through the sample and the concentration of the particles of sample, which absorb the UV-Vis light, respectively. Also, e is the molar absorbance or extinction coefficient, which is specific to materials.

$$A=\log_{10}(I_o/I)=e.c.l \tag{2.3}$$

With the reference of given formula of Beer-Lambert law, the solution concentration of the specimen is proportional to absorbance [47].

The UV/Vis spectrophotometer measures the intensities of lights which come to the sample (I_o) and pass through the sample (I). The relation between the ratio (I/I_o) also called as the transmittance and absorbance coming out from Beer-Lambert Law as follows (2.4):

$$A=\log_{10}\left(\frac{100}{\%T}\right) \tag{2.4}$$

By plotting the UV absorbance intensity to UV light wavelength, the information about the molecular structure can be determined [47]. The components of UV-VIS Spectrophotometer are the light source, the cells for samples, monochromator and detector.

2.1.4.3 Nuclear magnetic resonance spectroscopy, NMR

Nuclear magnetic resonance spectroscopy, NMR, is spectroscopic method, which defines the molecular structure based on the magnetic of definite nuclei. This method is relevant for spinning nucleus. When NMR is compared to infrared spectroscopy, NMR renders more information such as the number and type of chemical species which material contains.

Liquid and solid materials can be characterized by nuclear magnetic resonance spectroscopy (NMR). Nuclei, like ^{13}C or ^{1}H are determined as NMR active. They absorb at a frequency characteristic of the isotope in a magnetic field. Absorption energy, frequency of resonant and signal intensity is affected by magnetic field strength proportionally [48].

The protons in a molecule resonate at slightly dissimilar frequencies. The definition “chemical shift” is dimensionless and depends on the frequency shift and fundamental resonant frequency and it is measured with some reference resonance frequency. Chemical shift is a function of the nucleus and its environment. For the nuclei ^{1}H, ^{13}C, and ^{29}Si, tetramethylsilane (TMS) is commonly used as a reference [48].

Solid-state nuclear magnetic spectroscopy is a type of NMR, in which the solid samples are characterized by the presence of anisotropic (directionally dependent) interactions [48].

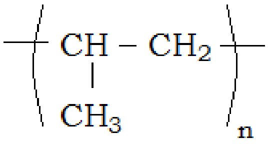
2.2 Polypropylene

Polypropylene (PP) is thermoplastic polymer which belongs to the family of polyolefins. PP is mostly very durable to chemicals, however is affected by strong acids, dry chlorine and bromine gas. It also swells, in presence of some organic solvents, such as benzene, toluene and mineral oils [49]. The ignition of polypropylene does not cause any smoke during burning. It burns rather like a candle and dripping occurs as well. The combustion product is not toxic.

Polypropylene is one of the most preferred thermoplastics because of its lightness, rigidity, toughness, heat resistance and chemical resistance. It has a wide usage area in different industries, such as textiles, packaging films, medical fibers, membranes, buildings, containers, coatings, etc.

Due to the usage area of polypropylene, it is also possible to find different type of polypropylene as commercial. The different molecular weights and molecular configurations give unique choices for production [49].

Polypropylene (PP) (Figure 2.7) was invented in the mid 1950's by Guillio NATTA's group in Italy through the polymerization of propylene (C_3H_6) in the presence of a catalyst mixture consisting of titanium tetra chloride ($TiCl_4$) and triethyl aluminum ($AlEt_3$) (developed by Karl Ziegler) [49].

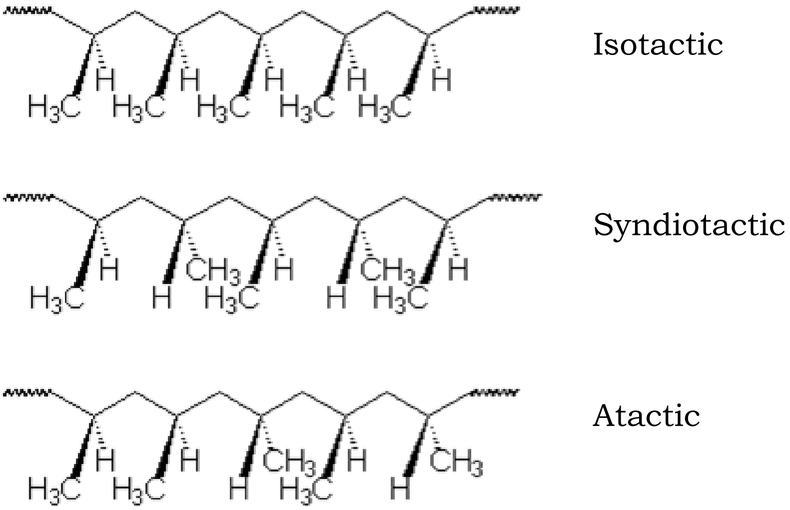


$$\left(\underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2\right)_n$$

Figure 2.7 Molecular structure of polypropylene

The growth in production and in usage of polypropylene (PP) increased during the latter half of the 20th century. From the early 1960s the growth rate was nearly 25% and during the period from about 1974 through 1999, the rate of consumption increased between 7% and 12% annually. Since the demand and consumption of polypropylene is growing, the production is rising as well [50]. Also, with the novel developments in polypropylene composites, new usage areas of polypropylene arise gradually.

Polypropylene shows stereochemical isomerism which is called tacticity. There are isotactic, syndiotactic and atactic polypropylenes due to spatial configuration of methyl groups bonded to carbon atoms in the backbone. When the methyl groups place on one side of chain and hydrogen atoms place on the other side, it is an “isotactic” polypropylene as seen in Figure 2.8. For a syndiotactic polypropylene, the methyl groups should be arranged opposite to each other. The random arrangement of methyl groups in polypropylene is referred to atactic polypropylene [51] (Figure 2.8).


Isotactic

Syndiotactic

Atactic

Figure 2.8 Tacticity of polypropylene [51]

Due to the tacticity degree of polypropylene, its physical properties vary as well. The industrial usage of polypropylene is mainly based on isotactic polypropylene, since it has high tacticity. The isotactic polypropylene is in solid phase and suitable for plastic processing techniques. However, atactic polypropylene is sticky and soft. Therefore atactic polypropylene is mainly used for applications in need of stickiness. On the other hand syndiotactic PP does not have a large volume of production [52].

2.3 Combustion of Polymers

Since polymers contain carbon and hydrogen in their chemical structure, they are considerably flammable [3].

Pearce and Liepins [53] determined the combustion mechanism as given in Figure 2.9. They pointed out that combustion of polymers is composed of four following steps: 1) preheating of polymer, 2) decomposition of polymer 3) ignition of polymer, and 4) combustion and flame propagation [50].

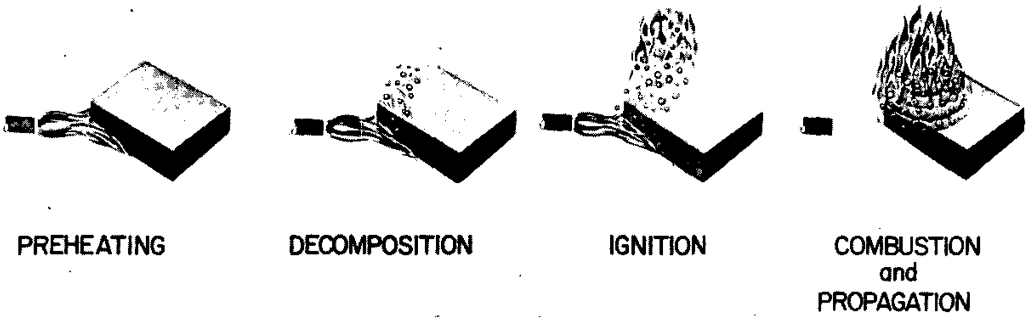


Figure 2.9 Process of polymer combustion [53]

The moment that the polymer faces with a heating source can be determined as preheating. Preheating step lasts till the material absorbs enough heat energy to decompose. It depends on thermal properties like the heat capacity, thermal conductivity, latent heat of fusion of material, i.e. polymer [53].

After the sufficient heat is absorbed by polymer it starts to decompose. First, the weak bonds break and the combustion products, which are gaseous and flammable, are released to environment.

These gases ignite in presence of the ignition source, if the concentration of oxygen and flammable gases are sufficient to initiate burning. The ignition of material provides the heat for combustion and propagation of flames during decomposition [53].

This process proceeds as long as any of the ingredients of fire triangle exists: fuel, heat or oxygen. Combustion maintains with presence of free radicals which are generated during fire in gas phase. As long as the material and enough heat energy are together, the combustion proceeds till an explosion. If the energy for fire is constant, there will be a “stationary flame”. In case of lower energy than required energy, the combustion rate decreases and after a while the flame extinguishes [54].

Since fire starts with thermal decomposition of material, it is also crucial to know the decomposition process of polypropylene (PP). The tertiary carbons in the backbone of polypropylene make it weaker and open to chemical attacks. During decomposition of polypropylene, chain reactions such as scission and transfer are crucial. The primary radicals occur at the tertiary carbon site, whereas secondary radicals at the secondary carbons. Also, the secondary radicals are more crucial than primary radicals, since they lead to the formation of side products during combustion such as pentane, 2-methyl pentene, etc. and thus contribute strongly to the decomposition of polypropylene [54].

During heating of PP, first the first weight loss can be observed around 220°C. Also oxygen affects the mechanism and rate of decomposition process. Polypropylene is also more resistive against oxidative pyrolysis below its melting temperature, since it has higher crystallinity and density than its melt has [55]. Although many researchers support the idea that the oxidation mechanism occurs during decomposition bases on hydrocarbon oxidation, Gijsman et al. [56] explain the fact differently. They claim that it is possible to happen because of decomposition of peroxy acids, which form from oxidation of primary decomposition products.

2.4 Flame Retardancy Mechanisms in Polymers

Flame retardancy has a great importance for protection from fire incidents and saving lives [57]. Since in today's world, there are lots of polymeric materials synthetic or natural, the fire risk should not be ignored.

The flame retardancy can be provided by following several mechanisms with flame retardant (FR) additives such as mineral FRs, halogenated FRs, phosphorous, silicon or nitrogen based FRs or nanoparticles.

Flame retardants take action as interfering with combustion process at any of these stages: during heating, decomposition, ignition, or flame spread. They act physically or chemically in solid, liquid or gas phase [57].

Physical action mainly depends on cooling the system by heat consumption. Some flame retardants like aluminum hydroxide or magnesium hydroxide decompose endothermically and release their water vapor at 200-300 ˚C. Also this action decreases the temperature of the system [3].

Another physical action is diluting the combustible gases in the gas phase. This kind of flame retardation can be obtained with inert gases like H_2O, CO_2, NH_3, etc. which also decrease the volumetric ratio oxygen needed for combustion of flammable gases [3]. For dilution action, the aluminum hydroxide ($Al(OH)_3$) is a good flame retardant. By heat, it converts to water vapor and aluminum trioxide (Al_2O_3). While water vapor dilutes the free radicals, the Al_2O_3 acts as productive layer [58].

Furthermore, physical flame retardancy system depends on the productive layer or barrier occurs during combustion. This barrier may be gaseous or in a solid for which insulates the “fuel”, i.e. polymer, from heat source [3]. This solid form is usually a char layer which separates the oxygen and fuel from each other. The gaseous barrier acts in a similar manner as well.

Chemical action mostly acts in gaseous phase as stopping the free radicals like H and OH by means of the interaction between these radicals and specific radicals (e.g. Cl, Br, P_2, PO_2 etc.) which are generated by flame retardant additives [3]. Obviously, it limits the propagation of flame which described in “combustion of polymers” section.

Furthermore, flame retardants may react with free radicals so that they decrease the concentration of free radicals. Thus, releasing of heat decreases and the system cools down. On the other hand this process can result in releasing toxic gases by halogenated flame retardants and releasing of CO gas due to partial combustion of polymer [58].

The flame retardancy can also occur in solid phase. The addition of some flame retardants into base polymers may decrease the inherent melting temperature of base polymer or may change its melt viscosity. Such additives may cause dripping during combustion of polymer. The disadvantage of this kind of burning is that the dripping may trigger the growth of flame because of the spread of flammable drops. Other type of solid phase flame retardancy is the char forming. The carbonaceous layer acts like an insulating barrier. It prevents the smoke formation and other gaseous products to environment. Mechanism of intumescent flame retardancy is similar. However, in this system there are blowing agents as well. They provide a thick barrier which yield better insulation (See also section 2.4.1.2 intumescent flame retardants) [58].

2.4.1 Additives for flame retardancy

Flame retardancy principle bases on lowering the heat release during combustion of polymer with several mechanisms and on providing a resistivity against ignition or propagation of flame by flame retardant additives. The principle is forming of a productive layer or diluting the radicals in system. Also some flame retardants behave as a heat sink due to their decomposition at low temperatures [53].

There are both inorganic and organic flame retardants. Antimony trioxide, zinc borate and magnesium hydroxide are some examples of inorganic flame retardants. Also phosphate esters and halogenated additives are some of the organic flame retardants. The halogens like chlorine and bromine are in many flame retardant additives. Also most commercial ones include elements such as phosphorus, nitrogen, silicon, antimony, aluminum, magnesium, etc. [59]. The classification of flame retardant additives is given in Figure 2.10. In general, it is possible to classify the flame retardants into six groups: Mineral, halogen, phosphorus, nitrogen, silicon containing flame retardants and nano-particles. Also, another classification can be made due to their type of flame retardant actions as mentioned in the previous section. In the selection of flame retardancy, the base polymer is very significant. Also, the environmental concerns should not be forgotten. As it is emphasized in previous sections, some flame retardants, especially halogen included ones, may cause releasing of toxic gases. However, there is not yet any international restriction for prohibition of their usage; some countries have already banned their usage, nationally. For instance polychlorinated biphenyls (PCBs) were banned in 1977 and polybrominated diphenyl ethers (PBDEs) were banned in 2008 by European Countries [60].

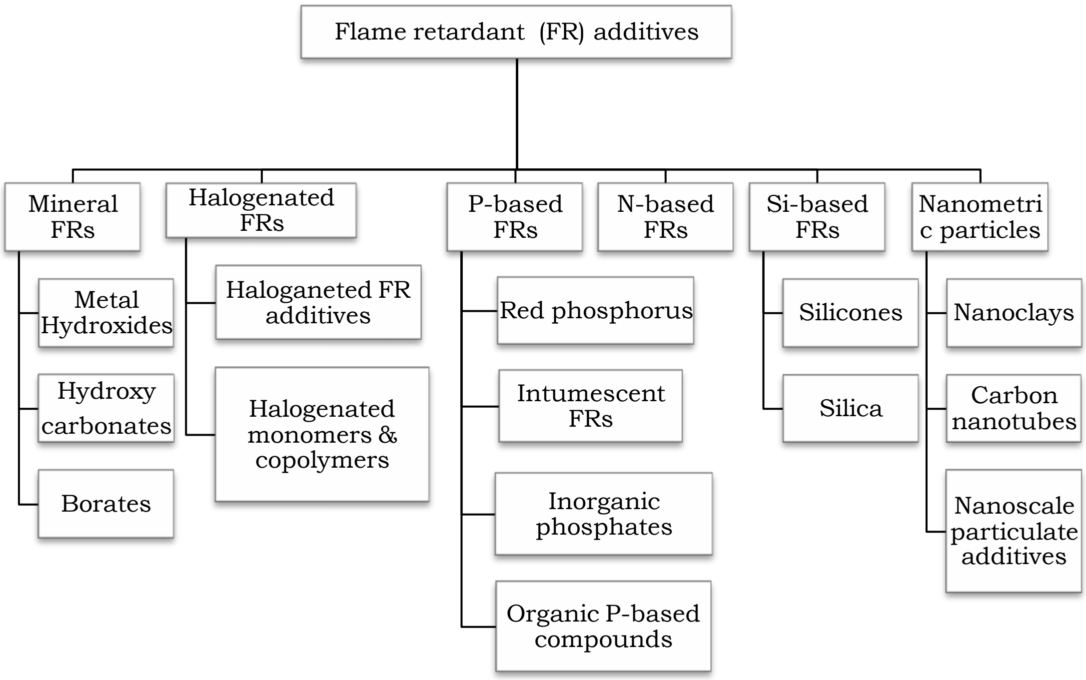


Figure 2.10 Classification of flame retardant additives [3]

The flame retardant additives can be introduced into base polymer either reacting the flame retardant monomer with the monomer/monomers of polymer or adding flame retardant additive into the polymeric melt or solution. In the first kind of flame retardancy, the flame retardant copolymers are produced and thus the base polymer becomes inherently flame retardant. This method provides less effect on the physical properties of polymer. Some kinds of reactive flame retardants are tetrabromobisphenol A, dibromoneopentyl glycol, vinyl chloride, and bromo- or dibromostyrene. The chemicals listed in Figure 2.10 are additive type flame retardants. They are usually introduced to polymer by melt mixing [59].

The halogen based flame retardants possessed a large market share among the flame retardants in 1997 as 49%. However because of environmental concerns, the amount of non-halogenated flame retardants has been increasing. Among non-halogenated flame retardants the most volume of consumption belongs to aluminum hydroxide (ATH) and magnesium hydroxide (MH) since they release water vapor only during burning. The advantage of magnesium hydroxide is that it has higher decomposition temperature than aluminum hydroxide. This property limits the usage of aluminum hydroxide especially for polymers which are processed at the temperatures close to decomposition temperature of ATH. For effective flame retardancy, ATH and MH should be introduced at high amount of loadings such as 60-65%. High loading obviously causes a decrease of physical properties, such as tensile and impact strength of base polymer [61].

2.4.1.1 Preceramic polymers for flame retardancy

2.4.1.1.1 Synergists with usage of preceramic polymers for flame retardancy

The preceramic polymers are inorganic polymers which become ceramics under heat. They are used as flame retardants because they convert to ceramic char while burning. This char is also very stable and prevents the propagation of flame. Ariagno et al. [62] invented a formulation of a heat-vulcanisable silicone elastomer, which can be used in electrical wires, cables. When it is used as flame retardant, during combustion it converts into a mechanically strength layer, which acts as flame retardant layer. Ariagno et al. have prepared a polydiorganosiloxane polymer composite which includes mica and ZnO. They also discovered the synergistic effect of mica and ZnO with silicone elastomers, according to a good elongation at break value (180%) and better ceramized residue [62, 63].

Phosphorus-containing flame retardants are one of the most preferred compounds since they are not only effective and have synergistic contribution but also they are environmentally friendly materials. Because of the weak bonds of phosphorates, these compounds decompose at lower temperatures than that of base polymers. Phosphorous based flame retardants produce a char layer upon the polymer, so they keep away the unburned sides of polymer from flame so that the polymer is protected from the oxygen attack and heat [64-67].

The nitrogen based flame retardants show synergistic effect with phosphorous-containing compounds. During combustion nitrogen-based flame retardants do not cause releasing toxic gases and they also produce inflammable gases. They are environmentally friendly additives and work with the principle of diluting combustible gases. Also the gaseous products act as blowing agents and the char layer swells, which provide a thicker layer and better insulation [68, 69].

Silicon-based flame retardants are also considered environmentally friendly, since they do not produce harmful gases to environment while burning. Another unique property is that during combustion they concentrate onto surface of polymer, since they have lower surface energy. During combustion, silicon containing flame retardants produce silica carbon, which is thermally stable and protects the material from further decomposition [70-72].

To sum up the phosphorous, nitrogen and silicon containing flame retardants are environmentally friendly additives, because they do not produce harmful gaseous products during fire. However the halogenated compounds cause harmful products such as HCl. On the other hand the environmentally friendly additives are not as much effective as halogenated additives. For this reason the synergism is important. They are usually added to polymers together due to several combinations and formulas. An effective combination is phosphorus (P), nitrogen (N) and silicon (Si) elements together for flame retardancy purpose. Each element has a different function. Phosphorus element contributes the char forming, nitrogen helps the swelling of char and silicon favors a thermally stable char [73-75].

Li et al. [76] synthesized a flame retardant compound including P-Si-N in order to investigate its effects on flame retardancy and char yield for polypropylene. They aimed to explore the effects of this flame retardant on the LOI and char yield values of polypropylene and also showed that effective flame retardancy can be achieved with environmentally friendly additives, in case of they were used together and at least two of them were introduced into the composites. They added this flame retardant at different weight percentages into polypropylene. They kept the PP concentration constant at 70% (w/w), and flame retardants containing P, N, Si at 10-30 % (w/w). The authors observed that the LOI value of PP increased from 17% to 26%, with the addition of the compound containing 20% phosphorus, 10% silicon and 10% nitrogen. Also, they characterized the composites by using TGA for char yield properties, and they found out 27 % increase in char yield at 800 °C [76].

Another multi-element formulation is represented by Istomin et al. [77]. They used a system containing phosphorus, nitrogen and halogen in order to achieve flame retardancy for polyethylene and polypropylene. They prepared the composites by melt mixing method.

Finally, they obtained LOI values of 27.1%-27.5%, so the polymer composites can be described as low-combustible [78].

Antimony trioxide (Sb_2O_3) has the largest market share among synergistic compounds. However, it is usually used with halogenated flame retardants. Antimony trioxide may react with the products which are produced by halogenated additives such as HCl and HBr. The reactions with these acids lead to formation of more Sb radicals. The reactions and synergistic mechanism are shown in Figure 2.11 [3, 79]. After the formation of SbCl products, the radicals occur in the reaction media. Sb radicals react with OH and H radicals, which lead to propagation of fire. Also SbOH radicals catch H radicals and dilute their concentration in gas phase [3].

$$SbCl_3 + H^{\cdot} \rightarrow HCl + SbCl_2^{\cdot}$$

$$SbCl + H^{\cdot} \rightarrow HCl + SbCl^{\cdot}$$

$$SbCl + H^{\cdot} \rightarrow HCl + Sb^{\cdot}$$

$$Sb^{\cdot} + OH^{\cdot} \rightarrow SbOH$$

$$SbOH^{\cdot} + H^{\cdot} \rightarrow SbO^{\cdot} + H_2$$

$$SbO^{\cdot} + H^{\cdot} \rightarrow SbOH$$

Figure 2.11 The reactions of antimony trioxide with HCl [3]

In the study of Eroglu et al. [80], the poly(methylsilyne) (PMSy) was used as flame retardant for polypropylene. PMSy is also a preceramic polymer with a network structure. They added 5% (w/w) PMSy into polypropylene, with synergists of 7.5% (w/w) triphenyl phosphate

(TPP) and 7.5% (w/w) metal oxides mixture. The LOI value of this composite was measured as 22.5% and LOI of neat polypropylene was determined as 17.5% [80].

2.4.1.2 Intumescent flame retardants

Intumescent flame retardants (IFRs) have gained great attention of scientific researches in last years [2-4, 54, 57, 63, 67]. This type of flame retardancy is a system which has at least two components: char forming and blowing agent. When the material is ignited, first, it swells and generates a pyrolysis product, which acts as a protective layer [81].

Intumescent flame retardants have several advantages: They are usually halogen free materials, release low smoke and no corrosive or toxic gases during burning. IFRs are usually used for flame retardancy of thermoplastics like polypropylene [82].

In a typical intumescent system formulation, there are a char forming agent, a catalyst for char formation and a blowing or foaming agent. Some IFRs contain all components together in their own formula, so that there is no need for other additives. For instance, melamine phosphates can form char, generates foam and act as a char forming catalyst at the same time [81].

For intumescent flame retardants the volume of char is very important for efficient flame retardancy. The more char amount is obtained, the more thermally stable polymeric composite is provided. In intumescent systems, additives including phosphorus and nitrogen are used for char forming. However it has been found that, when the char includes only these elements, the material looses weight at about 700°C in air, which means a reduction of thermal stability of char. Consequently, silicon based compounds may contribute as synergist in order to support thermal stability. Eventually, there is a synergism between IFRs and silicon-based compounds on flame retardancy of polymers [83].

The most preferred intumescent flame retardant systems are the systems which contain melamine derivatives. Melamine can be used for polyurethane foams; melamine cyanurate used for nylons; melamine phosphates, ammonium polyphosphate/pentaerythritol (PER) used for polyolefins [54]. Also melamine phosphates can be used with pentaerythritol for flame retardancy.

Most commonly used formulation in intumescent flame retardant system for polypropylene is pentaerythritol and ammonium polyphosphate (APP). Thus, APP acts as acid source and blowing agent; whereas PER acts as a carbonizing agent. Dogan et al. [84] used boron based synergists with IFRs: Zinc borate (ZnB), boron phosphate (BP) and silicon containing preceramic oligomer (BSi) in polypropylene. The ratio of APP:PER was 3:1 as this ratio provided the best flame retardancy for APP, PER systems. The authors have found out that the highest LOI for PP was 30% in the PP composite which consisted of 80% (w/w) PP, 19% IFR and 1% boron phosphate. They also measured the LOI value of neat polypropylene as 17.5%.

2.4.1.3 Other types of flame retardant additives

Nanotechnology submits useful tools for flame retardancy as well. There are flame retardant nanoparticles which can also provide very effective contribution in polymers mechanically and thermally. However, these nanoparticles should be distributed in polymer matrix very thoroughly which is very important since a random distribution may cause difficulties in polymer processing and uniform properties. The effects of nanoparticles for flame retardancy differ due to their geometric and chemical structure [3].

There are several kinds of nanoparticles used for flame retardancy. For instance nanoclays, carbon nanotubes, polyhedral oligosilsesquioxane (POSS) are some typical nanometric flame retardants [3]. In polymer composites the additives may decrease physical properties of materials especially because of their usage at high amounts. The advantage of nanoparticles is that obviously a small amount of additive can fulfill the required flame retardancy which can be achieved at high loadings of regular flame retardants. In particular, that is very crucial for polymeric fibers because their fiber property may easily be disturbed by additives.

Nanoclays provide protection of material during fire. Besides, there is no need for high amounts of nanoclays because of their nanometric size. Even 1% (w/w) addition of nanoclays can exhibit good flame retardancy in polymers [85]. The mechanism of nanoclays in a polymer depends on melting of polymer under flame. Under heat, the viscosity of polymer decreases and allows to the movement of additives. At this time, the nanoclays accumulate on the surface. The nanoclays protects polymer and provides thermal stabilization. Additionally, in organomodified nanoclays case, when the modifier is exposed to heat, there occur some catalytic sides on the surface of nanoclays due to its thermal decomposition. Because of this catalytic effect, the production of char increases as well [86, 87]. The thermally stable char provides not only protective layer against heat and oxygen attacks, but also keeping volatile materials on the surface.

Carbon nanotubes present considerable functions for development of polymer properties. They can be used in flame retardancy as well. As it is acceptable for most type of nanoparticles, carbon nanotubes implement good flame retardancy in low amount. In some studies, it has been denoted that they can be used for flame retardancy purposes in polymers such as polypropylene, polyethylene, polyamide, polystyrene, etc. at loadings less than 3 % by weight [3]. Isitman and Kaynak [88] studied the flame retardant properties of poly(methyl methacrylate) (PMMA) composites by addition of organo phosphorous with synergists of nanoclays and carbon nanotubes. They claimed that the carbon nanotubes have better impact on flame retardancy than nanoclays, of PMMA and organo phosphorous composites. The authors measured the LOI of neat PMMA as 17.3%. The greatest increase in LOI was obtained in the composite PMMA including 1% (w/w) carbon nanotube and 18% (w/w) organo phosphorous, from the LOI of 17.3% to 22.9%. When nano clay was used at 1% (w/w) in PMMA containing18% (w/w) organo phosphorous, the LOI was measured as 22.5%. They also pointed out that, since carbon nanotubes are mechanically strong materials, they prevent the swelling of char in presence of organo phosphorus. This inconsistency was determined as antagonism between carbon nanotubes and intumescent organo phosphorous additives [88].

Silsesquioxanes, like polyhedral oligosilsesquioxane POSS, are preceramic polymers which are precursors of ceramics. By heating they turn to thermally stable ceramic chars. These types of flame retardants are environmentally friendly and efficient [3]. As well as the POSS, other kind of silsesquioxanes such as poly(methylsilsesquioxane)s (PMSQ), are effective for flame retardancy purposes [89].

The nano-sized metal-oxides are also used for flame retardancy. In the study of Laachachi et al. [90], they used nano titanium dioxide and ferric oxide in poly(methyl methacrylate). They reported that addition of 5% nano metallic-oxides by weight improved the flame resistivity of polymer and provided thermal stabilization for poly(methyl methacrylate) polymer.

Baltaci et. al., also studied the flame retardancy of poly(ethylene terephthalate) (PET) with addition of zinc borates. They improved the LOI value of PET from 22.5% to 25.5% by using 2 % (w/w) zinc borate with 3 % boron phosphate (BP) [91].

2.5 Flame Retardancy of Polypropylene

Today, polypropylene (PP) is a very common plastic material and used in many applications such as disposable cups and dishes, home textiles, plastic bags, containers, etc. However, due to its chemical structure, it ignites easily in case of fire. Polypropylene melt can cause spread of flame. Since PP takes place in many applications, its flame retardancy is very crucial.

Self ignition point of polypropylene is 570 ˚C. Einsele et al. [92] have presented that the heat of combustion of polypropylene is 40 kJ/g. Polypropylene decomposes very rapidly when compared to wood or cellulosic materials.

Halogenated flame retardants have been the most preferred additives for polypropylene for years. They provide good flame retardancy even used at small amounts. In order to improve the efficiency of halogenated flame retardants, antimony oxide derivatives are used for synergism. However, the environmental concerns about this system are still being discussed, since usage of halogen-based additives together with antimony compound causes releasing halogen acids and metal halides. The releasing of toxic gases during fire is also dangerous for health [93]. Especially bromine based additives are being given up worldwide. For instance polychlorinated biphenyls were banned in 1977 and some bromine-based additives were banned in Europe in 2008 [93]. Thus, the researches about halogen-free flame retardants are increasing every day [64, 73, 74, 76, 78, 83].

The intumescent flame retardants are alternatives for halogenated additives, because they provide efficient flame retardancy and they are halogen-free. Chiu et al. [94] investigated the flame retardancy of polypropylene and achieved by addition of ammonium polyphosphate (APP), pentaerythritol (PER) and melamine into polypropylene. They have used 100 g PP, 14 g PER and 13 g melamine for all composites and these values were kept constant, whereas the amount of APP was 7, 15, 23 and 30 grams. The LOI of neat PP was measured as 17.8%. Maximum LOI value was observed in the composite with 30 grams of APP as 38.4%. On the other hand, they observed a dramatic decrease in tensile strength properties of polypropylene. They measured the tensile strength of neat PP as 20.91 Pa, but the tensile strength of composites decreased to 13.49 Pa. Chiu et al. [94] also proved that when the amount of APP increased in PP, the tensile strength decreased as well. They also have offered that this type of decrease might not be so important in some special applications, when the priority is the flame retardancy rather than mechanical strength.

Zhang and Horrocks [78] pointed out the percentages of additives in the polymer are very important for flame retardancy. When the amount of flame retardant is high, there can be obtained good flammability properties, however it is obvious that there would be a loose in mechanical properties. On the other side, when the amount of additives is less, the desired flame retardancy seems not to be effectively achievable. Zhang and Horrocks [78] offered an optimum amount of additives especially for PP fibers. They have claimed that, non-halogenated additives like phosphorus based additives should be loaded at least 15-20% (w/w) in PP fibers, otherwise the mechanical properties of polypropylene decrease dramatically.

Marosi et al. [95] proved that ammonium polyphosphate should be used with pentaerythritol (PER) for the purpose of intumescence. They added APP into polypropylene and tested with UL94 V method. This method bases upon the vertical burning properties of material. Basically, the material is ignited from bottom by using a flame source and it is exposed to flame for 10 seconds. The time required to extinguishing is saved. When the material extinguishes, the flame is applied for 10 seconds again. Burning time is saved again. According to these data, the material is classified as V-0, V-1, V-2. V-2 indicates that the material is flammable, where V-0 indicates flame retardant material [3]. In the UL94 V testing, the prepared composite by Marosi et al. could not achieve V-0 level. Thereafter, Marosi et al. prepared polypropylene composite with 18% (w/w) APP and 17% PER. For synergism they also added 1.5 % zinc borate and the composite achieved UL94 V-0 [95].

Zhang et al. [96] studied flame retardancy with surface grafting of polypropylene by using acrylamide, acrylic acid and metacrylic acid. They found out that acrylamide decreased flammability of polypropylene dramatically. Also they applied saponification to grafted polypropylene samples. As a result, char formation increased for polypropylene [96].

2.5.1 Silicon-Phosphorus-Nitrogen synergism in flame retardants for polypropylene

Li et al. [76] studied the synergistic contribution of phosphorus, silicon and nitrogen on the flame retardancy properties of polypropylene. They synthesized flame retardants consisting of phosphorus, nitrogen, and silicon, and prepared different composites with polypropylene (Table 2.1). They tested polypropylene based composites with limiting oxygen test and thermogravimetric analysis (TGA). The char yield of neat polypropylene is zero, because it does not leave a char residue while burning.

Table 2.1 Compositions of PP with P, Si, N, prepared by Li et al. [76].

Sample	**PP (wt%)**	**Phosphorus compounds (wt%)**	**Silicon compounds (wt%)**	**Nitrogen compounds (wt%)**	**LOI value (%)**
P-Si-0	100	0.0	0.0	0.0	17.0
P-Si-1	70	0.0	30.0	0.0	20.5
P-Si-2	70	30.0	0.0	0.0	20.5
P-Si-3	70	0.0	0.0	30.0	21.0
P-Si-4	70	10.0	20.0	0.0	22.2
P-Si-5	70	15.0	15.0	0.0	21.5
P-Si-6	70	10.0	20.0	20.0	22.9
P-Si-7	70	20.0	10.0	10.0	26.0
P-Si-8	70	22.5	7.5	7.5	24.0

Maximum LOI value was obtained as 26% in the composite which includes 70% (w/w) PP, 20% (w/w) phosphorous compound, 10%

(w/w) silicon compound and 10% nitrogen, whereas LOI of neat PP was measured as 17%. Plus, the char yield of this composite was found as 27% from TGA. Li et al. [76] reported that the synergism of P, N, Si elements can provide better flame retardant properties for polypropylene, when they used together rather than alone.

Environmentally-friendly flame retardant systems can be set up using nitrogen, silicon and phosphorous elements, because they do not affect the environment harmfully. They may also be used alone as flame retardant, however most studies show that they would provide better flame retardancy when at least two of them are added together in a polymeric material. In case three of those elements are used together, the best flame retardancy can be obtained due to the synergism. Synergism is explained with their actions during combustion of polymer. Char formation, blowing of char and thermal stability are provided by phosphorus, nitrogen and silicon, respectively [65, 73, 74].

2.6 Mechanical Properties of Polypropylene Composites

The effects of additives, such as minerals, in polymer matrix are attributed as reinforcement. The additives provide extra points within the matrix. Additives cause an increase in tensile modulus and stress at yield, because of their effects on the movements of molecular bondings. As a result the flame retardant additives render better mechanical strength rather than unreinforced polymers [97].

Some important properties of additives and polymers which influence the polymeric composites are listed below:

(1) The particle size of additive
(2) Surface properties and shape of additive
(3) Mechanical properties such as strength, toughness etc.
(4) Composite preparing process
(5) Bonds of additive to polymer depending on its dispersion in the polymer matrix
(6) The mechanical properties of polymer [97]

Zanetti et al. [85] reported flame retardant and mechanical properties of "polypropylene grafted maleic anhydride (PP-g-MA)" based polymer composites prepared by using additives of decabromodiphenyl oxide (DB) and antimony trioxide (Sb_2O_3) (AO). They added antimony trioxide because of its synergistic contribution with DB. Furthermore, they also prepared PP-g-MA based composites containing organoclay. However, Zanetti et al. kept organoclay composition constant at 5% (w/w). Elongation at break values of composites decreased distinctly compared to that of base polymer. They measured the elongation at break value of neat PP-g-MA as 5.4%. The elongation at break values of composites were reported as 4.2% for the composite containing 22% (w/w) DB , 5% (w/w) organoclay; as 4.2% for the composite containing 5% (w/w) organoclay and 22% (w/w) DB; and as 3.8% for the composite containing 6% (w/w) AO in PP-g-MA. On the other hand, Zanetti et al. observed also increase in yield stress and more dramatically improvement in elastic modulus. Adding 5% organoclay increased elastic modulus of neat PP-g-MA from 462 to 955 MPa. Also the incorporation of 5% (w/w) organoclay with 22% (w/w) DB and 6% (w/w) AO in PP-g-MA; improved the yield stress of PP-g-MA from 16.9 to 23.3 MPa [85].

2.7 Preparation of Polymer Composites

To prepare thermoplastic polymer based composites, the most preferred method is melt mixing. The additives are introduced in polymer melt mostly by using extrusion process. Another commonly used process for polymers is injection molding method. Such as plastic parts of automobiles, piping fittings, water bottles etc. And also the extruded composites are commonly formed by injection molding to obtain suitable samples for characterization tests of polymers.

2.7.1 Extrusion

Extrusion is a very common method among polymer processing techniques, since it is preferred in order to form polymer raw materials to obtain composites and/or final products. Polymer chips or powder is fed from hopper and move throughout the screw. Around the screw there are heating jackets which can be set as a temperature profile or constant temperature. While the screw turns around it creates pressure difference. The polymer melts with heat and shear stress at the same time [98]. Also screwing provides mixing, which is very crucial for composite preparation. Extruded polymer leaves the extruder from die (Figure 2.12). Melt polymer faces the cooling bath, which is usually cold water, and then the melt solidifies. With winders installed in the cooling bath, extruded polymer is spun along the bath and can be taken into a chopper for grinding.

By using extruder, it is also possible to have different shapes, from tubular shapes to thin films. Each part of screw has a specific mission during process. Feeding part takes the polymer from hopper into the extruder. The polymer melts in the compression part of screw with heat and shear forces. The metering part provides a consistent and homogeneous flow. It also supplies pressure to move the melt out from the die [98].

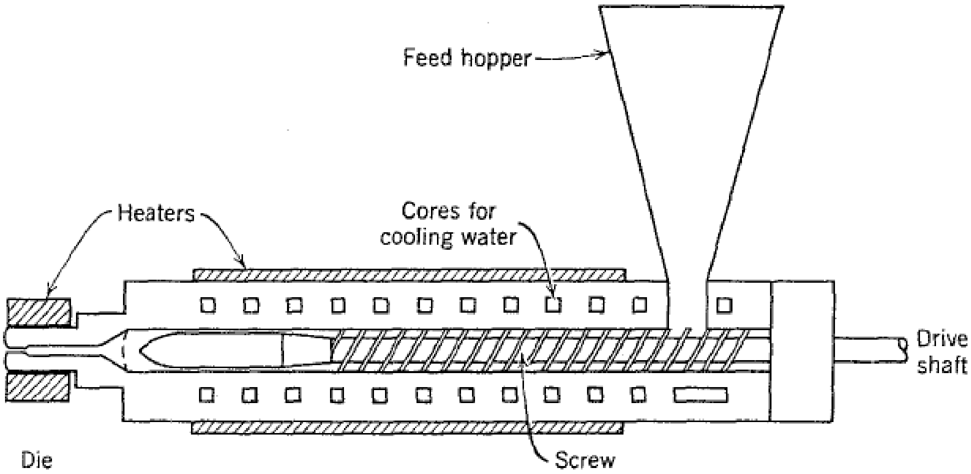


Figure 2.12 Diagram of a plastics extruder (single screw) [99]

Today, the twin or more screwed extruders are used. They provide more shear forces and uniform type of mixing [98]. Also, design of screw is another concept studied by researchers. Several types of screws having different lengths of screw steps, shapes and configurations exist in industry for various applications.

2.7.2 Injection molding

Injection molding process is a widely used polymer processing method for thermoplastic polymers. First of all, polymer is preheated to the sufficient temperature, at which polymer melts and becomes fluidic, in a barrel. After preheating polymer, melt is pushed with high pressure into a cold mold. In order to transfer polymer to the mold, it is possible using a piston or reciprocating screw. The screw works as it does in extrusion [98]. It takes the melt polymer from hopper and moves out to the cold mold. The polymer is cooled down in the mold and taken at which shape it is required, of course depends on the shape of mold. Then the screw goes back and takes a volume of polymer for next cycle of injection molding (Figure 2.13).

The opportunity of injection molding process is that products can be processed easily and quickly. It is known that a cycle lasts generally 10-30 seconds [98]. That is to say, it is possible to produce many kilograms of molded polymers in a short time. Since there are several types of molds in industry such as multi cavity molds, injection molding provides large production capacities.

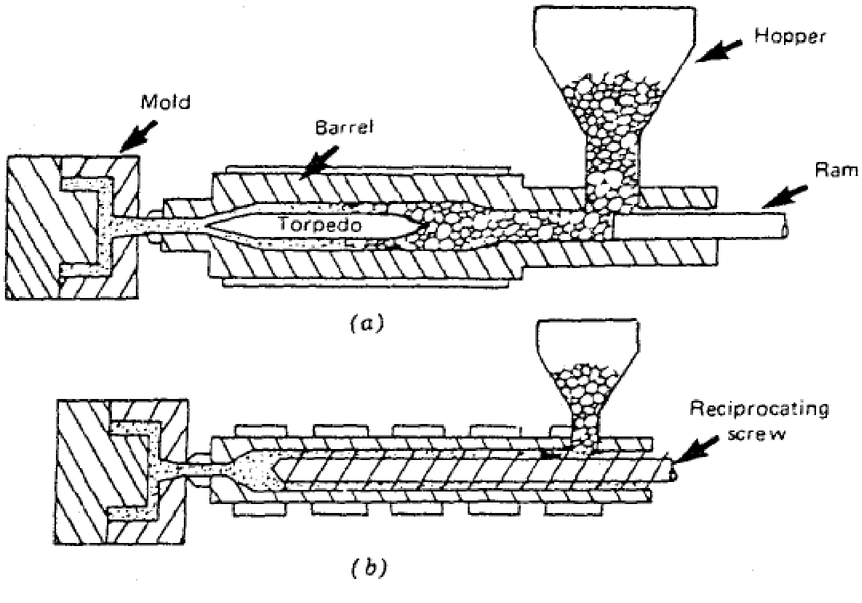


Figure 2.13 Sketch of (a) a ram-fed and (b) a screw-fed injection molding machine [98]

2.8 Characterization of Polymer Composites

Due to the property which is aimed to create in a polymer matrix, laboratory tests are done through some special methods such as flammability, conductivity, thermal tests, etc. Furthermore, in a polymer composite it is very crucial not to decrease the base polymers' inherent mechanical properties as well. For this reason characterization of polymer composites is essential.

2.8.1 Flammability tests

Minimum oxygen concentration to sustain burning, burning rate and heat release rates, are measurable flammability properties of polymers. These properties are mostly tested by limiting oxygen index, horizontal and vertical burning, cone calorimetry tests. There are also other flammability tests used in academic researches and industrial applications [3]. The most common tests are explained in the coming section.

2.8.1.1 Limiting oxygen index (LOI) test

Fenimore and Martin [100] introduced limiting oxygen index (LOI) test in 1966 as a test which can give information about relative flammability of materials. The standards for testing are ASTM D 2863 and ISO 4589.

Definition of limiting oxygen index (LOI) is that the minimum oxygen concentration in an oxygen/nitrogen gaseous mixture, in order to maintain burning of sample either 3 minutes or 5 cm. The sample must be in a vertical position and also it must be ignited from top (Figure 2.14) [101].

LOI value can be determined mathematically as given in Equation 2.5:

$$LOI = 100\ ([O_2]/([O_2]+[N_2])) \qquad (2.5)$$

The specimen with a size of 80x10x4 mm is replaced vertically in the middle of a chimney, which is generally made of glass. The oxygen/nitrogen gas enters from below of chimney and leaves it from top. The column should be purged at least 30 seconds. After a uniform distribution of gaseous mixture is obtained in the column, the specimen is ignited from top. If the specimen keeps burning for 5 cm or 3 minutes, the LOI value is fixed. If material extinguishes before 3 minutes, there should be let more oxygen which means its LOI value is higher than the guessed value. If it burns more rapidly than 3 minutes or 5 cm, the needed oxygen is less than set value, also sample has less LOI value [101].

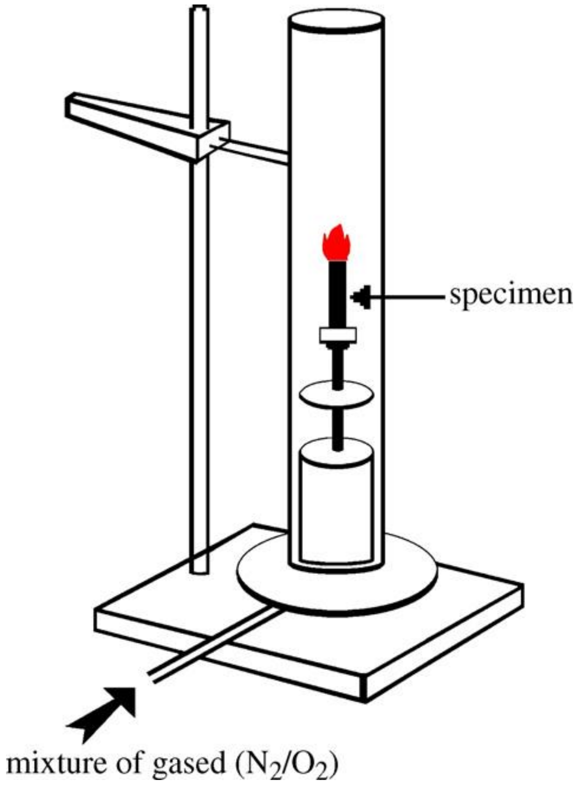


Figure 2.14 Experimental set-up for LOI measurement

Since air comprises 21% oxygen, the materials which have LOI values less than 21% are classified as combustible materials. If LOI value of material is higher than 21%, it is classified as self-extinguished material, because that material cannot be sustained combustion without any extra energy [101]. As a result, the higher LOI value materials have, the less they are flammable.

Today, there are lots of other developed flammability tests to measure flammability. However LOI is still a traditional method to show the relative flammability of materials and used as a reliable and comprehensible quality control test [3].

2.8.1.2 Horizontal burning test

The horizontal burning test gives the information about the materials burning rate when it is placed horizontally at the ambient temperature and atmospheric conditions.

The flame is fuelled by natural gas. The time required for the flame propagates and reaches to 100 mm of sample is recorded. The horizontal burning rates are reported as mm/min or in other units depend on the reporting techniques [102].

The test is applied according to ASTM D 635 standard. The specimen is placed vertically with a holder from one end of the sample. The other free end is exposed to flame for 30 seconds and flame is taken away. In case the specimen does not burn for 100 mm, extent of burning is reported. If the specimen burns to the 100 mm mark, the time for burning is reported as burning rate [102].

2.8.2 Mechanical tests

The most common mechanical properties for polymers are known as tensile strength, elastic modulus, elongation at break and impact strength. The tensile stress can be determined as the maximum stress that a material can stand until failure, while it is being pulled. Elongation at break values are obtained from tensile test as well, which is the maximum elongation percentage value of material just before it breaks down. The impact strength shows the required energy needed by materials against sudden hits or impacts and it gives information about the ductility or brittleness of material [103].

2.8.2.1 Tensile test

Tensile test (Figure 2.15) is known as one the most important mechanical test to determine the mechanical properties of materials. Tensile test or tension test gives information for applications of materials, quality control or determining the behaviors of materials under applied forces. From tensile testing; tensile strength or ultimate tensile strength, the tensile modulus (or Young's modulus), stress at yield, elongation at break of materials can be obtained [98].

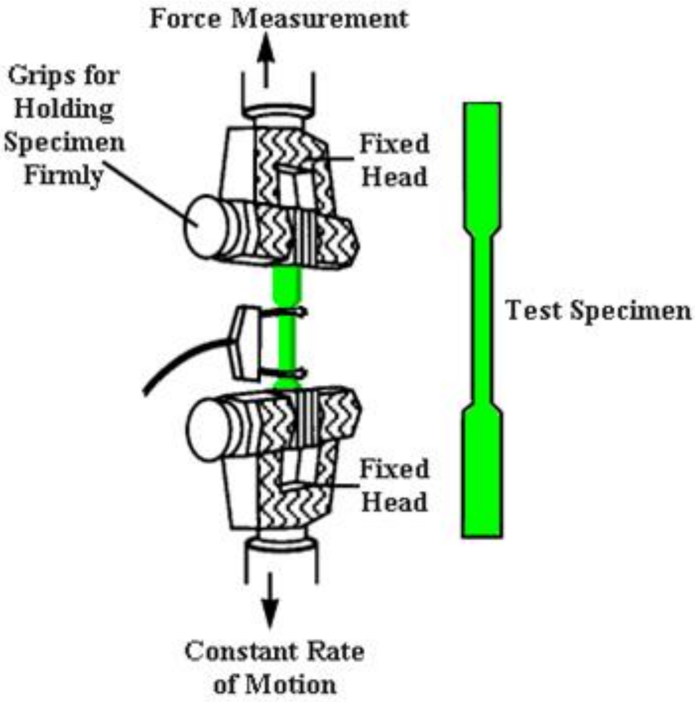


Figure 2.15 Schematic drawing of tensile testing system

The material is replaced with holders form both ends vertically and tightly. While the material is being stretched at a constant rate, the applied tensile force and elongation values are collected as data [104].

The test is applied until failure of material. A typical stress-strain curve of plastics is given in Figure 2.16.

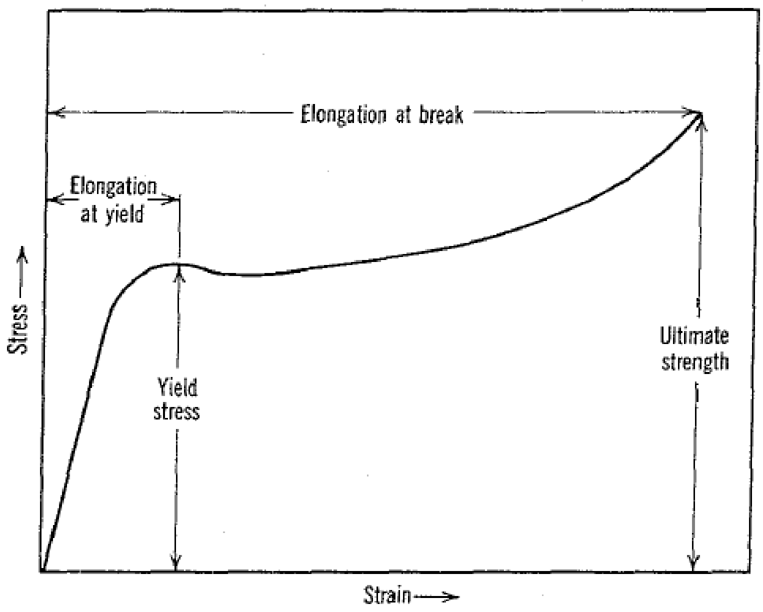


Figure 2.16 Generalized Stress-Strain curve for plastics [98]

Tensile strength or ultimate strength σ, is calculated from the equation given below in unit of pressure. (2.6) Here, F is the applied force and S is the cross sectional area of specimen.

$$\sigma = \frac{F}{S} \tag{2.6}$$

The initial slope of stress-strain curve is determined as elastic or Young's modulus given in Equation 2.7, where E is elastic modulus, and ε is elongation at break value. Elastic modulus is known in pressure unit, since the elongation at break value is without unit and stress value is in Pascals.

$$E=\frac{\sigma}{\varepsilon} \tag{2.7}$$

From data, the elongation at break or strain is calculated as follows, where ε is the elongation at break value, L_o is the initial length of material and L is the length of the material just before it breaks (2.8):

$$\varepsilon=\frac{\Delta L}{L_0}=\frac{L\text{-}L_0}{L_0} \tag{2.8}$$

2.8.2.2 Impact test

In impact strength test method, plastics are tested according to energy appearing as a result of being hit by a pendulum (Figure 2.17). The energy required to break down a specimen is calculated from the movement of pendulum [98]. The tested samples are generally notched so-called V-type notch according to ASTM D256 standard. The testing temperature should be constant during the test, because it directly affects the absorbed impact energy, since the materials can show different behaviors to impact stress at different temperatures. This is also explained with “brittle-to-ductile” transmission. In such a transition, at higher temperatures the impact energy is relatively large since the material becomes ductile. As the temperature is lowered, the impact energy drops over a narrow temperature range as the material becomes more brittle [105]. That is why it is crucial to do the impact test at a constant ambient temperature.

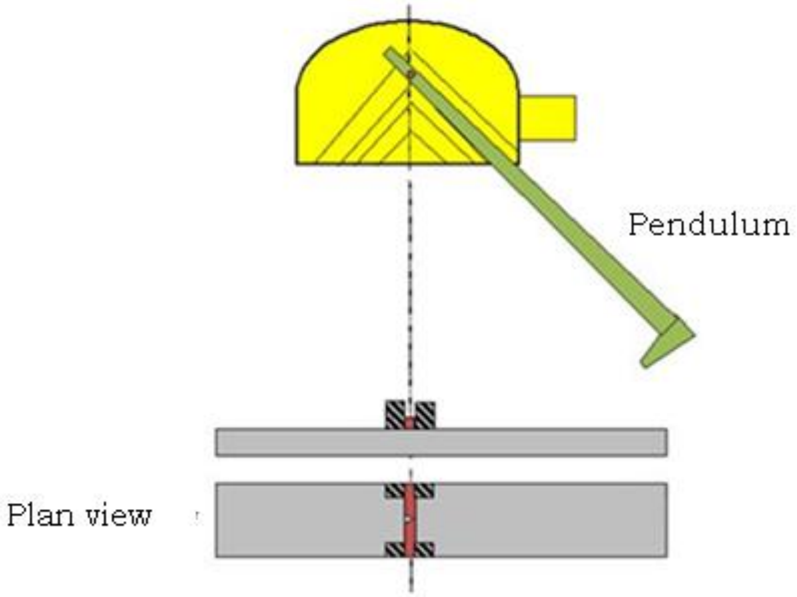


Figure 2.17 A schematic drawing of Charpy impact test instrument

The test can be done as either Charpy impact test or Izod impact test. The purpose of both methods is to measure the impact strength of sample. However, the difference is the placement of sample. In Charpy impact test, the pendulum hits the specimen, when it is located horizontally. In Izod impact test, the specimen is placed vertically (Figure 2.18).

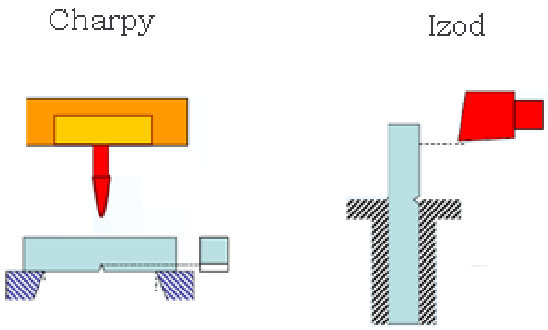


Figure 2.18 Differences between Charpy and Izod impact tests

There are two types of ruptures in polymers: ductile and brittle ruptures. If the material has elastic behavior, no yielding or drawing, it is “brittle rupture”. On the other hand, if material does not break when it is hit by pendulum, it has a ductile behavior against impact energy [98].

2.8.3 Thermal tests

2.8.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) gives information about the materials behavior under heating. By using a sensitive weight balance, the weight change of material is measured and reported as a function of temperature with TGA. Besides thermal properties, such as decomposition temperature of material, it is also possible to find out some information such as char yield, the amount of volatiles, composition of materials, etc. [98].

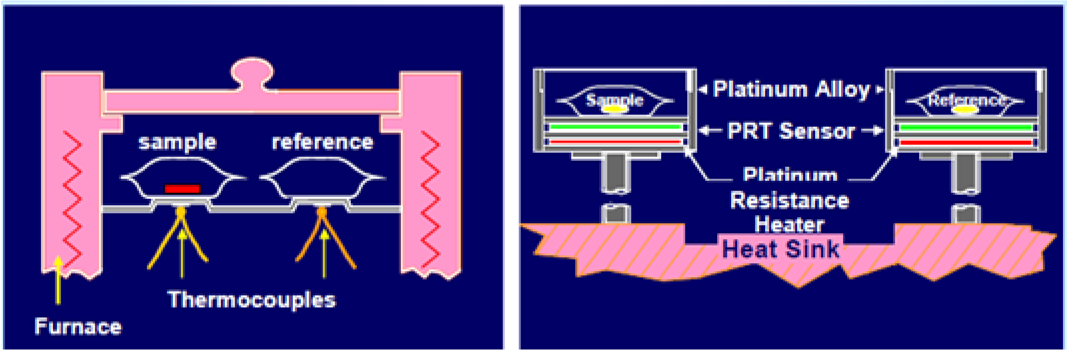
Thermal analysis is a very important test especially for polymer science. Since thermoplastics are widely used materials, TGA helps to investigate the thermal stability or flame retardant properties of polymers [106].

Thermogravimetric analysis (TGA) introduces assessments about decomposition of polymers under controlled circumstances. Many materials loose a very considerable mass at a certain temperature, which is known as ignition temperature. The significant mass loss can also be occurred, when there is any production of carbon monoxide on the surface of polymer. Obviously, carbon monoxide causes a decrease in oxygen concentration due to the reaction between carbon monoxide and oxygen [106]. Also if the sample contains additives, which have different decomposition temperatures, this can be monitored as well by many peaks shown in the TGA curve. Furthermore if these temperatures are completely and clearly known, their amount in the polymer can be calculated as well.

2.8.3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measures the temperatures and flowing heat and reports heat energy as a function of temperature and time. In other words, DSC gathers information from chemical and physical changes of material including endothermic or exothermic processes according to heat capacity of material. DSC is applicable both for liquid and solid samples. The test is done relatively fast, and sample preparation is easy. By using DSC it is also possible to study in a wide temperature range such as from -25 ˚C to 800 ˚C [107].

Heat flux type and power compensation type differential scanning calorimeters are widely used (Figure 2.19). When sample is put in one furnace, it is “heat flux” type DSC. As for “power compensation” DSC, sample and reference cells are put into two different furnaces.



Heat Flux DSC Power compensation DSC

Figure 2.19 Schematic drawing of heat flux DSC and power compensation DSC [105]

The properties which can be determined from DSC analysis are glass transition temperature, specific heat, boiling or melting temperature, crystallization point, percent of crystallinity, heat of fusion, heat of reaction, curing degree, curing rate, kinetics of reactions, percent of purity and thermal stability [107].

As the thermogravimetric analysis, differential scanning calorimetry is a very important test in polymer science. It is possible to determine thermal history of thermoplastics and its processing conditions. The results can be achieved analyzing the thermoplastic polymer at different heating rates in order to render its crystallinity degree. For thermosetting polymers the heat for curing can be associated with curing degree [107].

2.8.4 Morphological Analysis

2.8.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is a kind of electron microscope. SEM scans the sample with high-energy electron beam. The sample should be either conductive or coated with a suitable conductive material. Thus, the electrons act on the atoms on the surface of sample. This interaction makes the sample produce signals which carry information about the topography of sample or its composition etc. [108].

There are different types of detectors in scanning electron microscopes. The detectors are categorized by the signals such as secondary electrons, back-scattered electrons, etc. Most of SEMs have secondary electron detectors. Also some special SEMs have detectors which can be manipulated for several types of signals. By using secondary electron detectors, it is possible that having images of samples even at 1 nm size. Since there is a narrow electron beam, the SEM images or micrographs provide three-dimensional information about the surface. The required magnifications are also achievable from 10 times to 500000 times [108].

Back-scattered electrons (BSE) are used in analytical SEM. Its spectrum is generated from the typical X-rays. The electron beam is reflected by sample elastically. Also, the signal intensity of the back-scattered electrons is directly associated with the atomic number of the specimen. The analytical information can be gathered from BSE images is distribution of variant elements in the sample [108].

CHAPTER 3

EXPERIMENTAL

In the experimental part, the studies on poly(dimethylsilane) (PDMS), and polypropylene based composites are given. There are two sections in this chapter: In the first section, the electrochemical synthesis studies and characterization techniques of poly(dimethylsilane) are presented. In the second section, preparation of polypropylene based composites and their characterization methods are given.

3.1 Electrochemical Synthesis of Poly(dimethylsilane)

First, poly(dimethylsilane) was prepared from the dimethyldichlorosilane monomer via electrochemical reduction with solvent and supporting electrolyte. Then, the synthesis was carried out with a modification of removing solvent and supporting electrolyte from the system. Since the polymer was obtained in powder form, it is called as PDMS(p).

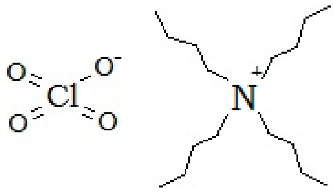
3.1.1 Electrochemical synthesis of poly(dimethylsilane) with solvent and supporting electrolyte

3.1.1.1 Materials

The monomer (>99%) and the solvent 1,2-dimethoxyethane (anhydrous, 99.5%) were purchased from Sigma-Aldrich. Tetrabutylammonium perchlorate (≥ 98.0%), which was used as supporting electrolyte, was a Fluka product. The chemical structures of chemicals used in the synthesis of poly(dimethylsilane) in powder form (PDMS(p)) are given in Figure 3.1.

Dichlorodimethylsilane

1,2 Dimethoxyethane



Tetrabutylammonium perchlorate

Figure 3.1 Chemical structures of materials used in PDMS(p) synthesis

3.1.1.2 Experimental parameters and procedure

The electrochemical synthesis of poly(dimethylsilane) was carried out in a 200 ml undivided cell under argon atmosphere. The electrodes were copper and with the size of 2.5x7.5x0.1 cm. After the copper electrodes were cleaned with 5% HCl solution, they were also cleaned with distilled water and acetone for purification. Then, they were put into the undivided electrolytic cell, in which the supporting electrolyte was filled. 1.88 grams of supporting electrolyte, tetrabutylammonium perchlorate, was dissolved in 50 ml solvent, 1,2 dimethoxyethane (DME). 5 ml monomer, dichlorodimethylsilane, was injected into cell under argon atmosphere. The ratio of monomer to solvent is 1/10 (v/v). The reaction was kept at 6 V constant potential for 30 minutes. After the electrolysis, 0.1 g $LiAlH_4$, which is reductive reactant, was added into the mixture, in order to remove possible remaining Si-Cl bonds under magnetic stirring and cooling process for 3 hours. After 3 hours, the mixture was evaporated by using a horizontal vacuum evaporator at 40°C. Evaporation continued till the solid polymer reached a constant weight and eventually a yellowish white poly(dimethylsilane) was obtained. PDMS(p) was dissolved in toluene and precipitated with methanol for purification, however the amount of obtained polymer was quite less. Thus, the synthesized PDMS(p) was used without purification. The polymerization efficiency, based on the ratio of polymer/monomer, was 35%. However, some impurities were observed. In order to remove impurities and have an efficient polymerization, other types of synthesis were investigated.

3.1.2 Electrochemical synthesis of poly(dimethylsilane) without solvent or supporting electrolyte

3.1.2.1 Materials

The monomer, dichlorodimethylsilane (> %99) was purchased from Sigma-Aldrich. The inert atmosphere was nitrogen (high purity). A single-compartment electrolytic cell (200 ml) equipped with copper electrodes (2.5x9x0.1 cm) was connected to Schlenk line (Figure 3.2) which provides the system to be airtight. The Schlenk system includes gas filters, which provide to filter the flowing nitrogen. The electrolytic cell is undivided and the copper electrodes are put into it via a power supply, the desired potential (32 V) is applied to the system, i.e. electrodes.

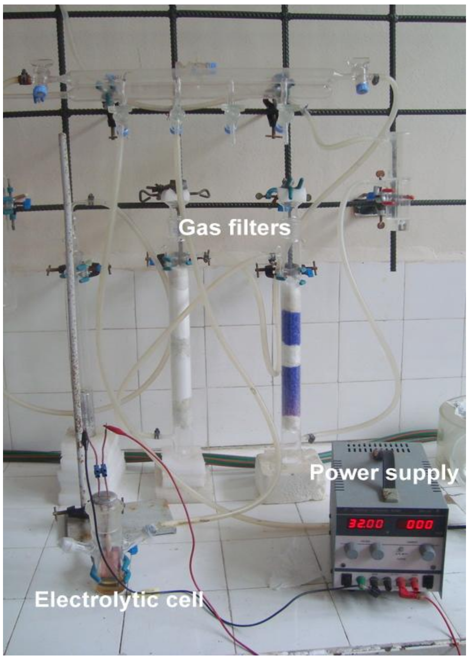


Figure 3.2 Picture of Schlenk system

3.1.2.2 Experimental parameters and procedure

Poly(dimethylsilane) was prepared from electrochemical reduction of dichlorodimethylsilane. Since this synthesis is air-sensitive, the experimental system was purged for 30 minutes with nitrogen gas in order to remove probable oxygen gas.

Copper electrodes were washed with 5 % (v/v) HCl aqueous solution and cleaned with distilled water before being inserted in cell. 30 ml of monomer was injected under nitrogen atmosphere into the electrolytic cell. The experiment was carried out under conditions of constant applied potential (32 V) at ambient temperature for 7 days. After the electrolysis a “highly viscous-gel like” polymer mixture with dense chlorine gas was obtained. After the electrolytic cell was opened, the chlorine gas was released and system was hold open about 1 hour to eliminate the gas under hood.

In order to remove the unreacted monomer from the viscous mixture, polymer was precipitated from methanol and filtered. Then it was dried in a vacuum dryer at 40°C and white colored-gel like polymer was obtained.

3.1.3 Characterization of poly(dimethylsilane)

The Fourier transform infrared (FT-IR) analysis of polymer samples was done by using a Shimadzu FT-IR spectrometer. For FT-IR measurements, solid samples were prepared with KBr and fluid samples were analyzed directly by FT-IR/ATR. Ultraviolet-visible (UV-VIS) analyses were done in tetrahydrofuran with ATI-Unicam UV2 spectrometer. For proton nuclear magnetic resonance (^{1}H-NMR) analyses, Varian/Mercury-200 machine was utilized.

Thermogravimetric analyses (TGA) were performed by using a a Shimadzu 60H-DTG. The morphology of Polydimethylsilane powder samples were obtained with the help of a scanning electron microscope (SEM) machine, Quanta 400F Field emission. The PDMS(p) specimens are coated with palladium and gold. The SEM analysis of poly(dimethylsilane) in viscous form cannot be done, since it was observed as unstable under electron beams.

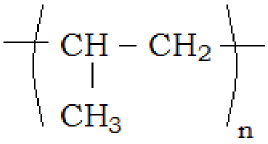
3.2 Preparation of Polypropylene/Preceramic Polymer Composites

The polypropylene and preceramic polymer blends were prepared by melt mixing process. The main preceramic polymer was poly(dimethylsilane) and in order to compare its impact on polypropylene, another preceramic polymer was used, poly(methylsilsesquioxane), which was synthesized in Karadeniz Technical University, Department of Chemistry [89]. Also for investigation of contribution for flame retardancy, different flame retardants such as P, N, B containing materials and intumescent additives (melamine phosphate and pentaerythritol) were used. The details are given in the coming section.

3.2.1 Preparation of polypropylene/poly(dimethylsilane) and polypropylene/intumescent additive composites

3.2.1.1 Materials

In this study, the base polymer is polypropylene (PP), PETOPLEN MH-418, which was purchased from PETKIM. Its chemical structure and properties are given in Figure 3.3 and Table 3.1, respectively.



$$\left[\begin{matrix} CH - CH_2 \\ | \\ CH_3 \end{matrix} \right]_n$$

Figure 3.3 Chemical structure of polypropylene

Table 3.1 PETOPLEN MH 418 specifications [109]

Properties	**Unit**	**Value**	**Test Method**
Contamination,100 g	g/10 min	4.0-6.0	ASTM D-1238
Tensile Strength			
- at Yield	MPa	34.3	ASTM D-638
- at Break	MPa	42.2	ASTM D-638

Poly(methylsilsesquioxane) (PMSQ), which is in the same class with PDMS, was used for comparison. PMSQ (Figure 3.4.b) has a network structure, where PDMS is a linear polymer.

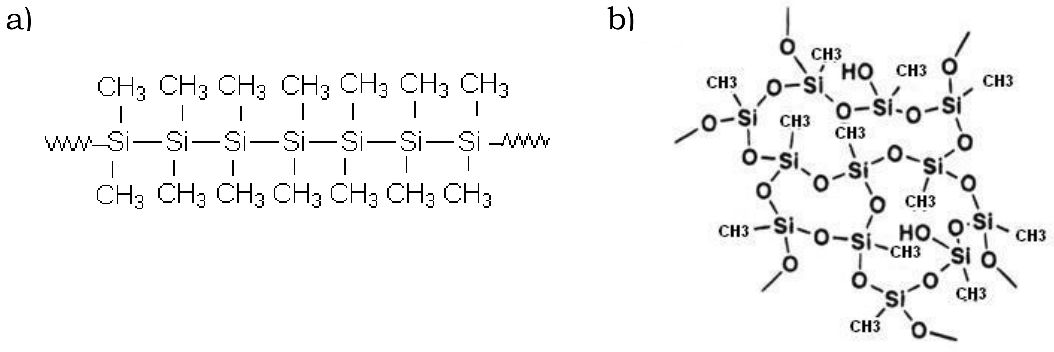


Figure 3.4 a) Poly(dimethylsilane) and b) Poly(methylsilsesquioxane)

PMSQ was synthesized by the emulsion polymerization of methyltrichlorosilane. The synthesis route is given in Figure 3.5. The average size of the polymer particles were between 0.7-1.1 μm.

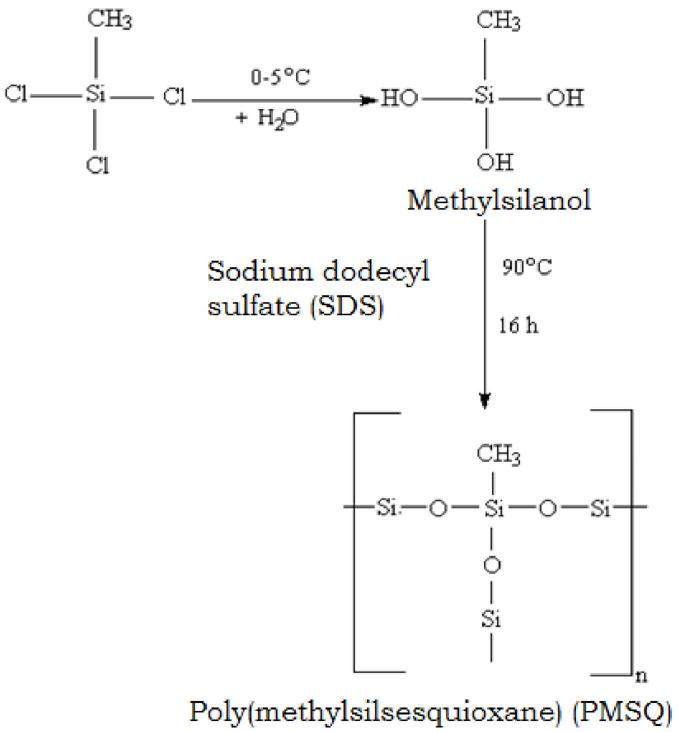


Figure 3.5 Synthesis of poly(methylsilsesquioxane)[89]

The additives were incorporated to polypropylene/preceramic additives composites in order to provide contribution for flame retardancy. Among these additives, boron phosphate (BP) was synthesized in the Department of Chemistry of Middle East Technical University (Fig. 3.6 (a)). Triphenyl phosphate (TPP) (trade name of Smokebloc AZ-12/BFR-4), which is a halogen free-additive (Figure 3.6 (b)); was supplied by Great Lakes Chemical Corporation. The other compounds such as magnesium hydroxide (MH) (Fig. 3.6 (c)) and antimony trioxide (Sb_2O_3) (AO) (Figure 3.6 (d)), were purchased from Sigma Aldrich. Pentaerythritol (PER) (Figure 3.6 (e)) is also a product of Sigma Aldrich and melamine phosphate (MP) with the trade name of Melapur MP is a product of Ciba Chemicals (Figure 3.6 (f)).

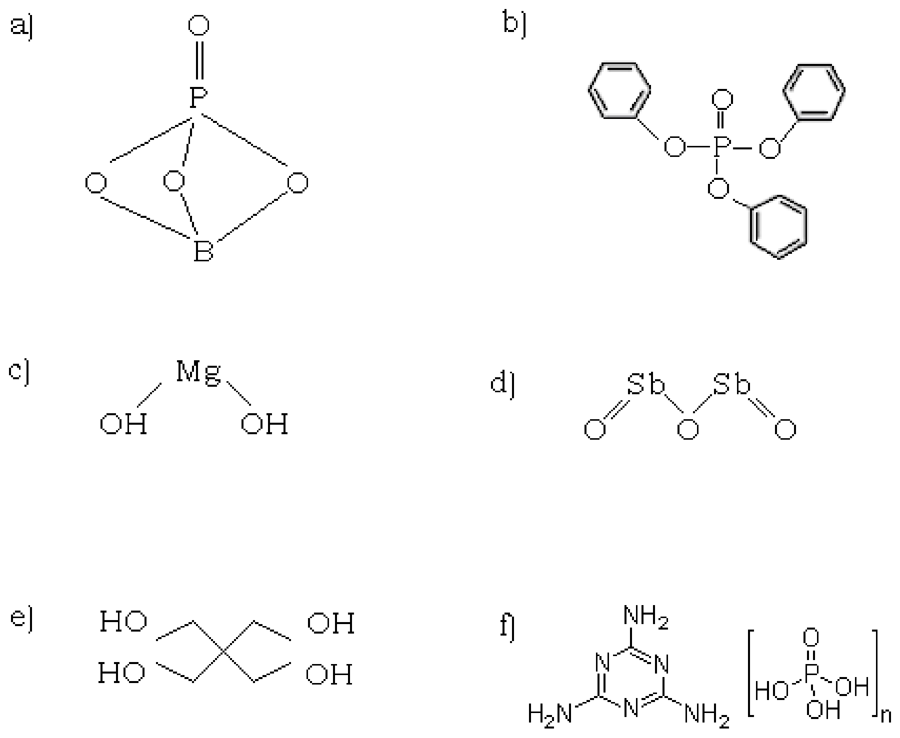


Figure 3.6 Chemical structures of additives: a) Boron phosphate (BP), b) triphenyl phosphate (TPP), c) magnesium hydroxide (MH), d) antimony trioxide (AO), e) pentaerythritol (PER), f) melamine phosphate (MP)

3.2.1.2 Composite preparation

Polypropylene was in granule form, whereas the additives were mostly in powder form. In order to achieve a good mixing of solids, it is better to have them about similar particle sizes. For this purpose polypropylene was ground with a Willey mill intermediate grinding machine, thus it became into powder form.

Before extrusion process (Figure 3.7) the materials were dried in a vacuum oven at 100°C for 2 hours. After drying they were mixed at certain concentrations. The compositions of polypropylene based composites are given in Tables 3.2 and 3.3. In Table 3.2, the preliminary experiments are seen and in Table 3.3 the studies done with intumescent additives are presented.

Figure 3.7 The picture of extruder used in this study

Table 3.2 Compositions of preliminary experimental systems

Composite (w/w %)	PP	PDMS	TPP	BP	MH
PP/1PDMS	99	1	-	-	-
PP/5PDMS	95	5	-	-	-
PP/5PDMS/5TPP	90	5	5	-	-
PP/10PDMS	90	10	-	-	-
PP/10PDMS/5BP/5MH	80	10	-	5	5

Table 3.3 Compositions of composites with intumescent and other additives

Composite/(wt%)	**PP**	**MP**	**PER**	**BP**	**AO**	**PMSQ**	**PDMS**
PP/10MP/10PER	80	10.00	10.00	-	-	-	-
PP/15MP/5PER	80	15.00	5.00	-	-	-	-
PP/5MP/15PER	80	5.00	15.00	-	-	-	-
PP/14.25MP/4.75PER/ 1BP (BP1)	80	14.75	4.75	1	-	-	-
PP/12.75MP/4.25PER/ 3BP (BP3)	80	12.75	4.25	3	-	-	-
PP/11.25MP/3.75PER/ 5BP (BP5)	80	11.25	3.75	5	-	-	-
PP/14.25MP/4.75PER/ 1AO (AO1)	80	14.75	4.75	-	1	-	-
PP/12.75MP/4.25PER/ 3AO (AO3)	80	12.75	4.25	-	3	-	-
PP/11.25MP/3.75PER/ 5AO (AO5)	80	11.25	3.75	-	5	-	-
PP/14.25MP/4.75PER/ 1PMSQ (PMSQ1)	80	14.75	4.75	-	-	1	-
PP/12.75MP/4.25PER/ 3PMSQ (PMSQ3)	80	12.75	4.25	-	-	3	-
PP/11.25MP/3.75PER/ 5PMSQ (PMSQ5)	80	11.25	3.75	-	-	5	-
PP/14.25MP/4.75PER/ 1PDMS (PDMS1)	80	14.75	4.75	-	-	-	1
PP/12.75MP/4.25PER/ 3PDMS (PDMS3)	80	12.75	4.25	-	-	-	3
PP/11.25MP/3.75PER/ 5PDMS (PDMS5)	80	11.25	3.75	-	-	-	5

The temperature profile in extruder was 180-185-195-205-215 °C from hopper to die. Since the materials were cooling in a water bath after extrusion, they were dried at 100 °C for 4 hours, before injection molding process (Figure 3.8).

Figure 3.8 The picture of injection molding machine used in this study

In the injection molding, the extruded composites were filled in a barrel which was at 210 °C. In this barrel it was waited for 3 minutes for melting. Then the melted composite was pushed with 13 bar pressure into the mold which is at 30°C. The samples were obtained at room temperature and ready to use in further polymer tests. The flow chart composite preparation is given in Figure 3.9.

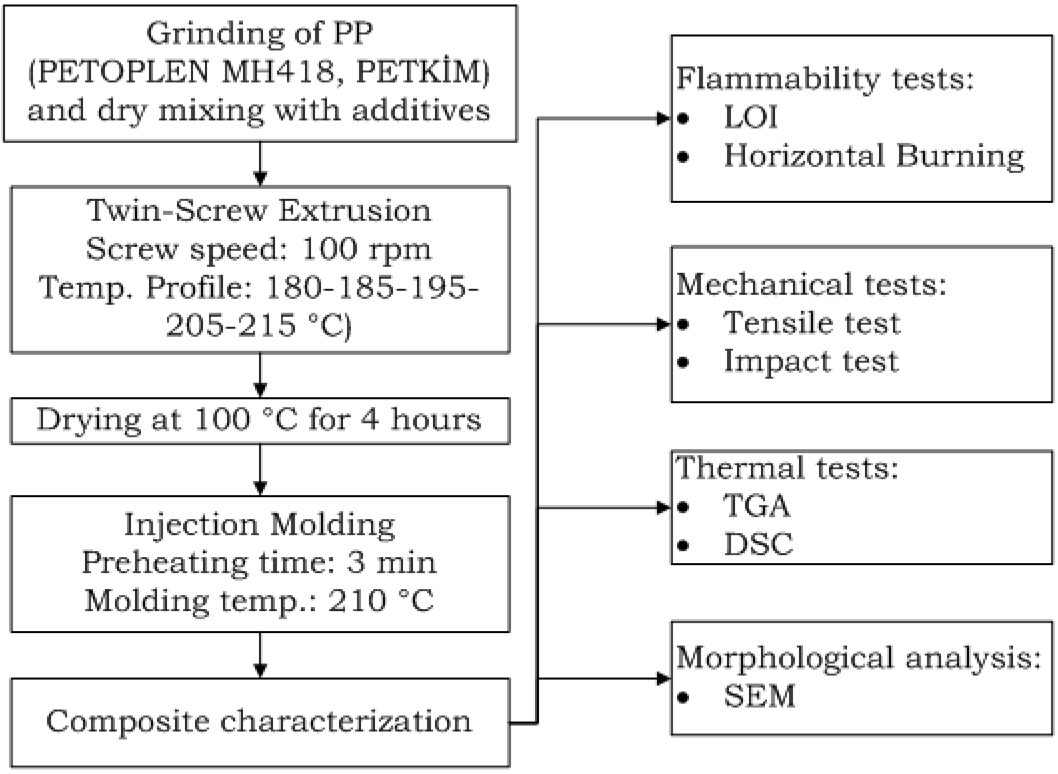


Figure 3.9 Flow chart of composite preparation

3.2.2 Characterization of polypropylene/poly(dimethylsilane) and polypropylene/intumescent additive composites

The flammability, mechanical and thermal behaviors, and morphology of prepared composites were characterized by using limiting oxygen index and horizontal burning tests, tensile and impact tests; thermogravimetric analysis and differential calorimetry tests; scanning electron microscope application, respectively.

3.2.2.1 Flammability tests

3.2.2.1.1 Limiting oxygen index (LOI) test

The limiting oxygen index (LOI) test is used to determine the minimum oxygen concentration in an oxygen-nitrogen mixture, required for continuing burning after ignition. In this study the test is performed according to the ASTM D2863 standard using an LOI test system, Dynisco Polymer LOI test instrument (Figure 3.10). Due to the standard, the dimension of samples is 80 mm in length, 10 mm in width and 4 mm in thickness. The samples were molded by using the injection molding machine with the mentioned dimensions.

Figure 3.10 Picture of Limiting Oxygen Index test instrument

The test specimen is put into the chamber vertically and with a burner it is ignited from the top [101]. The oxygen-nitrogen concentration is adjusted by needle valves and their flow is observed from rotameters. The gases, also coming from different gas tanks, come separately to the bottom of glass chimney, enter together into the chimney and flow upwards. After the ignition occurs, the sample is observed whether it burns for 3 minutes or 5 cm or not. If it extinguishes sooner, the oxygen concentration should be increased and the experiment should be done again. If it burns rapidly more oxygen should be in the chimney. The test is repeated to determine the LOI value correctly.

3.2.2.1.2 Horizontal Burning Test

In the horizontal burning test, the rate of burning and time of burning of materials are determined according to the standard of ASTM D635, when they are in horizontal position. Due to the standard, the dimensions of samples are 80 mm in length, 10 mm in width and 4 mm in thickness, such as the samples used in LOI measurements and the test is done at room temperature. The flame is applied for 30 seconds or in case of the specimen ignites immediately; it is applied until the specimen burns 25 millimeters. If the sample burns completely, the burning rate is calculated as the time per length. On the other hand, for the self-extinguished samples, the burning rate is calculated as the burning time per burning length. For each composite the test is repeated for 5 times and the averages of burning rates are given as horizontal burning test result.

3.2.2.2 Mechanical Tests

3.2.2.2.1 Tensile Test

In order to determine the tensile properties of composites the Schimadzu Autograph AG-100 KNIS MS Tensile Testing machine was used and the test was carried out according to the ASTM D638 standard. The specimen of tensile testing had a gauge length of 30 mm, the width of 4 mm and the thickness of 2 mm. The gauge length is the distance along the specimen upon which elongation calculations are made, also taken as initial length of material (Figure 3.11). The tensile test speed (crosshead speed) was 20 mm/min. From the results, stress versus strain curves were obtained, and the elongation at break, Young's modulus and tensile strength values are calculated. Tensile test was applied to 5 specimens of each composite and the results are calculated by being averaged and reported with their standard deviation values.

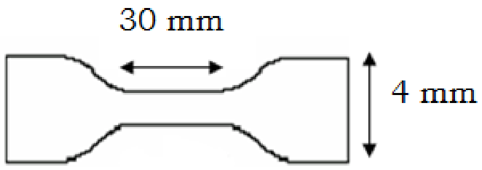


Figure 3.11 A schematic drawing of tensile test specimen

3.2.2.2.2 Impact test

The Charpy impact test (Figure 3.12) is used to determine the strength of material to the impact energy. The test was carried out at room temperature for all sets. The unnotched samples were tested by using a Pendulum Ceast Resil Impactor with 7.5 J pendulum according to ASTM D256 standard. The dimensions of samples were 80 mm in length, 10 mm in width and 4 mm in thickness. The energy per applied area, which is 40 mm^2 (width x thickness) is represented as impact strength. For each composition, the impact test was repeated for 5 specimens. The impact strength value was calculated as the average value of these 5 specimens and also reported with their standard deviations.

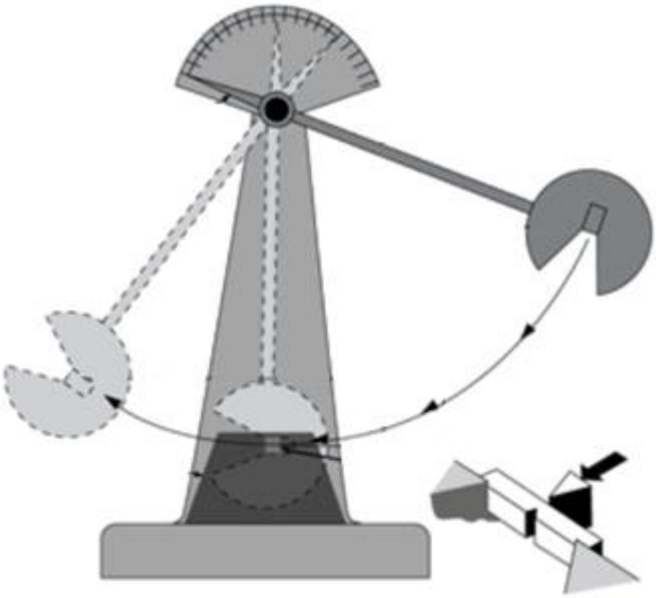


Figure 3.12 A schematic drawing of Charpy impact test and a notched specimen

3.2.2.3 Thermal tests

3.2.2.3.1 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) test was carried out with a Shimadzu DTG-60/DTG-60A machine under nitrogen atmosphere. The samples were heated from room temperature to 800 °C with a rate of 10 °C/min. From the curves of composites, the char yields were calculated, which is an important parameter for flame retardancy. Furthermore, the mass loss, which was observed between 400-480 °C, and decomposition temperature were determined from TGA curves.

3.2.2.3.2 Differential scanning calorimetry analysis (DSC)

The differential scanning calorimetry analysis (DSC) test was carried out by using a SHIMADZU DSC-60 Machine. The samples were heated from room temperature to 300 °C with a rate of 10 °C/min. From the DSC curves of composites, melting temperatures were determined.

3.2.2.4 Morphological tests

3.2.2.4.1 Scanning electron microscopy (SEM) analysis

For morphological analyses two SEM instruments were used: Quanta 400F Field Emission and SEM Zeiss EVO 40 machine. The impact fractured surfaces of polymers are investigated by SEM. Since the PP-based composites of the study are not conductive materials, for SEM analysis they were coated with gold and palladium. The SEM micrographs of polypropylene based composite samples were taken at different magnifications (x1000, x5000, x10000).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Electrochemical Synthesis of Poly(dimethylsilane)

4.1.1 Electrochemical synthesis of poly(dimethylsilane) with supporting electrolyte and solvent

Poly(dimethylsilane) (PDMS(p)) was synthesized from electro-reduction of dichlorodimethylsilane in 1,2 dimethoxyethane (DME) with supporting electrolyte and copper electrodes. PDMS(p) was obtained as dissolved polymer in DME, not on the surface of electrodes. The solution containing dissolved PDMS(p) was evaporated and PDMS(p) was attained as yellowish white powder. Since it was separated only from the solvent, it was possible that it might have some impurities coming from supporting electrolyte and unreacted monomer.

For purification, some traditional methods were examined such as dissolving of PDMS(p) with toluene and precipitating with methanol. However, this method did not succeed since huge amount of polymer loss was observed, because of dissolving of polymer as well as the impurities. Thus, PDMS(p) was used in polypropylene-based composites without purification.

The efficiency of PDMS(p) synthesis was calculated from product/reactant ratio. So, the conversion of monomer to product was found as approximately 35 %. However, the product might include impurities; the yield should actually be less than 35 %.

PDMS(p) was synthesized with supporting electrolyte tetrabutyl ammonium perchlorate (TBAP) in 1,2 DME solvent and obtained as yellowish powder after evaporation of solvent. The synthesized PDMS(p) was characterized by using FT-IR (Shimadzu FT-IR), UV-VIS (ATI-Unicam UV2), ^{1}H-NMR (Varian /Mercury -200 machine) spectrometers.. The morphology of PDMS(p) was observed by SEM (Quanta 400F Field Emission) and the thermal behavior was analyzed by TGA (Shimadzu DTG-60/DTG-60A).

The FT-IR spectrum of poly(dimethylsilane) (PDMS(p)) is given in Figure 4.1. The most distinctive peak is the Si-Cl peak which is observed near 662 cm^{-1} [10]. Elangovan et al. [10] have claimed that, the absence of Si-Cl peak in the FT-IR spectrum of PDMS shows the presence of Si-Si in the main chain. This is obviously an explanation about that the chlorine bonding was removed from the monomer and the desired radicals were created in reaction media.

The peaks at 2963, 2877 cm^{-1} indicate stretching of O-H and C-H. Also the peak at 1473 cm^{-1} is the asymmetric bending of CH_3 to carbon atoms. As mentioned before, poly(dimethylsilane) includes impurities, mostly caused by TBAP, supporting electrolyte. Its FT-IR spectrum is given in Appendix A, Figure A.1 (a) and the FT-IR spectra of PDMS(p) and TBAP is given in Figure A.1 (b) for comparison. The peaks of PDMS and TBAP show similarity. The IR absorption peaks of PDMS are at wavelengths 2963, 2877, 1473 and 1383 cm^{-1}, where as those of TBAP are appeared at 2966, 2878, 1474 and 1384 cm^{-1}.

These peaks of PDMS, most likely belong to IR absorption of TBAP. Also, during the reaction of poly(dimethylsilane), some oxygen joined into reaction of radicals, which is also understood from the peaks at 2963 and 1076 cm^{-1}. The peak at 928 cm^{-1} belongs to Si-H_2 vibration. The peaks at 883 and 802 cm^{-1} are attributed to Si-C stretching. In the study of Elangovan et al. [10], the typical peak is given as 882 cm^{-1} for Si-CH_3. Finally, the Si-Si vibration is appeared at 739 cm^{-1}.

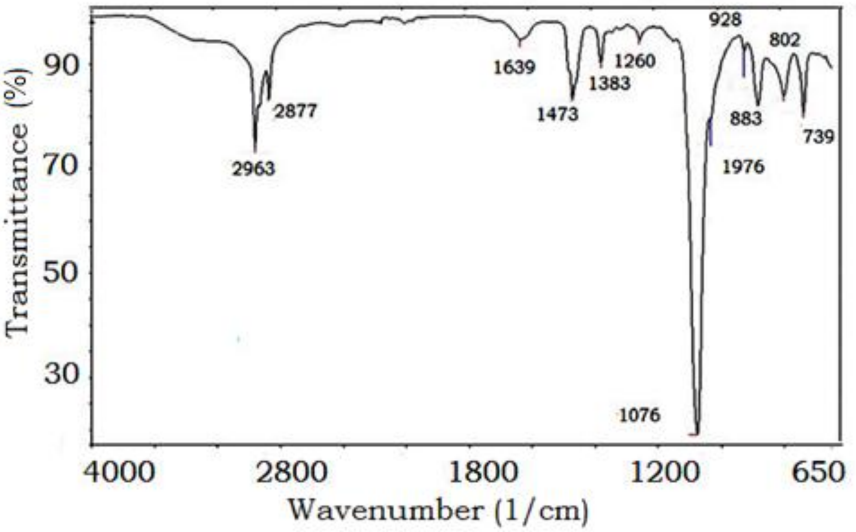


Figure 4.1 FT-IR Spectra of PDMS(p) (in KBr pellet) 2963 (O-H); 2877 (C-H); 1639 (C-C); 1473 (CH_3-C); 1383 (Si-CH_3;); 1260 (C-H); 1076 (Si-O-Si); 928 (Si-H_2); 883, 802 (Si-C); 739 (Si-Si).

The UV-VIS spectrum of PDMS(p) is given in Figure 4.2. The characteristic UV-VIS maximum absorption peaks of organo polysilanes are seen in the range of 280-350 nanometers [110]. The UV-VIS spectrum of PDMS(p) is seen between 317-368 nanometers. These peaks correspond to the trans and gauche states of Si-Si main chain. These results are also similar with those given in literature [10].

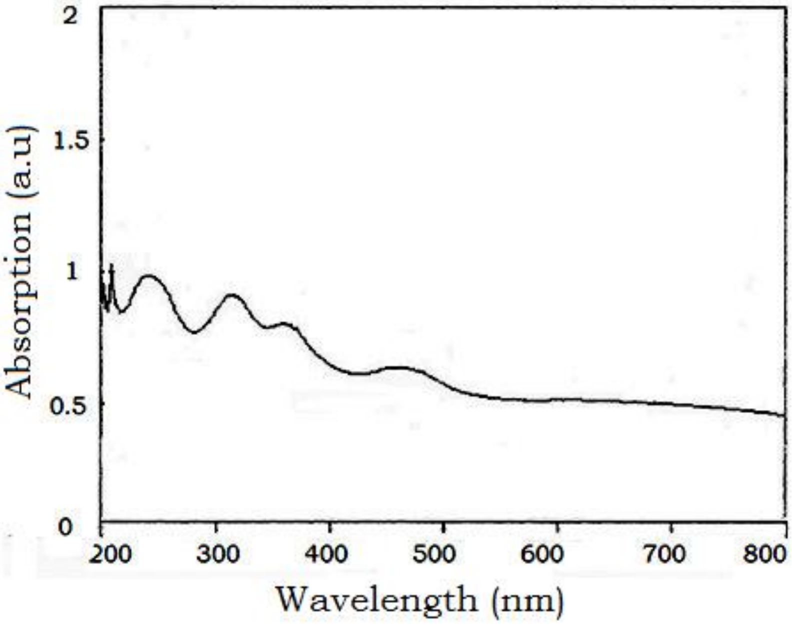


Figure 4.2 UV-VIS absorption spectra of PDMS(p) (in THF)

For further investigations of chemical structure of synthesized PDMS(p), the ^{1}H-NMR analysis was carried out in $CDCl_3$(Figure 4.3). In the study of Elangovan et al. pointed out that the ^{1}H-NMR chemical shifts for methyl groups bonded to silicon are seen between 0-0.04 ppm, methyl protons are seen at 1.009 ppm and Si-Si catenation is at 1.4 ppm [10]. In Figure 4.3, chemical shifts of PDMS(p) are seen at 0-0.044 ppm and they are attributed as $Si-CH_3$. The shifts near 0.976-1.007 ppm are appeared because of methyl protons. The peak at 1.394 ppm is related to Si-Si catenation. In the structure of PDMS(p) is also possible of presence of $(CH_3)_3-C$ groups (at 1.614 ppm) and CH_3-C (at 3.117 ppm) bonds. Also, there are hydrogens bonded to silicon atoms (at 4.993 ppm) within the chemical structure of PDMS(p) The shifts at 0.044, 1.007 and 1.394 ppm are similar to the study of Elangovan et al.

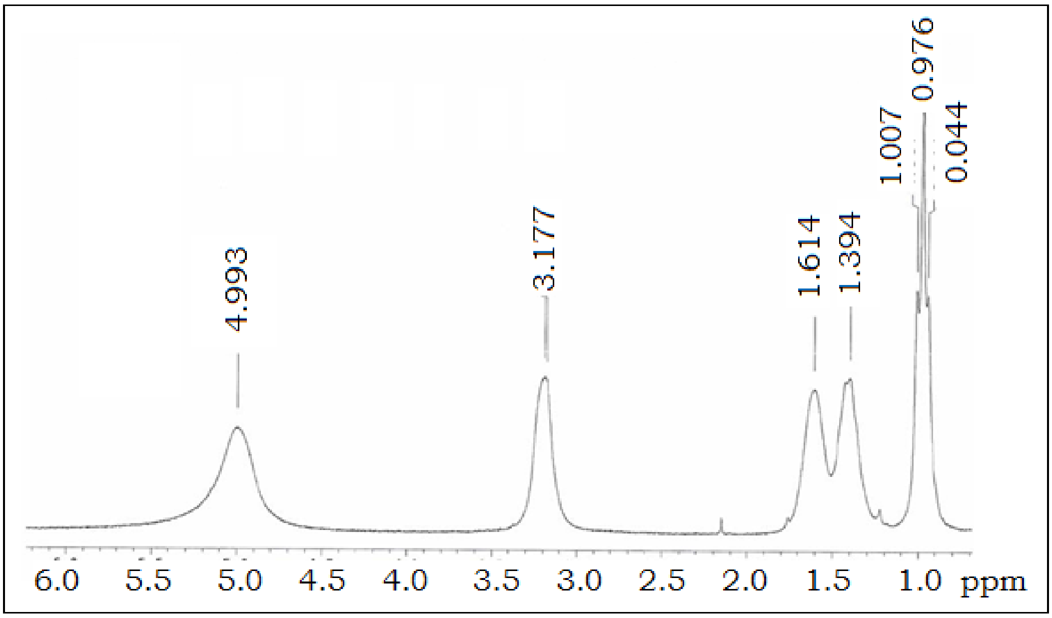


Figure 4.3 ^{1}H-NMR Spectrum of PDMS(p) ($CDCl_3$, δ ppm) 0-0.044 ppm (Si-CH_3); 0.976-1.007 ppm: (methyl proton); 1.394 ppm (Si-Si);-1.614 ppm ($(CH_3)_3$-C); 3.177 ppm: (Si-CH_3) ; 4.993 ppm (Si-H).

The surface properties of synthesized poly(dimethylsilane) are investigated by scanning electron microscope (SEM). The SEM micrographs are taken at 1000, 5000, 10000, 20000 and 40000 x magnifications and given in Figure 4.4.(a)-(e) As it is seen in SEM photographs, the particles of poly(dimethylsilane) tend to accumulate. The particle sizes are not clearly distinguishable. Since poly(dimethylsilane) may have little impurities coming from $LiAlH_4$ (reductive agent) and TBAP (supporting electrolyte), it is also possible that they interrupt the formation of polymeric domains. Also they can hardly be described as flat and oval type particles from Figure 4.4 (c), d) and e).

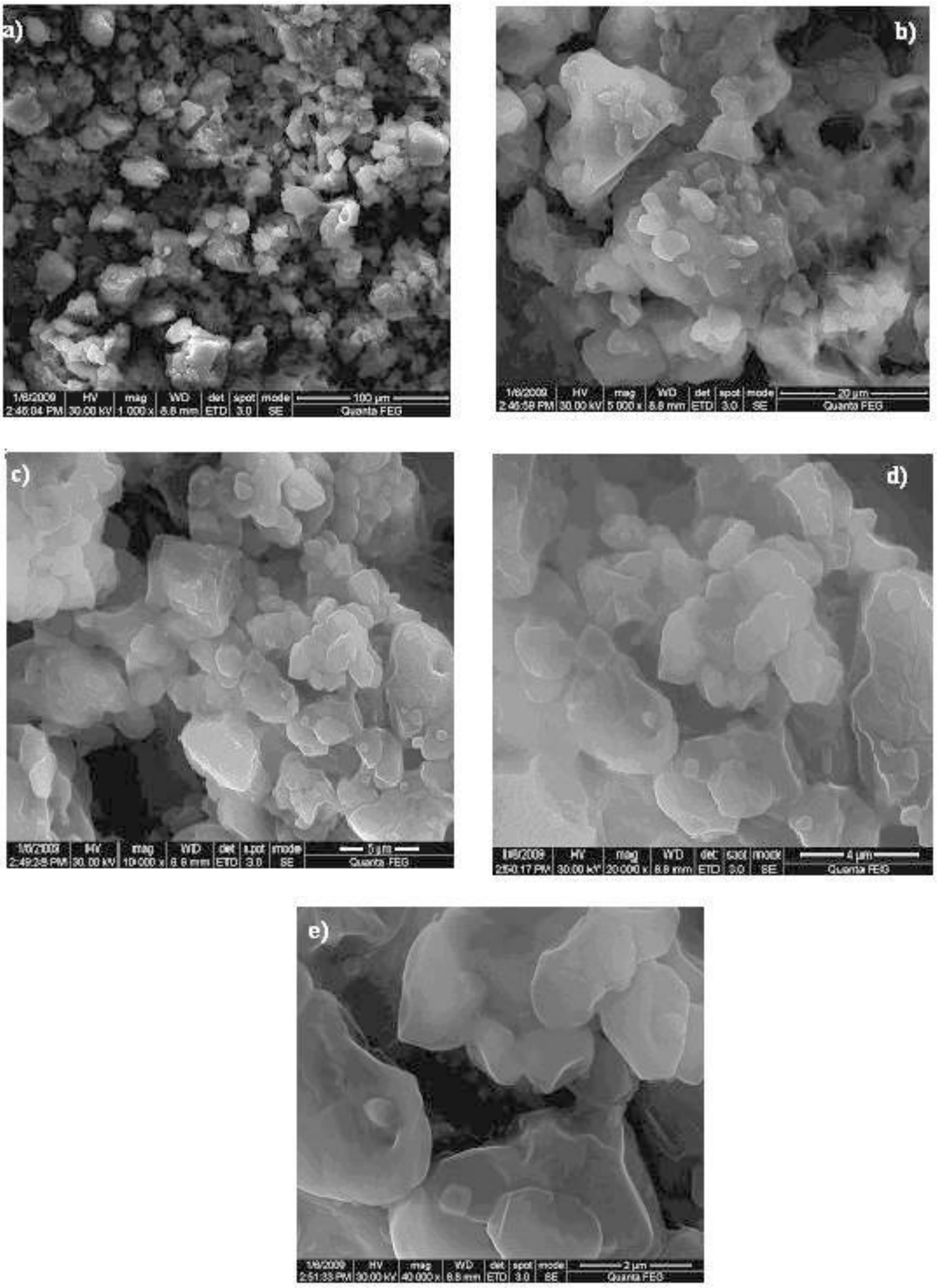


Figure 4.4 The SEM micrographs of PDMS(p) with supporting electrolyte and solvent (a)x1000 (b)x5000 (c)x10000 (d)x20000 (e)x40000 at magnifications

In order to analyze the thermal behavior and weight changes of PDMS(p) during heating, the TGA was applied. The results are seen in Figure 4.5. PDMS(p) begins to loose weight nearly at 50 ˚C. And also it loses 90 wt% of its weight around 260 ˚C. Then the weight of sample did not change till 800 ˚C. Shukla et al. [5] have synthesized the poly(dimethylsilane) by Wurtz coupling method. They also have made TGA for the resulting polymer. They have been observed the weight looses between 212-500 ˚C as 50% loss of polymer weight. The beginning temperatures of weight losses are not similar for both polymers. This may be related to the differences in synthesis methods and the impurities in present PDMS(p). The decrease till 274 ˚C in TGA curve is because of the vaporization of trapped solvent in polymer. At 274 °C, a sharp decrease occurs in weight loss, which can be determined as decomposition temperature of PDMS(p).

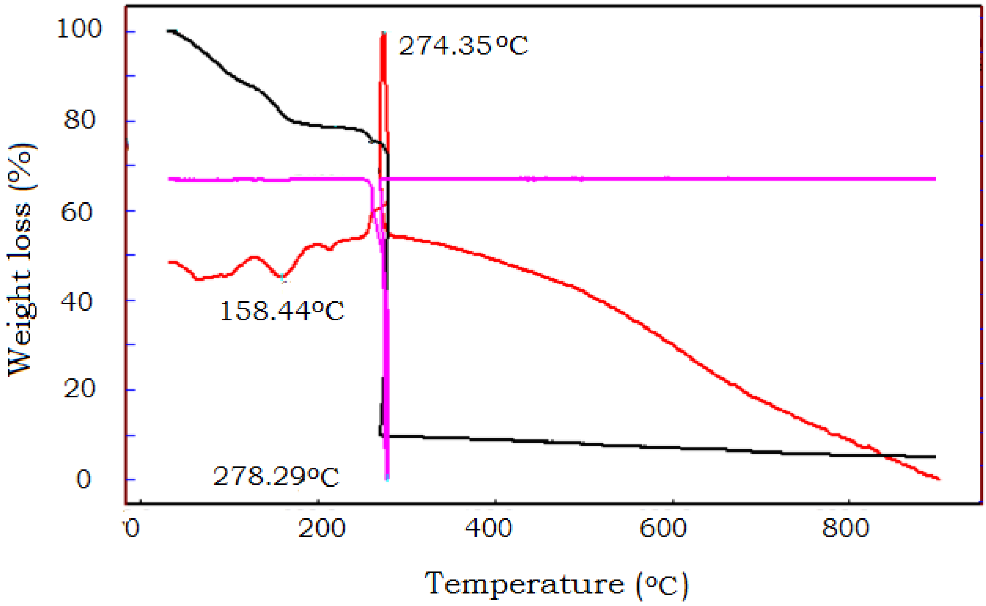


Figure 4.5 Thermogravimetric analysis curve of PDMS(p) (red line: first derivative, pink line: second derivative of TGA curve)

In the first trials of polymerization experiments, PDMS(p) was synthesized as reproducible. The synthesis was repeated for several times and the samples were characterized with the methods which were described above. However, since the polymer was lost at huge amounts after purification, a new method for the synthesis were investigated. The purpose was to obtain the polymer as pure as possible and without including any other materials such as supporting electrolyte, reductive agent or solvent and to get rid of any impurities in reaction medium.

4.1.2 Electrochemical synthesis of poly(dimethylsilane) without solvent or supporting electrolyte

In the present synthesis method, neither solvent nor supporting electrolyte was used for the production of poly(dimethylsilane). The study of Bordeau et al. [22] may be taken as an example. They did not incorporate any solvent in the electrochemical reaction media, however they used hexamethylphosphoric triamide (HMPA) or tris(3,6-dioxaheptyl)amine (TDA-1) as complexing agent and tetrabutyl ammonium bromide as supporting electrolyte, which may be ended as impurities in the final polymer [22]. To the best of our knowledge, the novelty of our study is that poly(dimethylsilane) polymer was synthesized by electrolysis of monomer, dichlorodimethylsilane, without using 1-2 dimethoxyethane as solvent or tetrabutyl ammonium perchlorate as supporting electrolyte for the first time. That is to say, in present polymerization reaction, there were not used any other chemicals, except the monomer. Thus, the resulted polymer is completely pure. The main problem is here about achieving impermeability of atmospheric gas into the system, since even a little amount of oxygen incorporation may cause oxidation and decomposition of monomer. Also, occurrence of free radicals due to the electrolysis tends to react with oxygen rather than themselves, which leads to production of undesired chemical structures in polymer chain. In order to prevent these undesired reactions, the Schlenk line system was used which was available in the Department of Chemistry in the Karadeniz Technical University. Poly(dimethylsilane) was synthesized from electro-reduction of dichlorodimethylsilane. The synthesis was carried out for seven days. After highly viscous fluid formation was observed, the current on the electrodes was cut and the system was opened to atmosphere. Because of involved chlorine gas as side product, the system was kept under sub-atmospheric pressure for 1 hour to get rid of the gas release. The final polymer was obtained in, highly viscous, adhesive and transparent gel-like form. The efficiency of synthesis was calculated as nearly 50%, according to polymer/monomer ratio.

For characterization of poly(dimethylsilane), the FT-IR, UV-VIS, ^{1}H-NMR spectroscopy, TGA and SEM analyses were applied as similar methods to which were carried out for previously synthesized PDMS(p) (with supporting electrolyte and solvent).

The FT-IR spectrum of poly(dimethylsilane) is given in Figure 4.6. The peak at 2974 appears due to C-H vibration. The characteristic bending of CH_3 group to C atoms are seen at 1471 cm^{-1}. The sharp peaks at 1740 and 1080 cm^{-1} indicates that in spite of the Schlenk system, synthesized polymer is still under attack of atmospheric oxygen. However, the intensity of this peak is lower than previously synthesized polymer, which is related to consisting amount of oxygen in polymer. At 813 and 611 cm^{-1} the Si-C and at 540 cm^{-1} Si-Si stretching are observed. Elangovan et al. [10] pointed out that, the absence of the peak at around 662 cm^{-1} indicates that the Si-Cl bonding in monomer disappeared, which shows the formation of desired radicals and also Si-Si catenation. The FT-IR of dichlorodimethylsilane also given in Appendix A, Figure A.2.

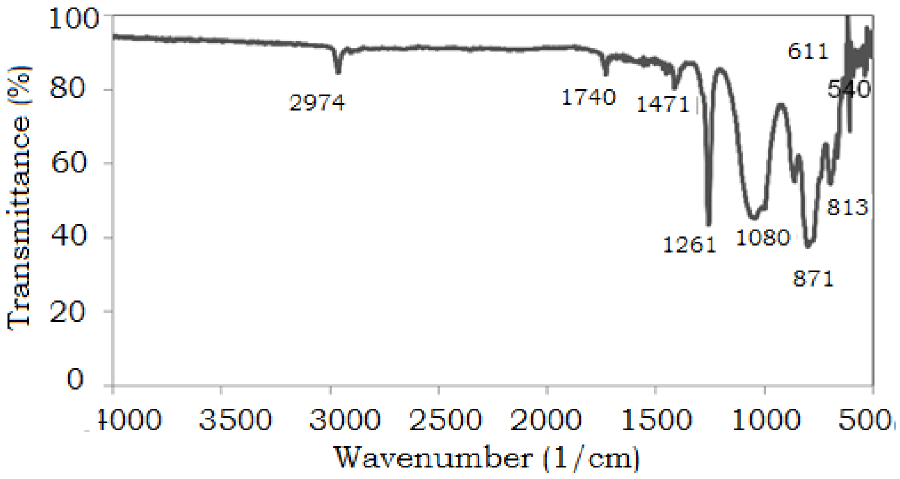


Figure 4.6 The FT-IR spectrum of PDMS (FT-IR/ATR). 2974 (C-H); 1740 (C=O); 1471 (CH_3-C); 1261 (C-H); 1080 (Si-O-Si); 871(Si-CH_3); 813, 611 (Si-C); 540 (Si-Si).

The UV-VIS spectrum of poly(dimethylsilane) is given in Figure 4.7. In this spectrum the absorption is observed between 250-300 nm which can be attributed to the linearity of Si-Si chain [9].

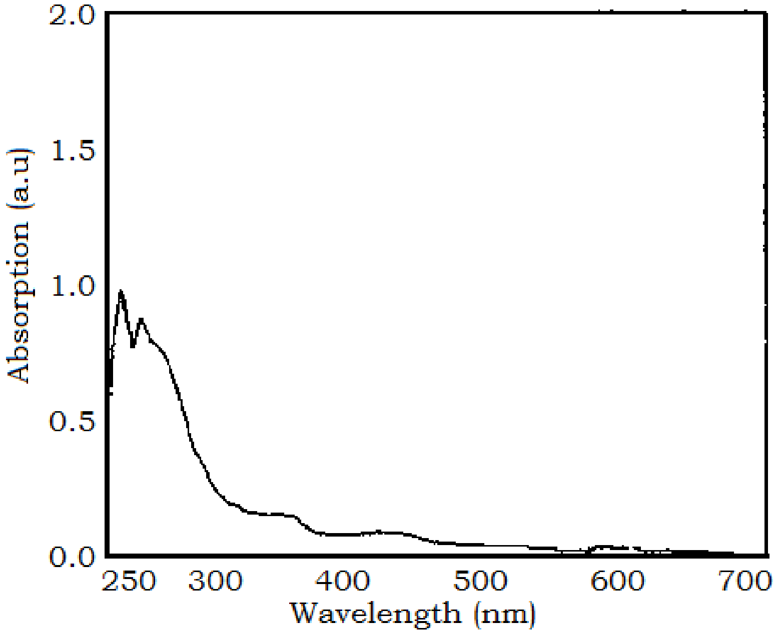


Figure 4.7 UV-VIS absorption spectrum of PDMS (in THF)

^{1}H NMR spectrum of poly(dimethylsilane) is given in Figure 4.8. It is similar to the results in the literature [10]. Elangovan et al. [10] pointed out that the chemical shifts between 0-0.4 ppm attributed to the Si-CH_3 group in the structure. So, the shift at 0.09 is appeared due to this group. They also observed a chemical shift at 1.009 ppm, which indicates methyl proton and in our case it is close to 0.9 ppm.The other chemical shifts are seen near 1.35-1.7 ppm (Si-Si); δ 4.25 ppm (Si-H).

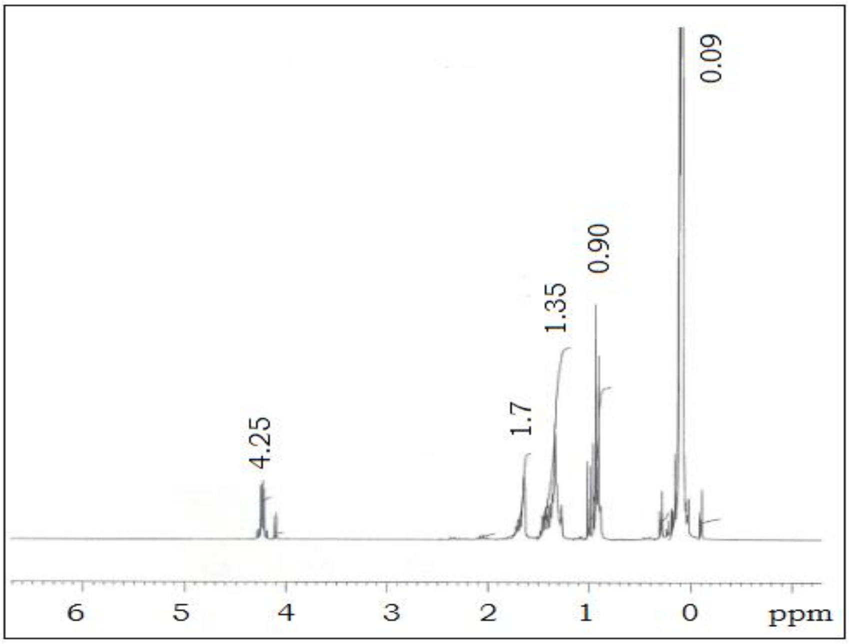


Figure 4.8 ^{1}H-NMR Spectra of PDMS ($CDCl_3$, δ ppm) 0-0.09 ppm (Si-CH_3); 0.9 ppm methyl proton; 1.35-1.7 ppm (Si-Si); 4.25 ppm (Si-H)

Since the poly(dimethylsilane), which was produced without solvent and tetrabutyl ammonium perchlorate as supporting electrolyte, was not stable under electron beams, its surface analysis with scanning electron microscope could not be carried out.

The pure PDMS has a relatively high decomposition temperature which is 548 °C (Figure 4.9). The first weight loss probably belongs to vaporization of water and unreacted monomer in the synthesized polymer. In comparison to previously synthesized poly(dimethylsilane), there is a great increase in decomposition temperature from 270 °C to 578 °C, which also improves the temperature of thermal decomposition of PP-based composites.

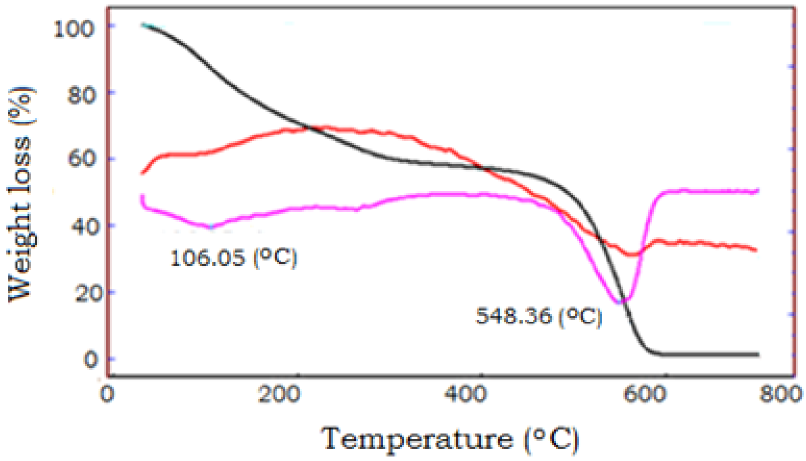


Figure 4.9 Thermogravimetric analysis curve of PDMS (red line: first derivative, pink line: second derivative of TGA curve)

4.2 Flammability, Thermal and Mechanical Properties and Morphologies of Polypropylene/Preceramic Polymer Composites

4.2.1 Flammability properties

4.2.1.1 Limiting oxygen index (LOI) test results

As mentioned before, the linear preceramic polymer, poly(dimethylsilane) (PDMS) was synthesized with two different methods: In the first synthesis method PDMS(p) was synthesized by electrochemical reduction of dichlorodimethylsilane monomer, in a 1,2 dimethoxyethane solvent mixture, which included tetrabutyl ammonium perchlorate as supporting electrolyte. The electrodes were copper and the resulting polymer was obtained in the form of powder with evaporation of solvent.. Since supporting electrolyte and trapped solvent cannot be removed by evaporation, the resulting polymer contained some impurities. Also, the purification caused huge amount of loss of polymer. In the second synthesis method, PDMS was synthesized by electrolysis of monomer only, so that the resulted polymer was pure and in a highly viscous form.

The limiting oxygen index test (LOI) results of neat PP/PDMS composites are given in Table 4.1. Poly(dimethylsilane), which was produced in powder form, was indicated as “PDMS (p)” and other “PDMS” abbreviation shows poly(dimethylsilane) synthesized without solvent and supporting electrolyte.

Polypropylene based preceramic polymer composites were prepared by using a twin-screw extruder. As stated in Chapter 3, for efficient flame retardancy, 20% (w/w) additive should be loaded in polypropylene and similar polymers. According to this information, totally 20% addition has been taken as basis. To achieve a contribution for flame retardancy, triphenyl phosphate (TPP) was added with PDMS(p) as well.

The inherent LOI value of polypropylene was measured as 17.5% (Table 4.1). Adding 1 % (w/w) PDMS(p) into polypropylene has increased the LOI of neat PP from 17.5% to 18.5%. This result obviously shows the flame retardant effect of PDMS(p) into a certain extent. As it is expected, when the concentration of PDMS(p) was increased from 1 % to 5 %, LOI of was increased from 18.5% to 19%. TPP can be used together with Si-based flame retardants. Because phosphorus and silicon elements provide contribution to flame retardancy, when they used together, the LOI value of PP/5PDMS(p)/5TPP was obtained as 19%. During the thermal decomposition of silicon-based additives, silicon dioxide is produced. It provides an insulating silica layer, which protects polypropylene from atmospheric oxygen and also further decompositions [111]. Also, silicon containing additives may act in vapor phase by trapping the flammable radicals, such as OH and H, since Si and CH_3 radicals may release during thermal decomposition of PDMS [112].

Table 4.1 LOI test results of PP/preceramic polymer composites, preliminary experiments

Composite	LOI (%)
PP	17.5
PP/1PDMS(p)	18.5
PP/5PDMS(p)	19.0
PP/5PDMS(p)/5TPP	19.0
PP/10PDMS	20.5
PP/10PDMS/5BP/5MH	21.0

The superiority of novel PDMS was also determined in LOI test. The LOI value of the PP composite with 10% (w/w) highly viscous pure poly(dimethylsilane) has been measured as 20.5%. When compared to PDMS(p)/TPP composites, the pure PDMS itself provided higher LOI value than that of the composite of PP/5PDMS(p)/5TPP (LOI 19%). Pure PDMS seemed also more efficient than PDMS(p), since it could decrease the flammability of polypropylene without addition of any compounds.

Investigation of suitable type and sufficient quantity of additives are crucial for flame retardancy research and development. This procedure mainly depends on experience in our laboratory [80, 91] and theoretical approaches [2-4, 53-58]. As a preliminary experiment, 5% (w/w) magnesium oxide, 5% (w/w) boron phosphate and 10%

(w/w) PDMS were added into PP. In this case the LOI was increased to 21%. These experiments show that there is a tendency of achieving better flame retardancy properties with convenient additives.

Referring to the studies about intumescent systems [2-4], the melamine phosphate (MP) and pentaerythritol (PER) compositions were examined with PDMS addition. The compositions and their LOI test results are shown in Table 4.2. In order to determine the optimum weight ratio of MP/PER, first the composites having 1:1, 3:1 and 1:3 of MP:PER were studied (seen in the first three rows of Table 4.2). The ratios of 1:1 and 3:1 were found out as the best compositions in comparison to 5MP/15PER with LOI value of 21.5%. Addition of 15 % MP together with 5 % PER, has increased the LOI value of neat polypropylene from 17.5% to 29% for polypropylene. The flame retardancy is provided by the elements of nitrogen and phosphorous, in MP. PER only acts as a carbonizing agent. That is why the higher MP loading results in higher limiting oxygen index.

Table 4.2 LOI test results of PP/IFR/preceramic polymer and PP/IFR/inorganic additives composites

Composite	LOI (%)
PP/10MP/10PER	27.0
PP/15MP/5PER	29.0
PP/5MP/15PER	21.5
PP/14.25MP/4.75PER/1BP (BP1)	26.0
PP/12.75MP/4.25PER/3BP (BP3)	22.5
PP/11.25MP/3.75PER/5BP (BP5)	22.0
PP/14.25MP/4.75PER/1AO (AO1)	28.0
PP/12.75MP/4.25PER/3AO (AO3)	25.0
PP/11.25MP/3.75PER/5AO (AO5)	21.0
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	25.0
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	22.0
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	21.5
PP/14.25MP/4.75PER/1PDMS (PDMS1)	24.0
PP/12.75MP/4.25PER/3PDMS (PDMS3)	23.5
PP/11.25MP/3.75PER/5PDMS (PDMS5)	22.5

For other intumescent flame retardant (IFR) composites, MP/PER:1/3 was kept constant and several compositions were studied. Other than PDMS preceramic polymer, poly(methylsilsesquioxane) (PMSQ), which is a preceramic polymer, but with a network structure, was also tried in order to compare the impact of poly(dimethylsilane) on flammability properties of polypropylene. As it is mentioned in previous chapter, there has been a synergism between phosphorus, nitrogen and silicon. Therefore silicon containing additives were added in the presence of melamine phosphate, which contains nitrogen and phosphorus elements.

According to weight ratio of MP/PER:3/1, composites were prepared and tested with limiting oxygen index test instrument. At the first sight, it is obviously seen that when the concentrations of additives (other than MP/PER) increase from 1 % to 5 % (w/w), the LOI value of composites decrease. This is because of the decrease of total IFR loading in composite. IFR systems provide flame retardancy with swelling of char. When any composite containing IFR additives are burned, the formed char is observed as spongy and voluminous. In Figure 4.10, PP/IFR (PP/15MP/5PER) specimens, before and after burning, are seen. The char formed acts as an insulating barrier and prevents the propagation of flame.

Figure 4.10 PP/IFR (PP/15MP/5PER) specimens, before and after burning

The other additives used with IFR systems should support or at least not prevent the swelling of char. Hence, for a good comparison between additives other than IFRs, it is better to deal with composites which include same amount of IFR. Accordingly, the highest LOI value among 1% additive containing composites, belong to the AO1 (80%PP/14.25%MP/4.75%PER/1%AO)) composite. The sequence among the composites containing 1% (w/w) additive and 19% (w/w) IFR can be arranged according to their LOI values from high to low as: AO1>BP1>PMSQ1>PDMS1. The LOI values of all composites are greater than LOI of neat PP, which is 17.5%. Furthermore, addition of 1% (w/w) PDMS into PP/IFR composite resulted in LOI value of 24% and provided a flame retardant composition. The LOI results of composites containing 3% additive and 17% IFR, can be arranged as AO3>PDMS3>BP3>PMSQ3, according to LOI results. It is seen that antimony trioxide (AO is still effective at 3% loading. 3% (w/w) addition of PDMS gives higher LOI than BP and PMSQ. This result also gives the idea of that PDMS is better than PMSQ, even though they both are preceramic polymers. When the total amount of IFR additive in PP composite is 15%, the order of results changed to: PDMS5>BP5>PMSQ5>AO5. The LOI value of composition with AO was determined as 21% for 5% (w/w) addition. However the LOI value of 3% AO in PP/IFR composite was 25%. As a result, the antimony trioxide addition should be 1% or 3% (w/w), because increase in amount of AO, causes antagonism rather than synergism. In PDMS case, the highest LOI value of 22.5% is obtained among all composites having 5% (w/w) additive and 15% (w/w) IFR.

To sum up, it can be understood that PDMS have better impact on flame retardancy than PMSQ. Pure PDMS affects more efficiently than non-purified PDMS. Antimony trioxide is a good synergist with phosphorus as well, but high loadings may affect contrarily to flame retardancy. Boron phosphate helps out to improve flame retardancy similar to PDMS. The LOI values of composites decrease when the total amount of IFR (MP and PER) additives decreases from 20% to 15% (w/w) and the amount of additives (AO, BP, PDMS, BP) increases as 1, 3, 5 % in PP/IFR compositions. This change may be related to the differences in flame retardancy mechanisms between IFR and other additives. The flame retardant impact of IFRs depends on the swelling of char during burning. However, the preceramic additives tend to form a ceramic char, which is quite rigid and non-porous. While burning, the PDMS or PMSQ additives convert to ceramic char and prevent swelling. This is also observed clearly during tests.

For investigations of flame retardancy, there are other important methods such as horizontal burning, vertical burning, etc. Assessing the LOI results with these methods provides more exact comments and consequences on flame retardancy. Also thermal studies give many clues about flammability and thermal properties of materials, in case they are handled together with flammability tests.

4.2.1.2 Horizontal burning test results

The polypropylene based intumescent flame retardant composites were characterized by horizontal burning test. The specimen was ignited under atmospheric conditions when it was placed horizontally and the burning time was then recorded. The burning rate was calculated burning length per burning time. Thus, burning rate shows how much has the specimen burned in a minute. Flame retardancy also provides less burning rate.

First, horizontal burning test was applied to neat PP and PP/MP/PER composites (Table 4.3). Only PP/5MP/15PER composite among the ones containing IFR only presents a burning rate of 21.27 mm/min (Table 4.3). The others did not burn, so the result was reported as not available (N/A). That supports the chosen ratio of MP/PER:3/1 (w/w) is appropriate for further compositions according to horizontal burning results like LOI results.

Table 4.3 Horizontal burning test results of PP/IFR/preceramic polymer and PP/IFR/inorganic additives composites

Composite	**Burning Rate (mm/min)**
PP	21.49 +/- 1.39
PP/10MP/10PER	N/A
PP/15MP/5PER	N/A
PP/5MP/15PER	21.27 +/-3.32
PP/14.25MP/4.75PER/1BP (BP1)	N/A
PP/12.75MP/4.25PER/3BP (BP3)	31.13 +/- 2.58
PP/11.25MP/3.75PER/5BP (BP5)	28.89 +/-3.89
PP/14.25MP/4.75PER/1AO (AO1)	N/A
PP/12.75MP/4.25PER/3AO (AO3)	30.36 +/- 4.37
PP/11.25MP/3.75PER/5AO (AO5)	38.13 +/-2.51
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	20.72 +/-0.69
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	38.31 +/-0.82
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	36.47 +/-2.83
PP/14.25MP/4.75PER/1PDMS (PDMS1)	16.83 +/-2.41
PP/12.75MP/4.25PER/3PDMS (PDMS3)	20.22 +/-2.09
PP/11.25MP/3.75PER/5PDMS (PDMS5)	20.43 +/-5.71

In LOI results, an arrangement from high to low LOI values of composites was done, in order to assess and compare them clearly. When the same arrangement is applied for 1% addition of additives into PP/IFR composition the horizontal burning results seem as: AO1=BP1>PDMS1>PMSQ1 according to from best to less flame retardancy among the studied samples. 1% AO and BP in the PP/IFR composite did not burn under flame. PDMS1 composite burned 16.83 mm in 1 minute, which is better than PMSQ1. For the composites containing 3% additive, the order is PDMS3>AO3>BP3>PMSQ3. When compared to LOI results given in previous section (also it is seen in Table 4.2), the LOI of AO3 composite is higher than PDMS3 composite. However, both composites burn in atmospheric condition and PDMS3 burns slower than AO3. The difference is about 10 mm between their burning rates. The LOI and burning rate is not properly relevant with each other. In other words, LOI gives information about the needed oxygen or atmosphere for burning, whereas horizontal burning provides information about the rapidity of flame propagation. When two materials are ignited at room conditions, the better way to distinguish the materials for flame retardancy is to look at their burning rates. Which means PDMS3 is more preferable than AO3 composite. Also, a material with LOI value of 21% is considered to be as “slow-burning'' material [113]. Also, the materials which have greater LOI value than 25% are “self-extinguishable” in air [114]. Thus, the composites, reported as N/A in horizontal burning test result, have also greater LOI values than 25%.

With the same aspect, the results for 5% (w/w) additive loading are arranged according to their horizontal burning results as: PDMS5>BP5>PMSQ5>AO5. These results are the similar to their LOI test values.

When the horizontal burning test and LOI test have been assessed together, it is obviously found out that, adding 5% PDMS with 15% IFR into PP provides efficient flame retardancy and shows better contribution than other additives. Also for PP composite with 5% BP it is possible to achieve flame retardancy. The amount of AO in PP/IFR composite should not be more than 3% (w/w) according to the difference in its LOI values (LOI of AO3: 25%, LOI of AO5: 21%) PDMS is more suitable and useful for flame retardancy purposes in comparison with PMSQ. In horizontal burning test results, the composite with PDMS have a better performance than PMSQ has (Table 4.3). On the other hand, the LOI results of composites with PDMS are higher than composites with PMSQ, except the composites with PMSQ1 and PDMS1. Both LOI results and horizontal burning results are related with the structures of polypropylene and additives. Polypropylene is a linear polymer containing carbon atoms in its backbone with–CH_3 side groups. The additives loaded into PP, also disperse within PP chains and do not react during polymer processing. The chemical actions occur in vapor phase with H and OH radicals during combustion and can be summed up as follows: Melamine phosphate and boron phosphate yield to form phosphorus oxides, which react with flammable radicals during burning and retard or prevent the propagation of flame. Antimony trioxide forms Sb radicals when used together with phosphorus and these Sb radicals capture flammable ones within the vapor phase. The Si-based additives also release Si and CH_3 radicals during thermal degradation, which reacts with OH and H radicals [112].

4.2.2 Thermal Properties

4.2.2.1 Thermogravimetric analysis (TGA) results

In order to determine the thermal properties of materials under heat, the thermogravimetric analysis is a useful tool. During heating, mass loses of composites are observed and recorded, which give large information about decomposition temperature and char yield of composite. As mentioned before, char yield is an important indicator for efficiency of flame retardants. Char acts as a heat insulator and barrier, so that it protects the material against the further decompositions and further production of free radicals. Furthermore, decomposition temperature is also important as at that temperature the flame propagation and further free radical reactions occur.

TGA results of preliminary experiments are given in Figure 4.11 and Table 4.4. In order to determine the decomposition temperature, the derivative of TGA curve is used. Also, the char yield is reported as the percentage ratio of material amount at 800 °C to that at the beginning of the analysis. The composites with 5%PDMS(p)/5%TPP and 10% PDMS have higher decomposition temperatures than neat PP. However, 1% (w/w) powder PDMS(p) in polypropylene, decreased decomposition temperature of neat PP (see Table 4.4). The decrease may be because of heterogeneous distribution of PDMS(p) within the polymer matrix. When the content of PDMS(p) increase from 1% to 5%, the decomposition temperature increases from 423 °C to 452 °C, however the char yield decreases. The decrease in char yield can be explained with the impurities in PDMS. When the concentration of PDMS(p) increases, the amount of impurities such as solvent and supporting electrolyte, increases as well. During heating, the solvent vaporizes with energy of heat and leaves the system, which causes a decrease in the amount of sample. Since the char yield takes into account the amount of material, which is left in the end of analysis, the char yield value decreases as well. Nevertheless their LOI values do not differ from each other (Table 4.1), since trapped solvent does not influence the combustion mechanism. In other words, the need of oxygen to continue burning is not affected by impurities. Addition of 5% PDMS(p) and 5% TPP (w/w) into PP improves the decomposition temperature of neat PP from 442 °C to 472 °C, however addition of 10% (w/w) PDMS alone, which was synthesized in pure form, increases the decomposition temperature to 473 °C. Pure PDMS seems more efficient than PDMS(p), since it provides better thermal property without using any other additives. Boron phosphate (BP) and magnesium oxide (MH) improve the char yield dramatically, whereas they do not perform well for decomposition temperature which is lowered even less than neat PP. The char yield of pure BP was found as 98% (see Appendix B, Figure B3), when analyzed with the same TGA conditions, so, it contributes to increase the char yield of PP. However, according to flame retardancy mechanism of magnesium hydroxide, it decomposes during heating and releasing water molecules as a result of reaction between OH and H radicals. Also, while $Mg(OH)_2$ helps out for flame retardancy, it lowers the decomposition temperature of polymer [61].

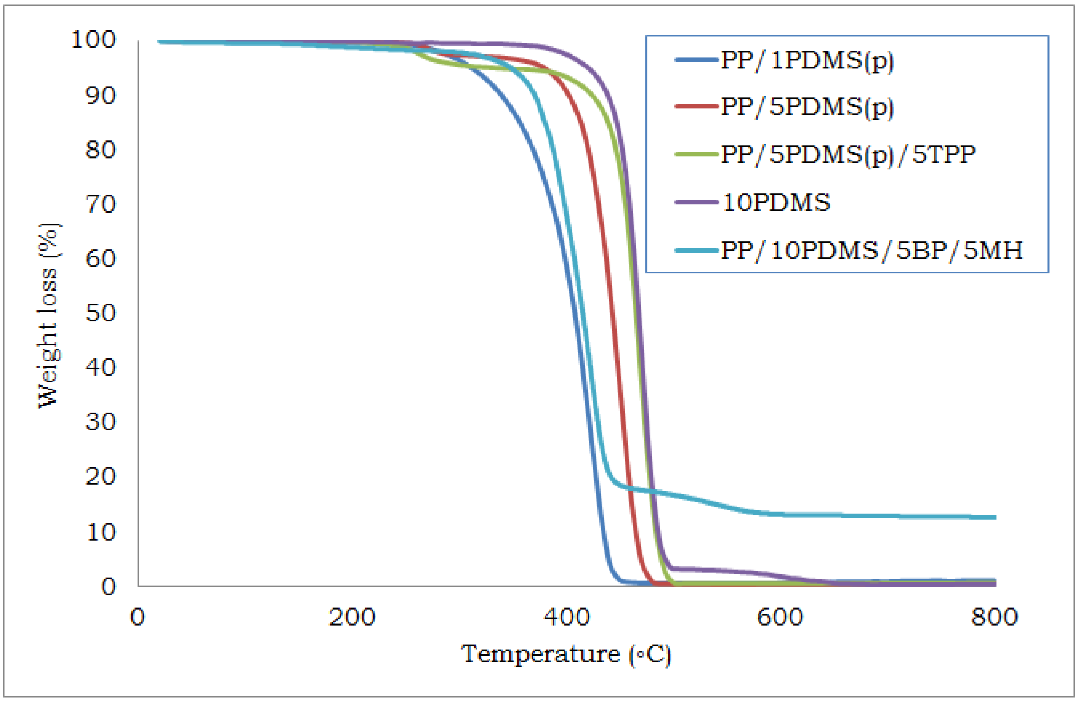


Figure 4.11 The TGA curves of PP/PDMS(p) and PP/PDMS composites (preliminary experiments)

Table 4.4 The decomposition temperatures and char yields of PP/PDMS(p) and PP/PDMS composites (preliminary experiments)

Composite	**Char Yield (%)**	**Decomposition Temperature* (◦C)**
PP	0.1	442
PP/1PDMS(p)	1.2	423
PP/5PDMS(p)	0.8	452
PP/5PDMS(p)/5TPP	0.9	472
PP/10PDMS	0.3	473
PP/10PDMS/5BP/5MH	12.7	423

* Decomposition temperatures are determined by derivative of TGA curve.

In intumescent system experiments, melamine phosphate (MP) and pentaerythritol (PER) were added into polypropylene at different ratios of MP/PER, 1/1, 3/1 and 1/3. Melamine phosphates can form char, generate foam and act as a char forming catalyst at the same time [73] and pentaerythritol (PER) acts as a carbonizing agent [79]. Their impacts on char forming and thermal decomposition are obviously seen in Figure 4.12 and Table 4.5. As it is expected maximum char yield is obtained with 13.5% in the PP/15MP/5PER composite, since the content of MP or char forming agent is highest among them. Also, the carbonizing of polymer is performed well by 15%PER addition in PP/5MP/15PER composite, so that the decomposition temperature was found as 461 °C, since the carbonizing of materials increases the decomposition temperature and makes the materials more thermally stable.

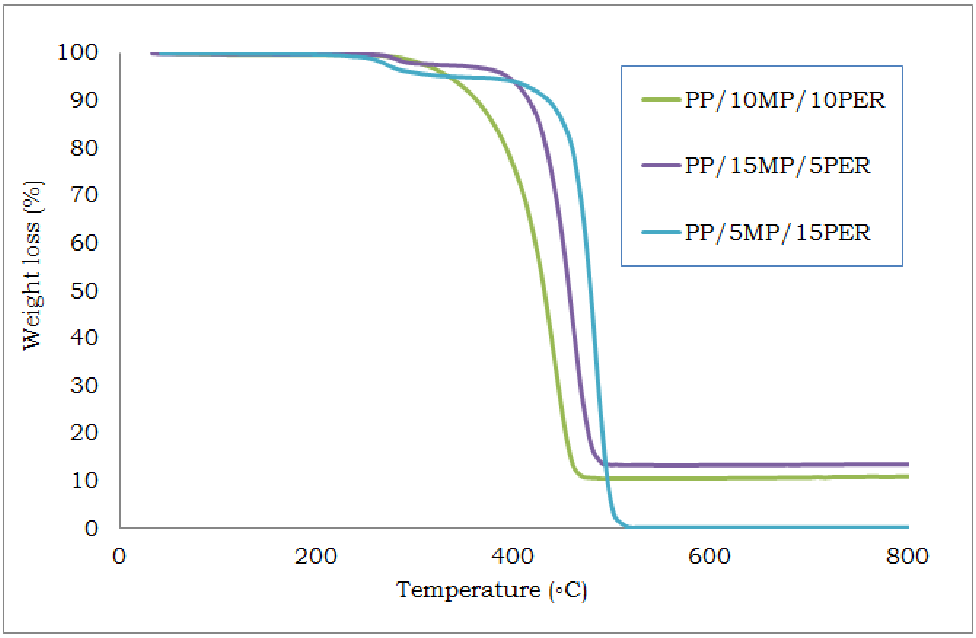


Figure 4.12 The TGA curves of PP/IFR (preliminary) polymer composites

Table 4.5 The decomposition temperatures and char yields of PP/IFR polymer composites

Composite	Char Yield (%)	Decomposition Temperature* (◦C)
PP/10MP/10PER	10.8	444
PP/15MP/5PER	13.5	448
PP/5MP/15PER	0.1	461

* Decomposition temperatures are determined by derivative of TGA curve.

TGA curves of PP/IFR/BP and PP/IFR/AO composites are seen in Figure 4.13. The best char yields are obtained in PP/IFR/AO composites (Table 4.6). Although boron phosphate (BP) and IFR, increases the char yield of PP from 0.1% to 12.7% in preliminary experiments (Table 4.4), it does not affect synergistically with intumescent flame retardants. Also, another important result comes out from these experiments is the proportional decrease in char yields with decreasing total amount of IFR additives. For instance when the BP content is 1% and IFR content is 19%, the char yield results in 9.6% in BP1 (Table 4.6). However in BP5, which contains 5% BP and 15% IFR, the char yield is found as 4.4 %, related to decreasing amount of char promoter, MP, from 14.25%(w/w) to 11.25%(w/w). Also since BP thermally decomposes at higher temperatures than 800 °C (Appendix B, Figure B.3). The decomposition temperatures of BP composites increase, when BP content increases in polymer (from 425 to 467 °C). The AO1 and AO3 composites have nearly the same values both for char yield and decomposition temperature. Also, the highest decomposition temperature is observed in AO5 composite with 462 °C. Since the decomposition temperature of pure AO was determined as 655 °C (Appendix B, Figure B.9), the increasing amount of antimony trioxide, provides an increase in thermal decomposition temperature.

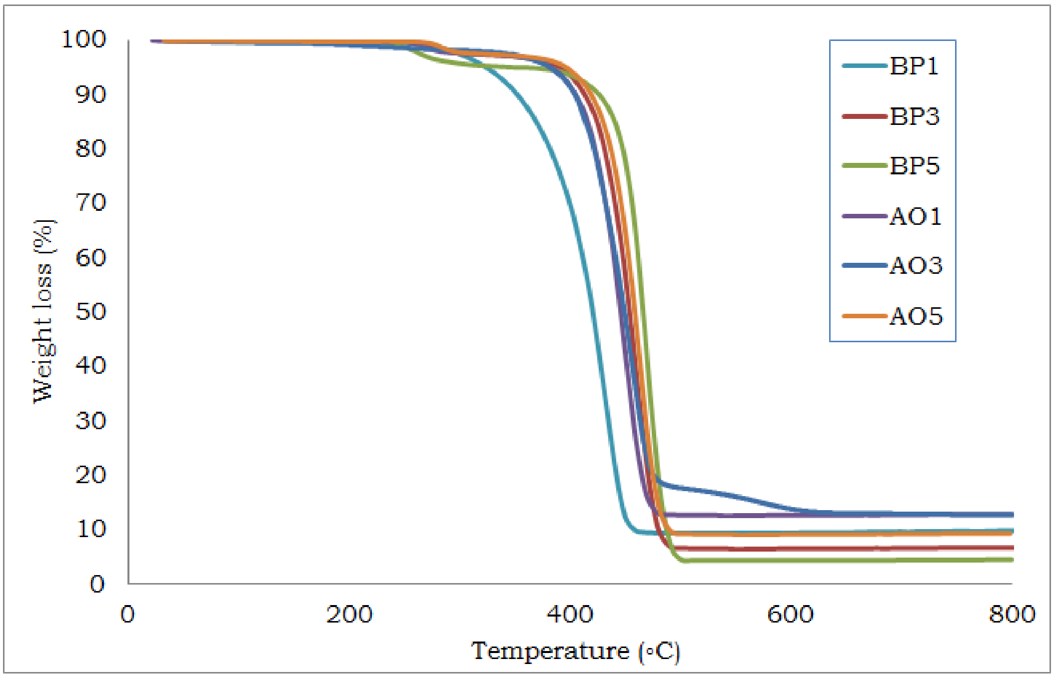


Figure 4.13 The TGA curves of PP/IFR/BP and PP/IFR/AO composites

The TGA results of PP-based IFR composites with preceramic additives are seen in Figure 4.14. Addition of PMSQ improves the decomposition temperature of neat polypropylene due to its preceramic structure. The preceramic polymers are well known with their thermal stabilization effects. Also, it is expected that the thermal decomposition temperature is improved by preceramic polymers for polypropylene [5]. All studies of preceramic composites give higher temperatures of decomposition than neat PP. The best char yield among preceramic polymer composites belongs to PMSQ1 with 12.9%. Alike the BP and AO composites, the decrease in IFR content causes a decrease in char yields as well. According to LOI results, PMSQ1 has a LOI value of 25%, whereas PDMS1 was 24%. This difference may depend on the higher char yield of PMSQ1 than

PDMS1. Also when the PMSQ3 and PDMS3 are compared, their char yields are equal. LOI of PDMS3 may be higher than PMSQ3 since it decomposes at higher temperature than PMSQ3 does. Also the horizontal burning results support the TGA results. Among the whole experiments the highest decomposition temperature is achieved with PDMS5; however its char yield is still low. Both PDMS and MP/PER systems provide thermally stable char. However their mechanisms are different from each other. PDMS converts to a dense and rigid char [70-72], whereas MP/PER tends to convert a voluminous char [2], as it explained in section of flammability tests. This difference between their char formation mechanisms may cause an antagonism.

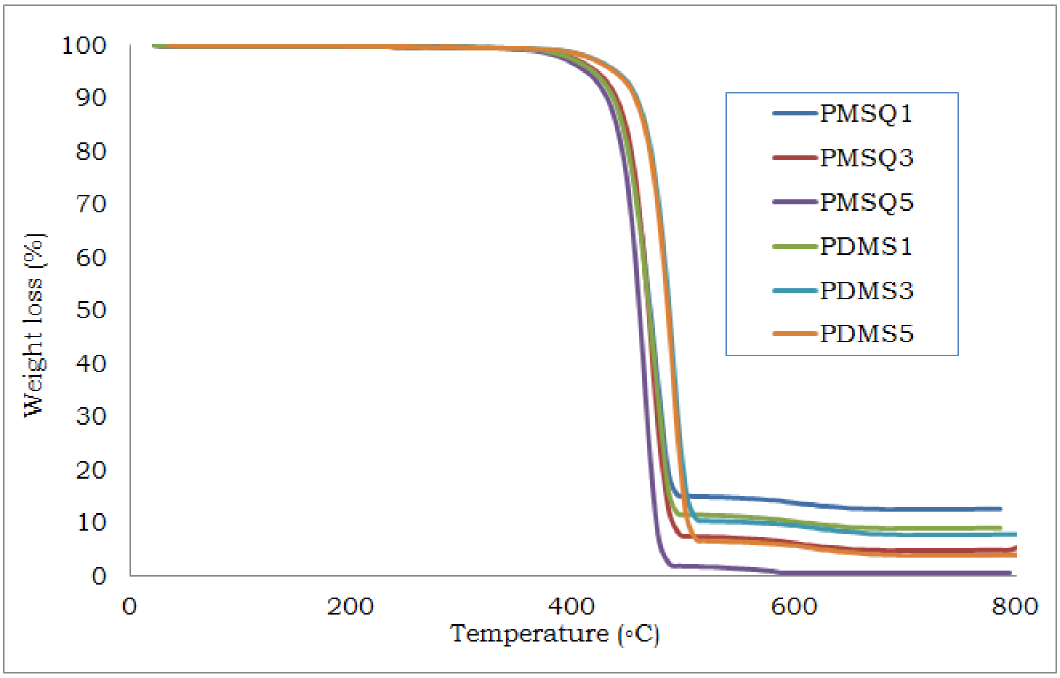


Figure 4.14 The TGA curves of PP/IFR/PMSQ and PP/IFR/PDMS polymer composites

Table 4.6 The decomposition temperatures and char yields of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS polymer composites

Composite	Char Yield (%)	Decomposition Temperature[*] (◦C)
PP	0.1	442
BP1	9.6	425
BP3	6.8	449
BP5	4.4	467
AO1	12.8	444
AO3	12.8	446
AO5	9.2	462
PMSQ1	12.9	469
PMSQ3	5.3	467
PMSQ5	0.9	468
PDMS1	9.0	469
PDMS3	5.3	483
PDMS5	0.9	491

[*] Decomposition temperatures are determined by derivative of TGA curve.

4.2.2.2 Differential scanning calorimetry (DSC) results

The overall results of differential scanning calorimetry tests of all the composites are listed in Table 4.7. It is reported that the DSC analysis gives crucial information about the thermal behavior of composites for the processing, since thermoplastic polymers are processed generally at approximately 10-20 °C higher temperatures than their melting temperatures. If any composite has higher melting temperature than 215 °C (our extrusion profile was 180-215 °C), the additive would not melt in extruder and it may cause increase of the torque obtained in the extruder. During extrusion, such an increase was not observed and the additives are considered to melt at this temperature range. This issue is supported by DSC analysis as well. The melting points of composites in DSC analysis are resulted in lower values than processing temperature in the extruder.

By addition of boron phosphate, the melting point of neat PP increases above 170 °C. Boron phosphate melts around 1400 °C [91]. The highest value among melting points of composites is the result of PDMS5 with 181.1 °C. PDMS5 appears as the most thermally stable material according to the thermal analyses. In TGA analyses of PDMS5, the decomposition temperature was determined as 491 °C, which is the highest temperature among all composites studied in our case. Since PDMS is the precursor of ceramic materials (preceramic), it is expected the materials to have high thermal properties. Preceramic materials convert into ceramic, when they are heated above their decomposition temperatures [12]. According to that when the amount of PDMS in the polymer composite increases, the thermal stability of polymer should increase, too. For both in DSC and TGA results, this proportional increases are seen accordingly.

Table 4.7 The melting temperatures of PP/PDMS preliminary, PP/IFR, PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS polymer composites

Composite	**Melting Point, T_m(°C)**
PP	167.8
PP/1PDMS(p)	170.8
PP/5PDMS(p)	166.5
PP/5PDMS(p)/5TPP	164.5
PP/10PDMS	166.2
PP/10PDMS/5BP/5MH	168.8
PP/10MP/10PER	171.3
PP/15MP/5PER	172.5
PP/5MP/15PER	166.3
BP1	171.6
BP3	172.2
BP5	172.4
AO1	169.2
AO3	170.8
AO5	173.2
PMSQ1	166.8
PMSQ3	166.3
PMSQ5	165.0
PDMS1	169.1
PDMS3	170.4
PDMS5	181.1

4.2.3 Morphological results

The scanning electron microscopy image of neat PP is given in Figure 4.15 at x1500 magnification. The SEM image of base polymer is a reference for comparison to their composites with additives. Thus, the morphological changes caused by additives can be investigated clearly.

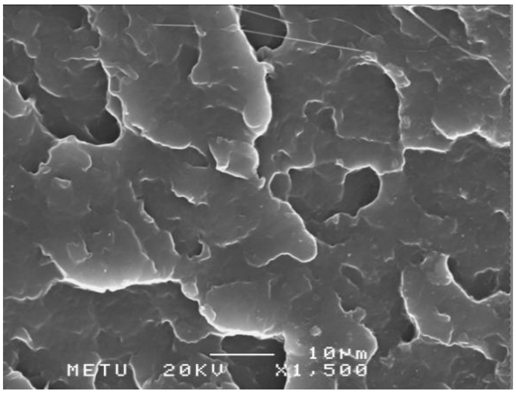


Figure 4.15 SEM micrograph of neat polypropylene at x1500 magnification

The electron microscopy images of preliminary PP/poly(dimethylsilane) composites are seen in Figure 4.16 and the SEM micrographs of pure additives are given in Appendix C. Generally, all of the SEM micrographs seem similar to each other. In the images, the white points indicate the poly(dimethylsilane) particles. Therefore it can be said that PDMS particles are homogenously distributed in PP matrix. In Figure 4.16 (a) and (b), the cross-sections of composites are quite alike, for PP/10PDMS composite, some pores are seen in PP (Figure 4.16 (c)). The pores might be generated because of vaporization of unreacted monomer content in the composite, which comes from poly(dimethylsilane). During extrusion, monomer might be vaporized due to the high processing temperature. There is also a very little mass loss at 173 °C, in derivative of TGA curve of PP/10PDMS. Therefore, the pores are related to unreacted monomer removal.

SEM micrograph of PP/5PDMS(p)/5TPP is given in Figure 4.16 (d). The shape of rectangular prism is the indication of TPP addition. This shape is a characteristic physical property of TPP (Appendix D, Figure D.5) and also analyzed by EDX. In the EDX result, the phosphorous peak is obtained as sharp and intense peak (Appendix D, Figure D.4).. Also, the white spots are seen in Figure 4.16 (e) belong to PDMS polymer and the other structures belong to magnesium hydroxide and boron phosphate. The magnesium peaks are appeared in EDX analysis; however boron peaks are unable to detect with EDX, instead the phosphorus peaks are seen, which correspond to boron phosphate additives (Appendix D, Figure D.5).

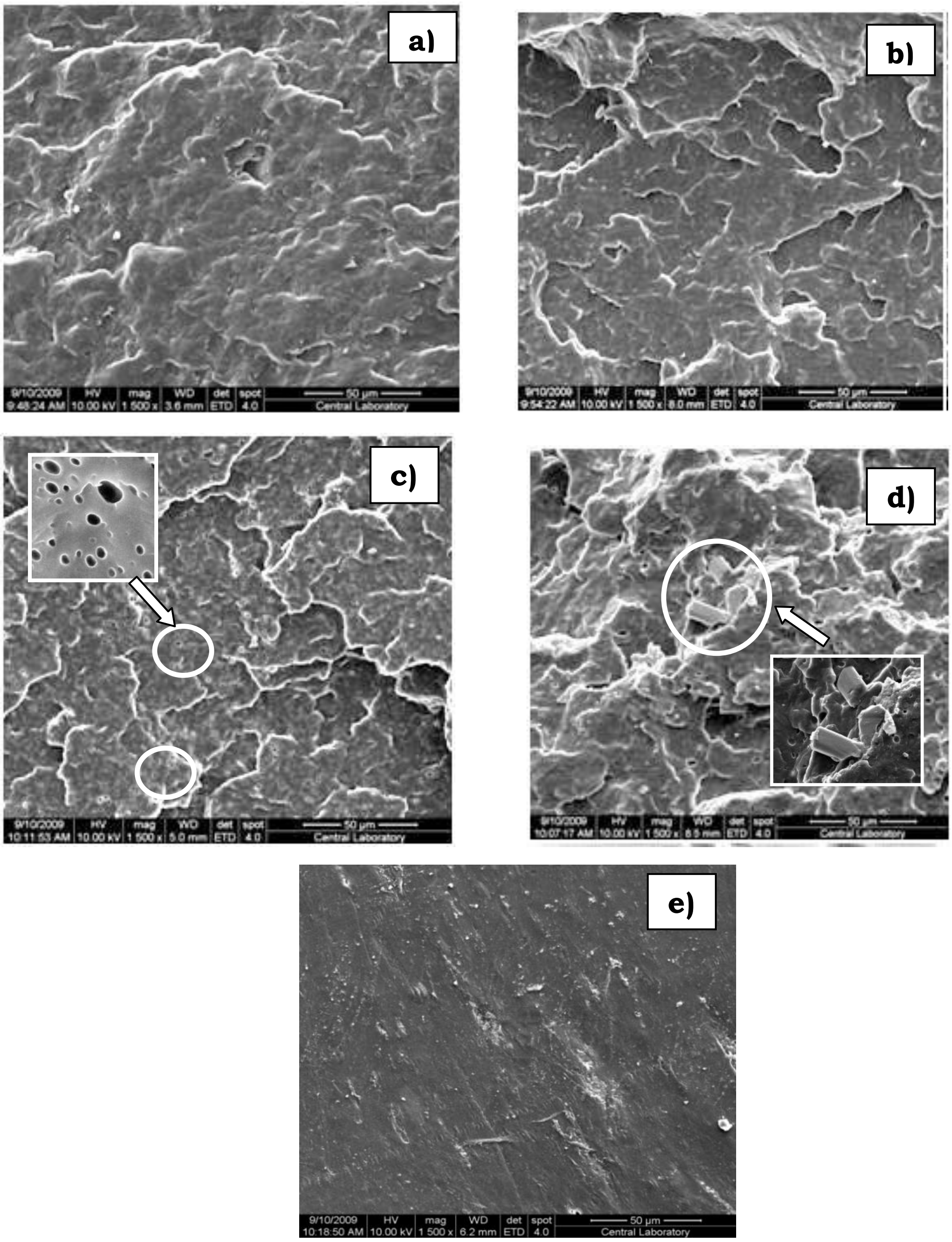


Figure 4.16 The SEM micrographs of preliminary experimental composites at x1500 magnification (a)PP/1PDMS(p) (b)PP/5PDMS(p) (c)PP/10PDMS (d)PP/5PDMS(p)/5TPP (e) PP/10PDMS /5BP/5MH

The PP/IFR composites, prepared with melamine phosphate (MP) and pentaerythritol (PER) additives were also examined with SEM and the micrographs are seen in Figure 4.17. Also, the SEM micrographs of MP and PER are given in Appendix C, Figure C-4 and C-5 as well. The morphologies of both PP/10MP/10PER and PP/15MP/5PER are similar to each other (Figure 4.17 (a) and (b)). Increasing the MP amount in PP does not affect the morphology of composite, however PER did. Some holes in a non-uniform distribution are seen in the micrograph of PP/5MP/15PER (Figure 4.17 (c) and Figure 4.18). According to neat PP, MP and PER micrographs, the particles of PER are more distinguishable in the SEM images of composites (Appendix C).

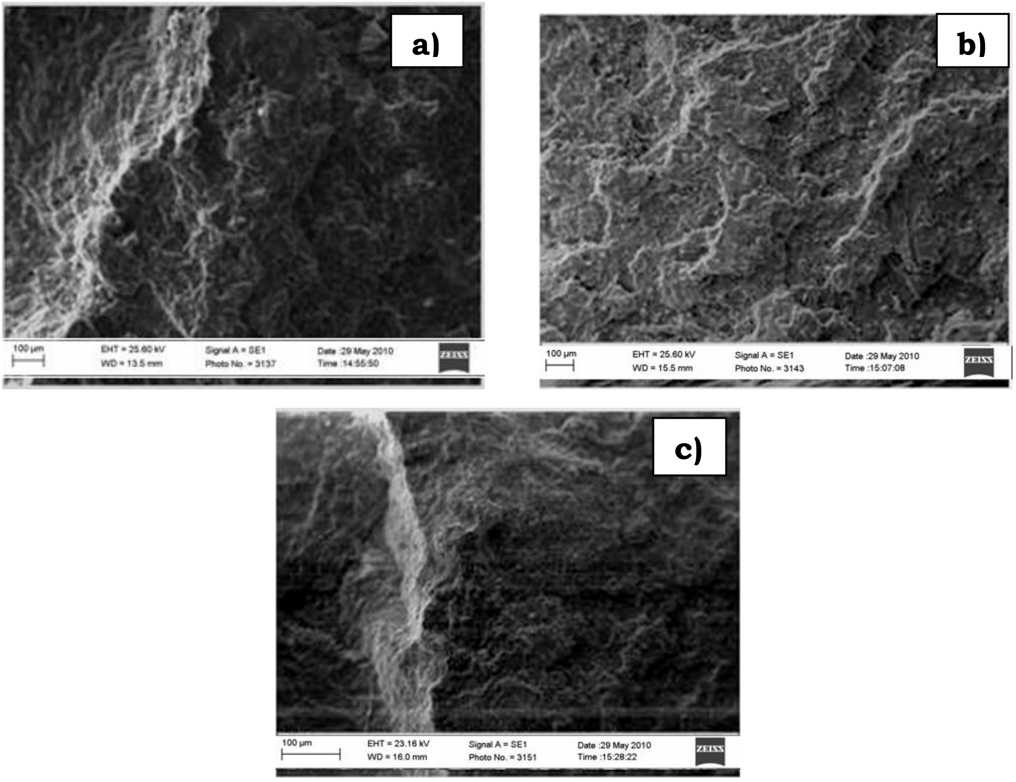


Figure 4.17 The SEM micrographs of PP/IFR composites a)PP/10MP/10PER b)PP/15MP/5PER c)PP/5MP/15PER

The distribution of MP and PER seems homogenous according to Figure 4.18. MP particles are observed as the white spots, determined by EDX (Appendix D, Figures D.1 and D.2). For SEM images, the most featured particle is PER, since its dimension is larger than MP. The PER particles are clearly seen in Figure 4.18.

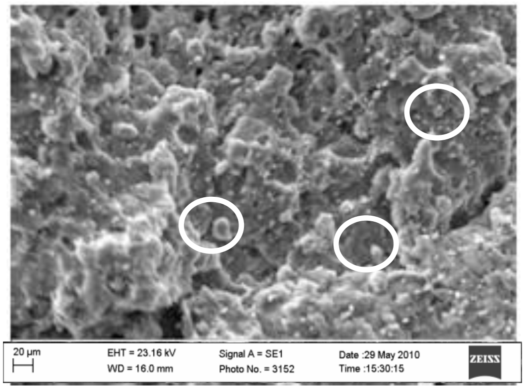


Figure 4.18 The SEM micrograph of PP/5MP/15PER at x5000 magnification (PER marked with circles)

The SEM images of PP/IFR/BP and PP/IFR/AO are presented in Figure 4.19. MP, PER and BP particles are seen in the micrographs of PP/IFR/BP composites. As a reminder, the composites with BP, AO, PDMS and PMSQ contain MP/PER as 3/1 weight ratio. In these SEM micrographs the white spherical particles are obviously seen and their distributions are uniform. The adhesion between additives and matrix is well which contributes to obtain good mechanical properties for polypropylene composites. There are also some agglomerated particles. The smallest white spheres on the rough surface of polymer indicate melamine phosphate, which is analyzed by EDX analysis (Appendix D, Figure D.1).

The relation between SEM micrographs and the mechanical properties is explained in the next sections. In pictures, AO particles are seen as the smallest white spherical particles. Since the AO particles are nano-sized, due to well-distribution within polymer matrix, they are denser than the other additives (Figure 4.19) The AO peaks were also detected with EDX analysis (Appendix D, Figure D.3)

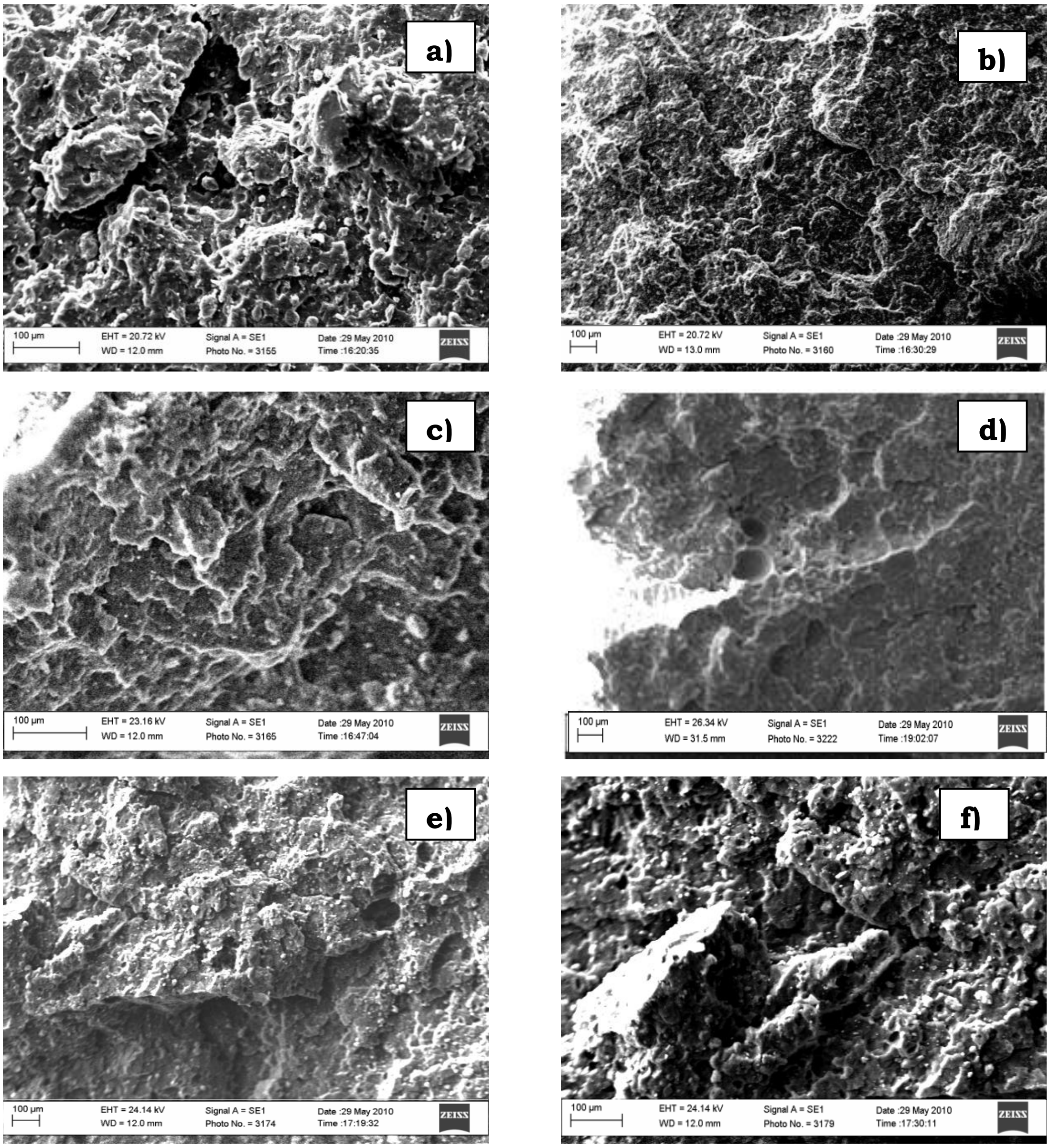


Figure 4.19 The SEM micrographs of PP/IFR/BP and PP/IFR/AO composites (a)BP1 (b)BP3 (c)BP5 (d)AO1 (e)AO3 (f)AO5

The micrographs of the composites of PP/IFR/PMSQ are given in Figure 4.20 (a), (b) and (c). For PMSQ1, the BSD (back scattering electron) detector was used, because the analysis could not be done with SE (secondary electron) detector only for this composite. Poly (methylsilsesquioxane) polymer has a spherical structure (Appendix C, Figure C.1). Its particles are embedded in PP matrix and they were surrounded by PP as it is seen in Figure 4.20 (a), (b) and (c). The particles show non-uniform dispersion within the PP domain. Since these spherical particles may absorb the impact energy applied to composite, the impact strengths are improved compared to the others. In Figure 4.20 (a), there are some cracks on the surface, which may occur as a result of impact test fracture. The pictures, in Figure 4.20 (b) and (c) are similar to each other; also their impact strength values are very close. The impact strength test results are discussed in the coming section. The MP, PER and PMSQ particles are embedded in PP matrix and have a homogenous distribution, that is why they increase the impact strength of neat polypropylene.

There is no significant difference among the morphologies of PDMS composites in Figure 4.20 (d), (e) and (f). Homogenous distribution is observed at this magnification. It is known that PDMS is a linear polymer with Si atoms in the backbone. Theoretically, it is expected to observe an improvement in mechanical properties. This is actually proven by tensile tests of preliminary experiments and PP/IFR/PDMS composites, in the next section of this study.

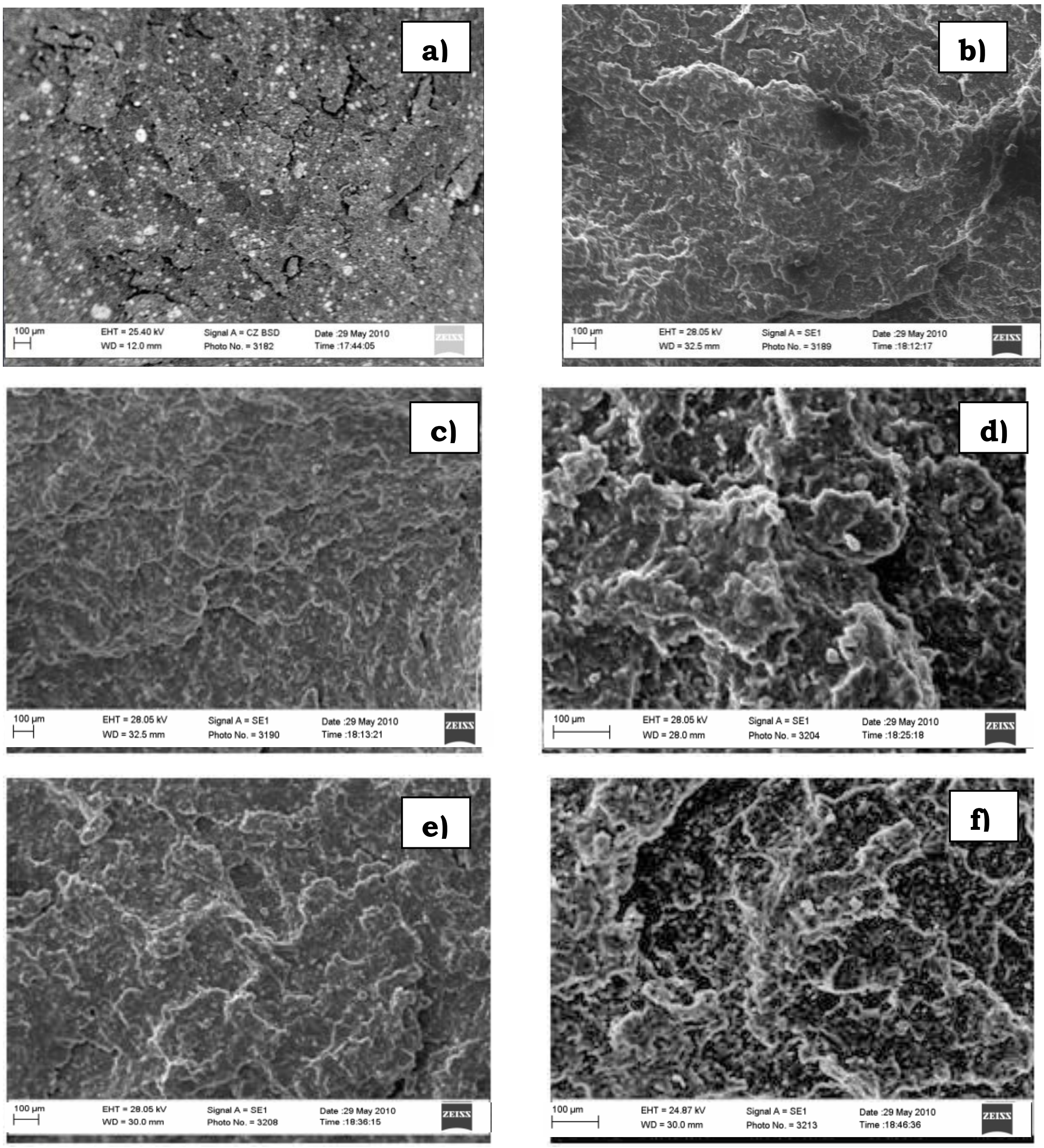


Figure 4.20 The SEM micrographs of PP/IFR/PMSQ and PP/IFR/PDMS composites (a)PMSQ1 (b)PMSQ3 (c)PMSQ5 (d)PDMS1 (e)PDMS3 and (f)PDMS5

4.2.4 Mechanical properties

The aim of this study is to obtain polypropylene composites by using preceramic additives for flame retardancy purposes. On the other hand, the mechanical properties of polypropylene should be preserved with the additives. Since this study aims to develop an improved flame retardant polypropylene composite, the mechanical properties are important for potential applications of polypropylene. Tensile strength and impact strength of polymer give crucial information about polymer processing and application areas. For instance, when the additive decreases the mechanical strength of a polymer, during molding processes, the final product may break and deform. Also, this product has limits for usage area.

4.2.4.1 Tensile properties

In order to determine the tensile properties of polypropylene, tensile test was applied to the polypropylene based composites.

The tensile strength values of PP, PP/ PDMS(p) and PP/PDMS materials from preliminary experiments are given in Figure 4.21 (Appendix E,Table E.1). Tensile strength increases in PP/1PDMS(p) when compared to neat PP from 50.3 MPa to 55.5 MPa. Since PDMS has a linear molecular structure as well as PP has, the polymer chains of both polymers move coherently during stretching. Thus, the addition of PDMS improves the tensile strength of polypropylene. On the other hand, the addition of TPP 5%(w/w) into PP with PDMS 5%(w/w), causes a significant decrease in tensile strength to 37.6 MPa. However, the tensile strength value of PP/10PDMS composite has a greater value than PP/5PDMS(p)/5TPP with a little amount of deviation. For both composites the total amount of additive is 10%

(w/w). The difference between them promotes the idea of linear structure consistence. Nevertheless, except 1% PDMS(p) composite, all the composites shows lower strength under tensile loading. When the total amount of additives is increased from 10% to 20% in PP/10PDMS/5BP/5MH composite, the expected value is much lower than the PP/1PDMS(p), PP/5PDMS(p), PP/5PDMS(p)/5TPP, PP/10PDMS composites. However, the difference is not so significant with PP/10PDMS. As a result, BP and MH addition, even at 10% (w/w) in PP totally, does not cause considerable decreases in tensile properties, whereas TPP does at 5% (w/w) alone. TPP compound has larger domains than BP and MH particles, as it is seen in SEM micrograph of Figure 4.16 (d). Because of its structure, TPP particles may disturb the alignment of polymer chains during stretching. Thus, it creates weak points on polypropylene chains, so that chains become weak and break easily. Also, the decrease can be related to the weak adhesion of additives to PP matrix. It is clearly seen in Figure 4.16 (d) that the adhesion between TPP and PP matrix is not strong enough, since TPP particle is not covered by PP. Therefore, this results in a decrease in tensile strength.

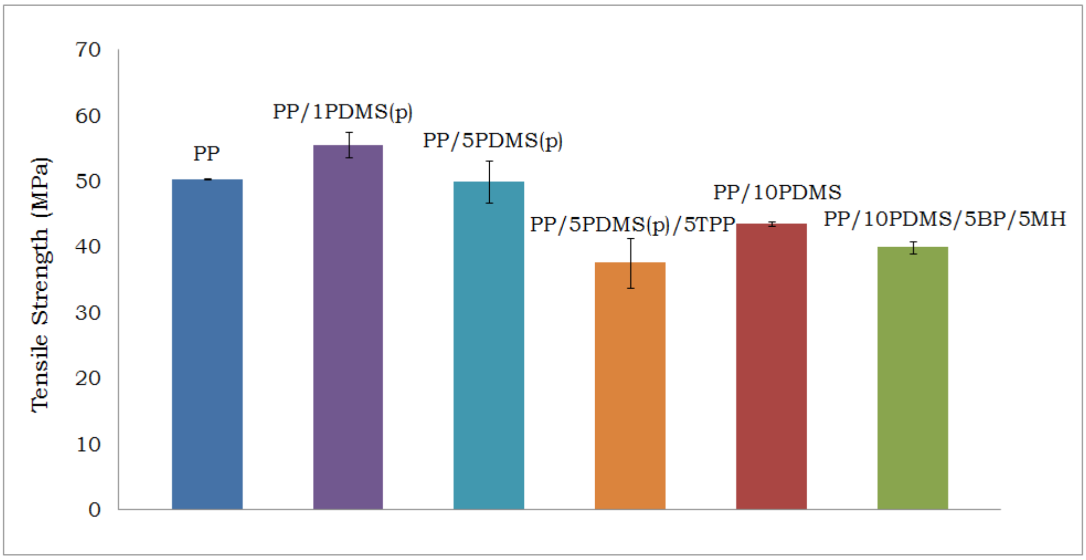


Figure 4.21 Tensile strength values of PP/preceramic polymer composites (preliminary experiments)

Elastic modulus values of PP and PP/preceramic polymer composites are shown in Figure 4.22 (Appendix E, Table E.2.) Elastic modulus of polypropylene, which is measured as 735 MPa, is improved in all the composites. At the first sight, the trend of graph seems to that of with Figure 4.20. 1% (w/w) PDMS(p) powder addition, results in about 30% increase in neat polypropylene, from 735 MPa to 945 MPa. In the composite of PP/5PDMS(p), elastic modulus is quite close to PP/1PDMS(p) with 921 MPa and again greater than neat PP. The addition of TPP decreases elastic modulus of PP/5PDMS(p) as that it is observed in tensile strength behavior. The same reasons, which are explained for the decrease of tensile strength caused by TPP, can be related with elastic modulus results. As a reminder, TPP has larger particles and low adhesion with PP matrix. That causes a loss in mechanical properties such as tensile strength and elastic modulus. The highest elastic modulus value is obtained in

PP/10PDMS/5BP/5MH composite. Boron phosphate (BP) and magnesium hydroxide (MH) increase the elastic modulus value of PP/10PDMS from 871 MPa to 1067 MPa. When it is compared with neat PP, elastic modulus increases about 45%. This can be attributed to the possible higher moduli of BP and MH.

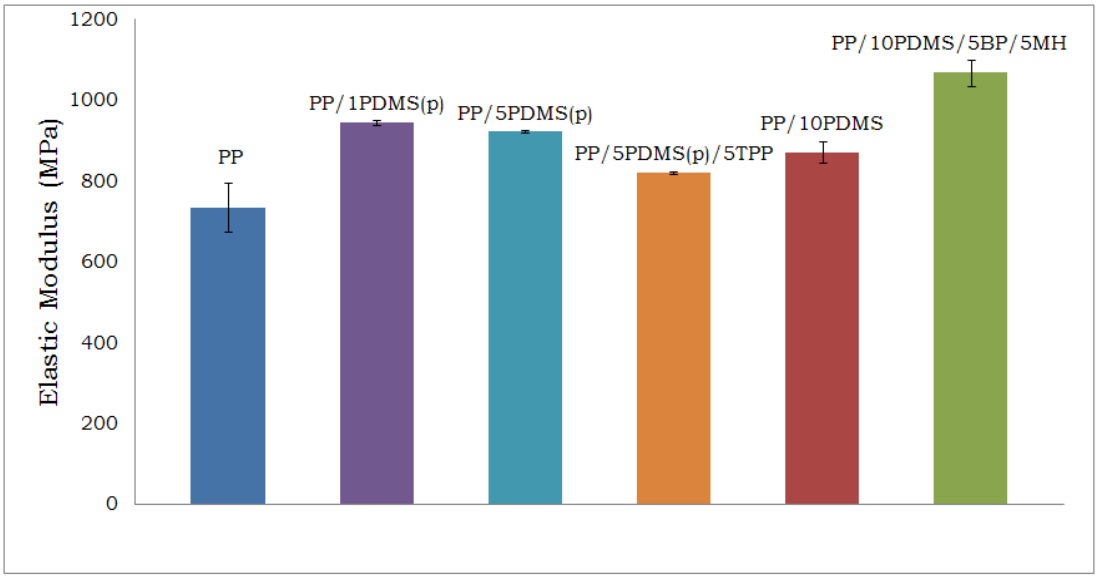


Figure 4.22 Elastic modulus values of PP/preceramic polymer composites (preliminary experiments)

Another important property, which is gathered from tensile test, is elongation at break values. Decrease in elongation property of polypropylene is obtained for all the composites studied (Appendix E, Table E.3). While stretching polymer, the polymer chains, which are mainly in spaghetti form, start to align and become more ordered. During this process, the polypropylene chains may be disturbed by particles of additives. As a result of the friction between additive particles and polymer chains, there occur some weak points, which tend to break down. Therefore, the similarity between chemical structure of additive and base polymer is very important in elongation. For instance, in Figure 4.23 the decrease of elongation at break of polypropylene from 765% to 524% is obviously seen even at 1% PDMS(p) addition. The analogous result exists in PP/5PDMS(p) and PP/5PDMS(p)/5TPP as well. The superiority of pure PDMS, which is synthesized without any supporting electrolyte and solvent, is seen in elongation of break with a value of 707%. Also, this is the highest value among all the preliminary composites. Since PDMS(p) includes impurities, the decreases in this property are reasonable. Despite the fact that PP/10PDMS provides higher elongation at break values, addition of BP and MH compounds causes a significant decrease, since they are disturb the polymer chains (both of PP and PDMS) and prevent the elongation.

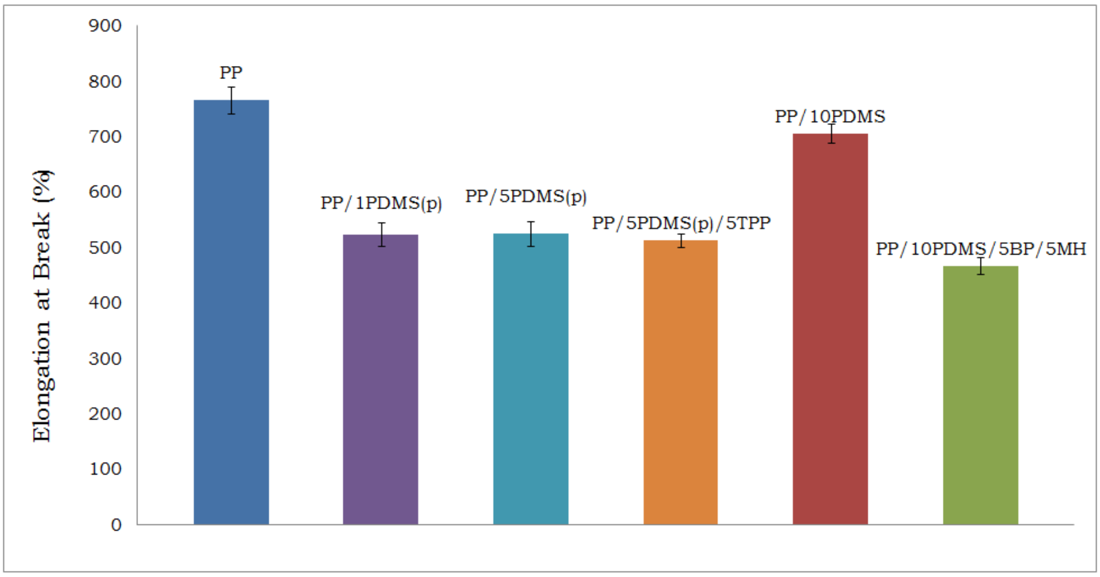


Figure 4.23 Elongation at break values of values of PP/preceramic polymer composites (preliminary experiments)

When all the tensile test results of preliminary experiments are assessed together, the composite with optimum tensile properties can be mentioned as PP/10PDMS. To sum up, 10% (w/w) PDMS addition into polypropylene has resulted in the following tensile properties: For tensile strength, PP/10PDMS:44 MPa versus PP: 50 MPa; for elastic modulus, PP/10PDMS: 871 MPa versus PP: 735 MPa and for elongation at break, PP/10PDMS: 707% versus PP: 766%.

Zhang and Horrocks [78] claimed that the additives might cause losses in mechanical strength and based on previous researches in literature, they have offered to load the additives maximum at range of 15-20% (w/w) into base polymers. In this study, in the coming experiments the total loadings of additives were kept at 20% (w/w) in polypropylene. Tensile test was carried out with PP/IFR composites as well (Figure 4.24). As a reminder, according to flammability tests, the MP/PER : 3/1 (w/w) composition was chosen as the best composite among the other IFR composites. The tensile strength results of the composites are lower than that of neat PP, as it is seen in Figure 4.24 (Appendix E, Table E.1). The decrease is about 20% for all the MP/PER compositions. Similar 20% decrease has been seen in PP/5PDMS/5MH/5BP composite as well. This is related to presences of relatively high amounts of additives, which cause weakness and irregular stress distribution in polymer.

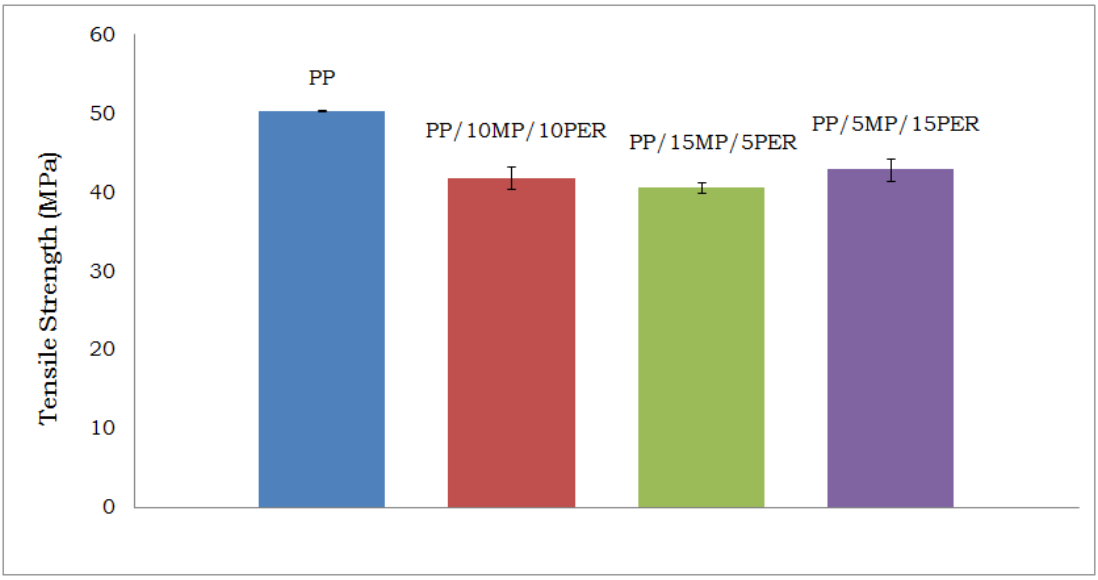


Figure 4.24 Tensile strength values of PP/MP/PER composites

When the elastic modulus values of PP/MP/PER composites are examined (Appendix E, Table E.3), it can said that the additives improved the elastic modulus of polypropylene dramatically (Figure 4.25). As it is seen in Figure 4.25, the increase in MP loading in PP matrix, cause a decrease in elastic modulus compared to PP/MP/PER composites. This trend appears in tensile strength results as well (Figure 4.24). That may be related with the uniform distribution of MP particle within the PP domain. The highest elastic modulus result was obtained for PP/5MP/15PER with 54% improvement, which means an increase from 783 MPa (neat PP) to 1692 MPa (PP/5MP/15PER).

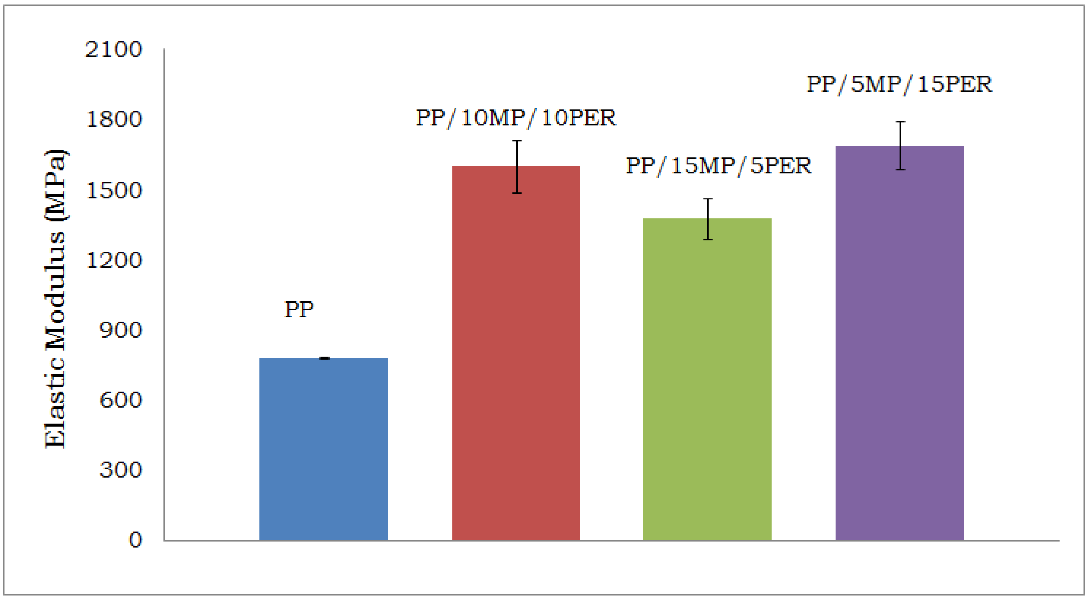


Figure 4.25 Elastic modulus values of PP/IFR composites

Lv et al. [2] have claimed that the IFR systems have some drawbacks such as being sensitive to moisture and not being able to compatible within the base polymer matrix. Thus, they tend to decrease the mechanical properties of polymer [2]. This is understood clearly, from Figure 4.26 in elongation at break values. Neat polypropylene has 765% elongation at break value, whereas PP/10MP/10PER and PP/15MP/5PER could not achieve even 100% elongation level.

In the SEM micrographs, the fractured surfaces of PP/10MP/10PER, PP/15MP/5PER and PP/5MP/15PER are given (Figure 4.17 (a) -(c)) The analogy between the mechanical test results of PP/10MP/10PER and PP/15MP/5PER can be related to their similar morphologies as well.

Although according to tensile test, the best MP/IFR composite was found as PP/5MP/15PERregarding to the flame retardancy aim of this study, the 15MP/5PER is chosen as optimum concentration. And it is expected that PP/15MP/5PER should recover its mechanical properties into a certain extent due to PDMS and/or other additives.

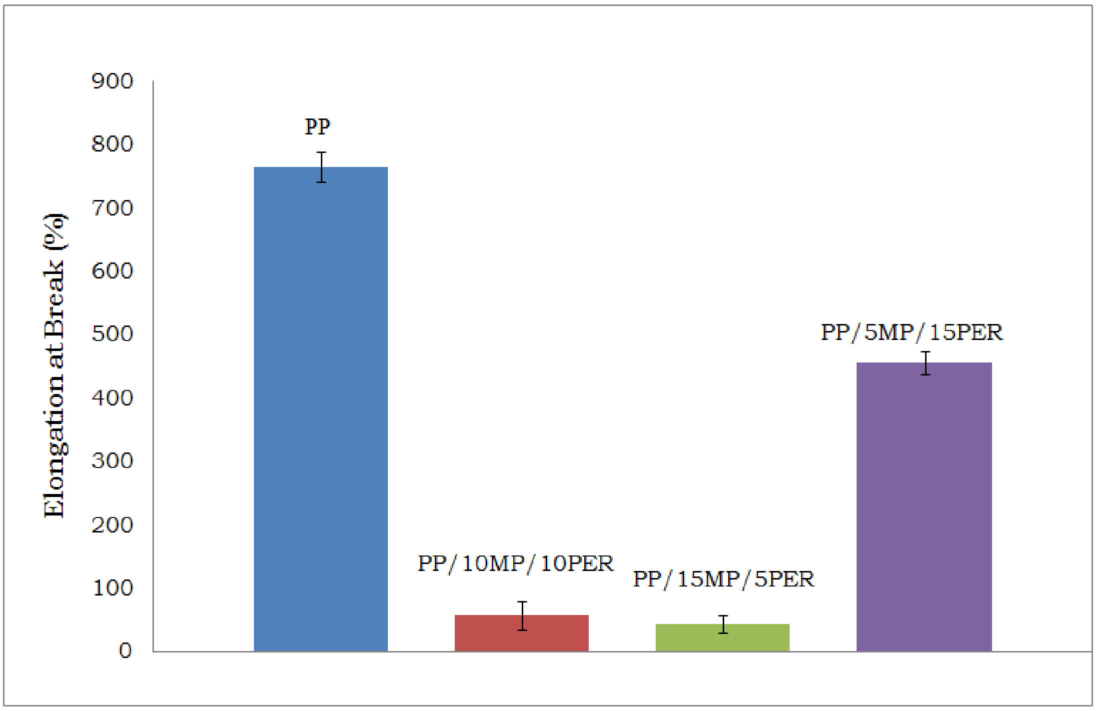


Figure 4.26 Elongation at break values of PP/IFR composites

As mentioned above, the optimum MP/PER ratio is chosen as 3:1 according to flammability test results. PP/15MP/5PER has an LOI value of 29% and does not burn in air atmosphere according to horizontal burning test. Tensile stress at break values of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS are given in Figure 4.27. The tensile strength values of these composites are lower than neat polypropylene, since the additives form agglomerates, whichdisturb the alignment of polypropylene chains under tensile loading and lower the mechanical strength of polypropylene. The level of decrease is about 28%. There is not a distinguishable difference between the tensile stress at break values of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS composites.

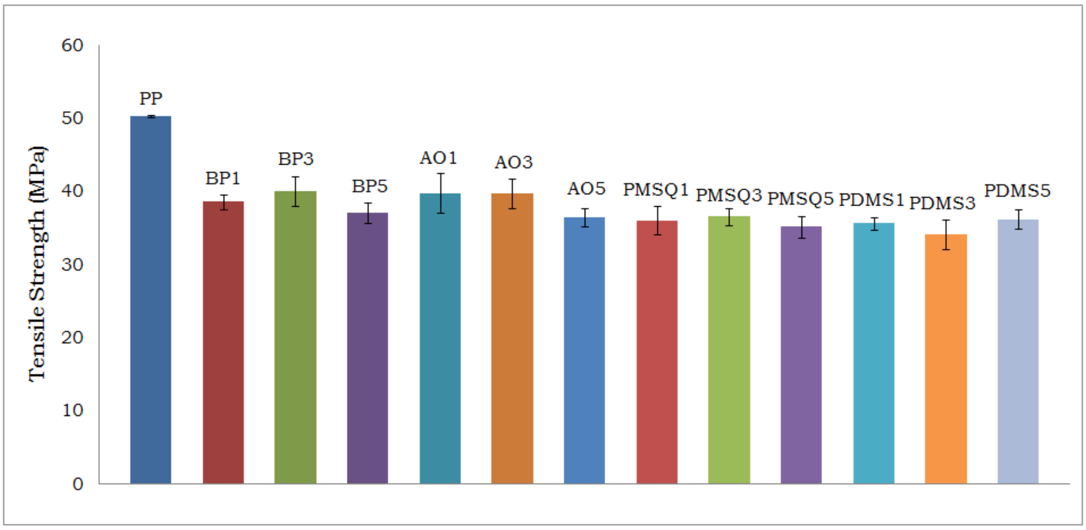


Figure 4.27 Tensile stress at break values of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS

It has been confirmed that the additives used in polypropylene based composites cause an increase in the elastic modulus of PP. Likewise, the composites prepared with different percentages of IFRs together with BP, AO, PMSQ and PDMS improve elastic modulus of polypropylene, as it is seen in Figure 4.28. By addition of 1% (w/w) AO and BP, elastic modulus of polypropylene is substantially increased. That may be because of the high elastic moduli of these additives. When the amounts of AO and BP in PP are increased from 1% to 5% by weight; the elastic modulus values of AO1 and BP1 decrease. In that case, it is probably because of higher agglomeration at higher additive loading. In case of PMSQ, the addition of 5% PMSQ to IFR composite causes a decrease in elastic moduli when compared to PMSQ1 and PMSQ3. As reported before PMSQ is nano-sized (Appendix C, Figure C.1). Thus there exists higher agglomeration at 5% PMSQ, which indicates lower degree of dispersion in matrix. On the other hand, addition of PDMS improves the elastic modulus of PP much less, when compared BP, AO and PMSQ composites. But, there still exists certain improvements with PDMS. The PDMS has analogous polymer chain structure to PP, since it has linear structure and CH_3 groups bonded to Si backbone. PDMS seems a compatible additive with polypropylene in case of mechanical tests. .As concentration of PDMS increases elastic modulus values, decrease due to agglomeration occurring in the structure.

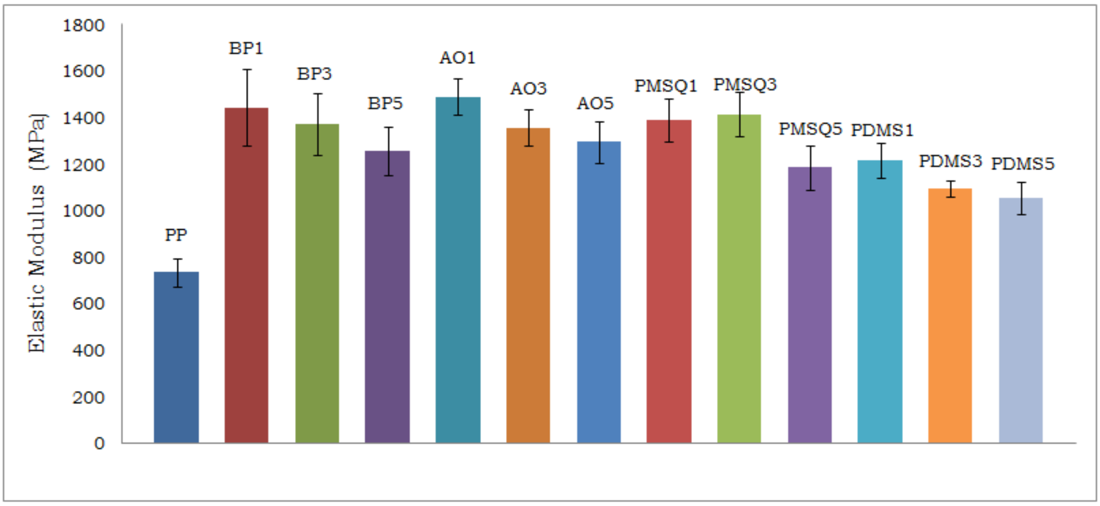


Figure 4.28 Elastic modulus values of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS composites

As it is seen in Figure 4.29, the most distinctive diversity was in elongation at break values among tensile properties of PP/IFR/additive composites. At the first sight, the dramatic decrease of AO composites is very remarkable. The elongation at break values of AO1, AO3 and AO5 are measured as 53%, 65% and 48%, respectively, which are lower than of all others, because of extensive distribution of AO particles in PP matrix (SEM micrograph, Figure 4.18 (d), (e) and (f)). Its distribution disturbs the alignment of PP chains during stretching in tensile test, which causes a decrease in that property. In case of BP, it is found that, increasing BP content in PP has a positive impact on elongation at break values. Nevertheless, this impact might be related to the decreasing IFR content in PP. Oppositely, the increasing amount of PMSQ in PP (1; 3; 5% (w/w)), results decrease in break values for these composites. PMSQ is a polymeric additive the same as PDMS; however it has a network structure. This structure may cause derangement of stress loading, during alignment of PP chains. PDMS has a positive impact on elongation at break values compared to the other composites. Since it has a linear structure, it shows a harmony with polypropylene, while being pulled or stretched, due to the alignment of polymer chains. The similar result is obtained with 10% (w/w) PDMS alone with 90% (w/w) PP, in preliminary experiments (see Figure 4.23). It has the highest elongation at break value among the other composites and provides 27% higher elongation than others. Also, in SEM micrographs of PDMS composites, the uniform distribution of PDMS particles is seen (in Figure 4.20 (d), (e) and (f)).This may contribute to the increase in especially elongation at break values.

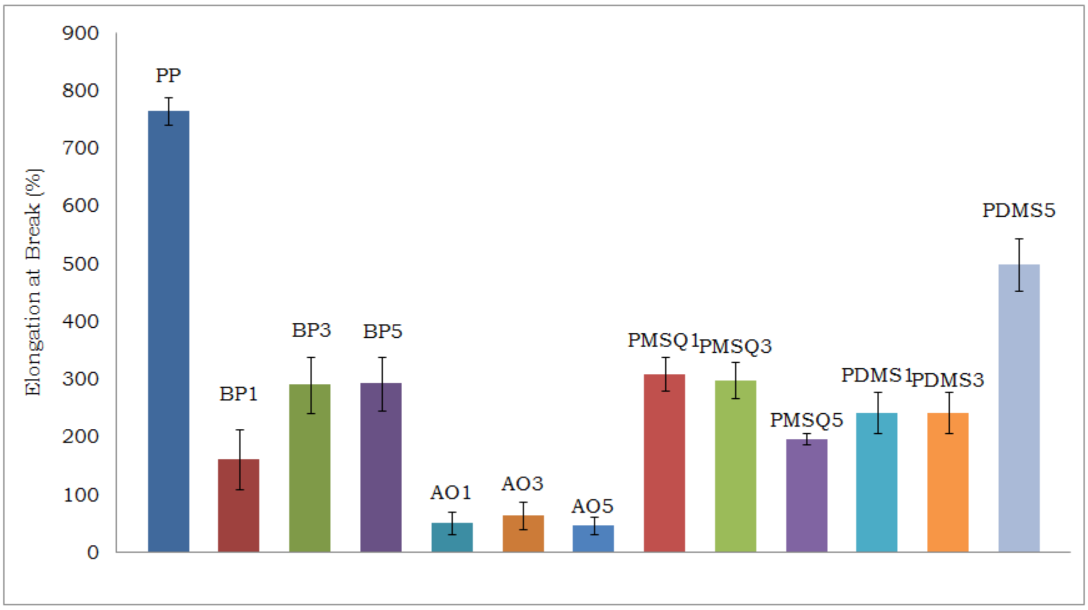


Figure 4.29 Elongation at break values of PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS

4.2.4.2 Impact strength

In Figure 4.30, the impact strength values of preliminary experimental composites are given (Appendix E, Table E.4). 5% (w/w) PDMS(p) increases the impact strength of polypropylene from 24 to 29 kJ/m^2. However, in tensile test, the composite with TPP has decreased tensile strength. As commented before, TPP has a negative impact on mechanical properties of PP, since it may create stress concentration points. On the other hand, PDMS synthesized without supporting electrolyte and solvent show positive effect on impact and tensile properties of PP. The PP/10PDMS improves the impact strength of PP about 190%, due to its linear structure as the similar linear structure of PP PDMS, which is synthesized as pure form, increases inherent impact strength of polypropylene, from 23 kJ/m^2

to 67 kJ/m^2.Magnesium hydroxide and boron phosphate decrease the impact strength of PP/10PDMS, because of low adhesion between MH, BP and PP.

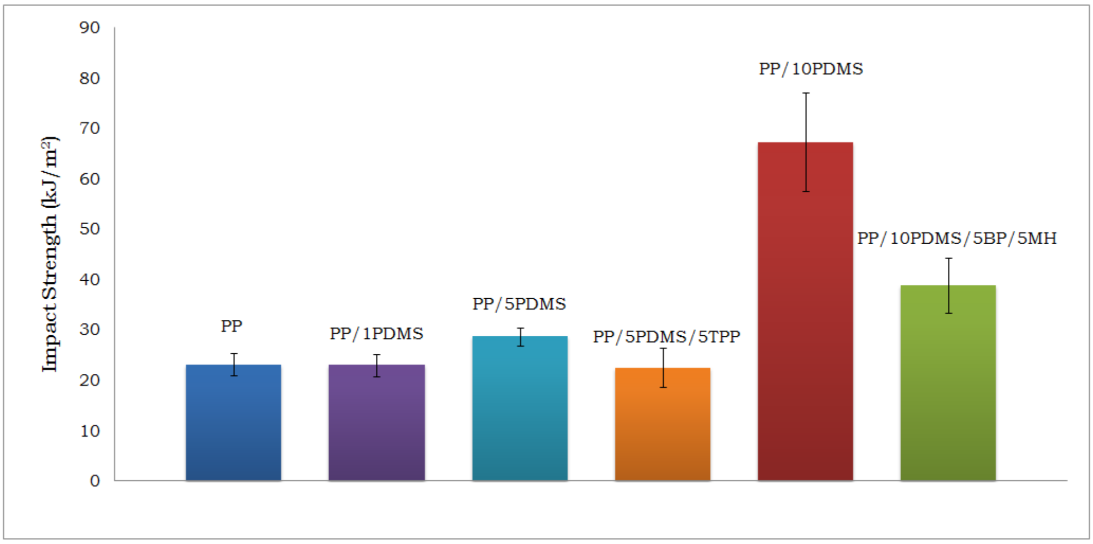


Figure 4.30 Impact strengths of PP/preceramic polymer composites (preliminary experiments)

In intumescent flame retardants with polypropylene composites, the impact strength of polypropylene increases slightly (Figure 4.31). The chosen composite among IFR systems was PP/15MP/5PER, which has an impact strength value of 24 kJ/m^2. It is better to say that no significant change is observed among IFR composites, when compared to neat PP (23 kJ/m^2).

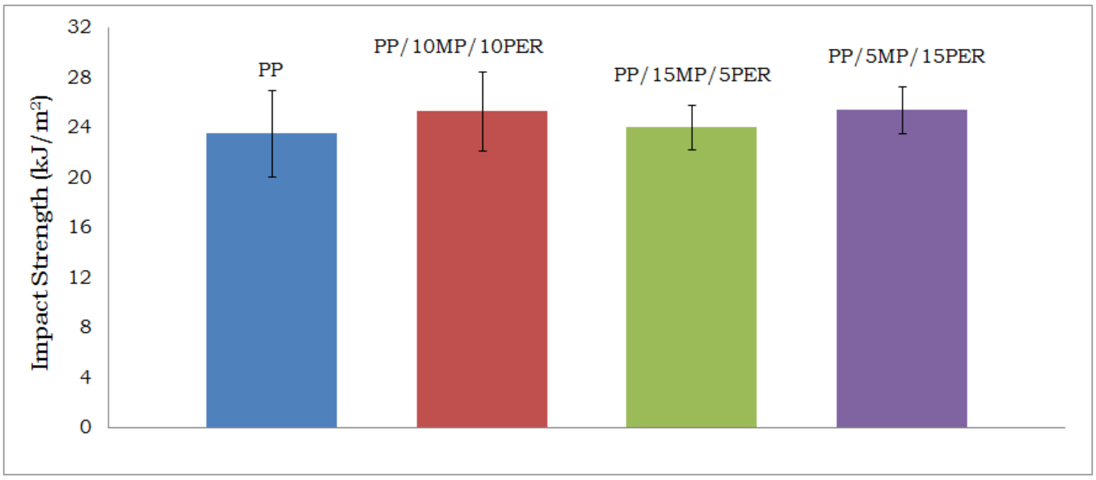


Figure 4.31 Impact strengths of PP/IFR composites

In Figure 4.32, the impact test results of PP/IFR/additive composites are given. Addition of 1 % (w/w) boron phosphate in polypropylene matrix increases the impact strength of neat polypropylene a little. However, there is no significant change between PP/BP composites and neat PP. Also, PP/IFR composites with AO addition show similar impact strength results with PP/IFR/BP composites. PMSQ addition supported PP composites better than AO and BP additives. The addition of 1% PMSQ into PP increases the impact strength of polypropylene about 14%, due to its network structure. The highest impact value was obtained in the composite PDMS5 with 95% increase with respect to PP. PDMS5 may be determined as the best composite among PP/IFR/BP, PP/IFR/AO, PP/IFR/PMSQ and PP/IFR/PDMS composites according to tensile and impact test results. PDMS exhibits improved mechanical properties due to the presence of Si atoms in the backbone [5].

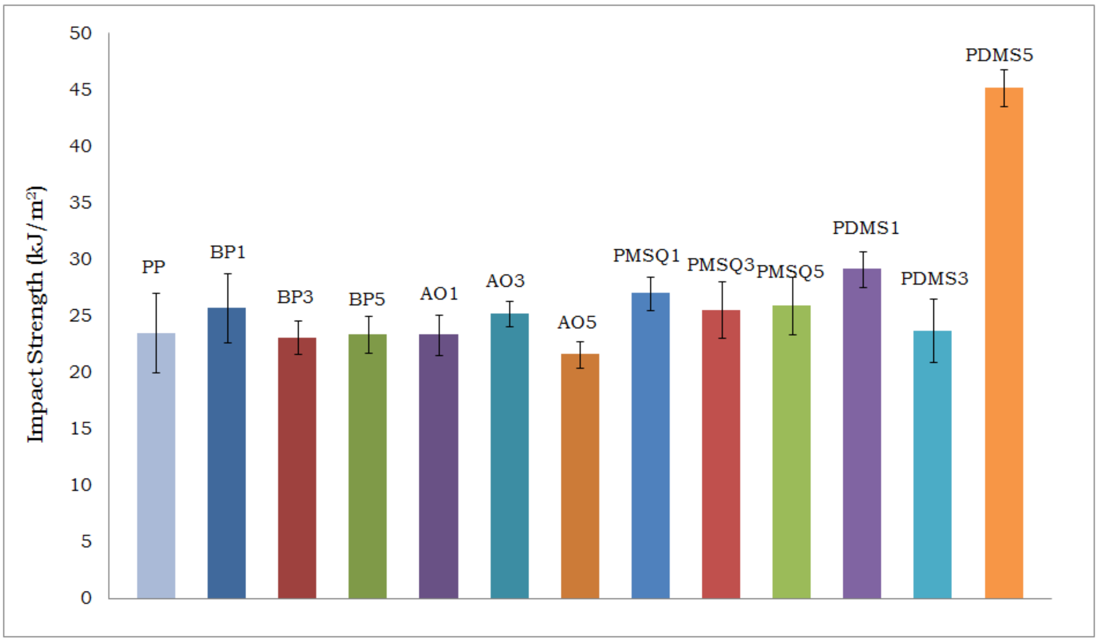


Figure 4.32 Impact strengths of PP/IFR/AO, PP/IFR/BP, PP/IFR/PMSQ and PP/IFR/PDMS composites

CHAPTER 5

CONCLUSIONS

The aim of this study is to develop polypropylene (PP) composite with preceramic polymers and other additives mainly for flame retardancy purposes. The preceramic polymer, poly(dimethylsilane) (PDMS) was synthesized and the PP based composites were prepared and characterized in terms of morphology, flame retardant and mechanical properties. The following conclusions can be drawn:

- The poly(dimethylsilane) preceramic polymer was synthesized with electrochemical polymerization of the dichlorodimethylsilane monomer in the solution of 1,2 dimethoxyethane (DME) and supporting electrolyte, tetrabutyl ammonium perchlorate (TBAP). It was characterized by FTIR, UV-VIS, ^{1}HNMR, TGA and SEM methods. The results were compared with literature, and it was observed that PDMS was successfully synthesized.

- However, because of these chemical compounds and difficulties during purification the first synthesized PDMS was not completely pure and the effects of impurities were observed in the characterization tests as well.

- Alternatively, PDMS was produced by means of direct electrochemical reduction of dichlorodimethylsilane alone, without using any solvent, supporting electrolyte, etc., in order to have PDMS in pure form. For this synthesis, also, a Schlenk-line system was used, which means an impermeable experimental set-up. After seven days polymerization, a highly viscous polymer (Pure PDMS) was obtained and the resulting polymer was characterized by FT-IR, UV-VIS, ^{1}HNMR, TGA and SEM methods.

- The synthesized PDMS polymer was added into PP in 1, 5, 10 wt % with additives such as triphenyl phosphate (TPP), boron phosphate (BP) and magnesium hydroxide (MH) by processing in a twin-screw extruder in order to prepare PP/PDMS blends. This trial was called as preliminary study. The LOI value of neat PP was measured as 17.5%, whereas the highest LOI result for this preliminary studies was obtained as 21% in the composite containing 10% pure PDMS, 5% BP, 5% MH and 80% PP.

- The intumescent flame retardant systems were investigated by using melamine phosphate (MP) and pentaerythritol (PER).

- In order to decide the optimum concentration ratio of MP/PER (w/w), the PP-based composites, which included totally 20% IFR with the ratios of MP/PER, as 1/1, 3/1 and 1/3 (w/w), were prepared. Also, the effects of boron phosphate (BP), antimony trioxide (AO), poly(methylsilsesquioxane) (PMSQ) and PDMS on flame retardant and mechanical properties of PP were investigated.

- The most effective composite composition was determined as MP/PER:3/1 (80%PP/15%MP/5%PER) with respect to LOI results (LOI of 29%) for PP/IFR composites.

- The additives of BP, AO, PMSQ and PDMS were added into PP/IFR composites at 1, 3 and 5% (w/w) concentration, whereas the IFR content was varied as 19%, 17% and 15% (w/w). The total additive loading was kept constant at 20% (w/w).

- The highest LOI value was obtained in AO1 (1% AO (w/w), 19% IFR (w/w), 80% PP(w/w)) composite as 28%, however it lowered sharply the tensile strength and elongation at break properties of neat polypropylene. Furthermore, its concentration should not be larger than 3% (w/w) with IFRs for effective flame retardancy in polypropylene.

- The PDMS with IFR composites decreased the flammability of polypropylene. The best LOI result obtained among PDMS composites was PDMS1 (1% PDMS, 19% IFR, 80% PP) composite with a value of 24% which is assessed as flame retardancy level of self-extinguishable material, according to ASTM standard.

- Also the other prominent composition was obtained for the case of PDMS5 composites (5%PDMS with 15%IFR). It did not only act as a flame retardant compound, but also it acted as a reinforcing additive according to the mechanical test results.

- In intumescent systems, the main problem is the loss in mechanical properties of base polymer. Furthermore, this novel synthesized PDMS, substantially improved the mechanical strength of polypropylene or at least did not cause further losses.

CHAPTER 6

RECOMMENDATIONS

Following recommendations can be given to the researchers focusing on poly(dimethylsilane) synthesis and its usage as polymeric additive:

- Characterization of semi-conductive properties of poly(dimethylsilane),

- Usage of poly(dimethylsilane) as an additive in different polymeric matrices such as engineering plastics, and investigations of mechanical, thermal and flame retardancy properties of these composites.

REFERENCES

1. Blatz, P.S., “The chemistry and uses of fire retardants”, French Patent, 1355064, (1964).

2. Lv, P., Wang, Z., Hu, K. and Fan, W., “Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives” Polymer Degradation and Stability 90, 523-534, (2005).

3. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.-M., and Dubois, Ph., “New prospects in flame retardant polymer materials: From fundamentals to nanocomposites”, Material Science and Engineering, 63, 100-125, (2009).

4. Lu, S.-Y. and Hamerton, I., “Recent developments in the chemistry of halogen-free flame retardant polymers”, Progress in Polymer Science 27, 1661–1712, (2002).

5. Shukla, S.K., Tiwari, R.K., Ranjan, A., Saxena1, A.K., and Mathuri, G.N., “Some thermal studies of polysilanes and polycarbosilanes”, Thermochimica Acta 424, 209–217, (2004).

6. Roy, A. K., Inorganic high polymers, “Kirk-Othmer Encyclopedia of Chemical Technology”, John Wiley and Sons, Inc., New York (2000).

7. Tamao, K., Sun, G.-R., Kawachi, A., and Yamaguchi, S., “Regioselective synthesis of polyfunctionalized alkyltrisilanes and

tetrasilanes via reductive cross-coupling reaction of aminoalkylsilyl chlorides with lithium", Organometallics 16, 780, (1997).

8. Sanji, T., Kawabata, K., and Sakurai, H., "Alkoxide initiation of anionic polymerization of masked disilenes to polysilanes", Journal of Organometallic Chemistry 611, 32–35, (2000).

9. Suzuki, M., Kotani, J., Gyobu, S., Kaneko, T., and Saegusa, T., "Synthesis of sequence-ordered polysilane by anionic ring oppening polymerization of phenylnonamethyl cyclopentasilane", Macromolecules, 27, 2360–2363, (1994).

10. Elangovan, M., Muthukumaran, A., and Anbu Kulandainathan M., "Comparison of solid state studies and electrochemical behavior of poly (dimethylsilane) and poly (dimethylstannum) film electrodes", Materials Letters 60, 1099–1105, (2006).

11. Ishifune, M., Kogai, Y., and Uchida, K., "Effect of disilane additives on the electroreductive polymerization of organodichlorosilanes", Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 42, 921–929, (2005).

12. Lichtenhan, J.D. and Gilman J.W., "Preceramic additives as fire retardants for plastics", US Patent 6362279, (2006).

13. http://www.sps.aero/Key_ComSpace_Articles/TSA008_White_Paper_Ceramics_From_Polymers.pdf, last accessible 30 October 2011.

14. Burns, G.T., Zank, G.A. and Ewald, J.A., "Preparation of high density boron carbide ceramics with preceramic polymer binders" US Patent 5545687, (1996).

15. Yajima, S., Hayashi, J., and Omori, M., "Continuous Silicon Carbide Fiber of High Tensile Strength", Chemistry Letters 9, 931, (1975).

16. Hasegawa, Y. and Okamura, K., "SiC-C composite materials synthesized by pyrolysis of polycarbosilane", Journal of Material Science Letters 4, 356, (1985).

17. Srinivasan, R., "Ablation of polymers and biological tissue by ultraviolet lasers", Science 234, 559, (1986).

18. Miller, R.D., Willson, C.G., Wallraff, G.M. Clecak, N., Sooriyakumaran, R., Michl, J., Karatsu, T., McKinley, A.J., Klingensmith, K.A. and Downing, J., "Polysilanes: Photochemistry and Deep UV Lithography", Polymer Engineering and Science 29, 882, (1989).

19. Miller, R.D., Willson, C.G., Wallraff, G.M. Clecak, N., Sooriyakumaran, R., Michl, J., Karatsu, T., McKinley, A.J., Klingensmith, K.A. and Downing, J., "Polysilanes: solution photochemistry and deep UV lithography", Polymeric Materials Science and Engineering, Proceedings of the ACS Division of Polymeric Materials Science and Engineering 60, 49-53 , (1989).

20. Kashimura, S., Ishifune, M., Bu, H.-B., Takebayashi, M., Kitajima, S., Yoshihara, D., Nishida, R., Kawasaki, S., Murase, H. and Shono, T., "Electroreductive synthesis of some functionalized polysilanes and related polymers", Tetrahedron Letters 38, 4607-4610, (1997).

21. Bortolin, R., “Polysilanes”, US Patent 4882450, (1989).

22. Bordeau, M., Biran C., Marie-Pierre Leger-Lambert and Dunogues J., “Competitive Electrochemical Synthesis of Polydimethylsilane without Solvent”, Journal of Chemical Society Chemical Communications, 1476-1477, (1991).

23. Sanji, T., Kawabata, K., and Sakurai, H., “Alkoxide initiation of anionic polymerization of masked disilenes to polysilanes”, Journal of Organometallic Chemistry 611, 32–35, (2000).

24. Kim H. K., K. Matyjaszewski, “Preparation of Polysilanes in the Presence of Ultrasound” Journal of American Chemical Society 110, 3321-3323, (1988).

25. Kepler, R.G. and Soos, Z.G., “Electronic excitations of poly(methylphenylsilane) films” Physics Review B 43, 12530, (1991).

26. Hasegawa, T., Iwasa, Y., Sunamura, H., Koda, T., Tokura, Y., Tachibana, H., Matsumoto, M. and Abe, S., "Nonlinear optical spectroscopy on one-dimensional excitons in silicon polymer, polysilanes, Physical Review Letters 69, 668, (1992).

27. Tachibana, H., Matsumoto, M., Tokura, Y., Moritomo, Y., Yamaguchi, A., Koshihara, S., Miller, R.D. and Abe, S., “Spectra of one-dimensional excitons in polysilanes with various backbone conformations”, Physical Reviews B47, 4363, (1993).

28. Agarwal, R., Tandon, P., and Gupta V.D., “Phonon dispersion in poly(dimethylsilane)”, Journal of Organometallic Chemistry 691, 2902–2908, (2006).

29. Majima, Y., Kawata, K., Nakano, Y., and Hayase ,H., “Polysilane spherulites and their high photoluminescence quantum yields”, Journal of Polymer Science, Part A: Polymer Chemistry 35, 427, (1997).

30. Birot, J.-P., Pillot, J., Dunogues, Comprehensive Chemistry of Polycarbosilanes, Polysilazanes, and Polycarbosilazanes as Precursors of Ceramics, Chemical Reviews 95, 1443, (1995).

31. Idesaki, A., Narisawa, M., Okamura, K., Sugimoto, M., Morita, Y., Seguchi T. and Itoh M., “Application of electron beam curing for silicon carbide fiber”, Radiation Physics and Chemistry 60, 483–487, (2001)

32. Okamura K., “Ceramic fibers from polymer precursors”, Composites 18, 107, (1987).

33. Matson D.W., Petersen R.C. and Smith R.D., “The preparation of polycarbosilane powders and fibers during rapid expansion of supercritical fluid solutions" Materials Letters 4, 429 (1986)

34. Matyjaszewski, K., Greszta, D., Hrkach, J.S., and Kim, H.K. “Sonochemical synthesis of polysilylenes by reductive coupling of disubstituted dichlorosilanes with alkali metals” Macromolecules 28, 59–72 (1995).

35. Tilley, T.D. “The coordination polymerization of silanes to polysilanes by a “s-bond metathesis” mechanism. Implications for linear chain growth” Accounts of Chemical Research 26, 22–29 (1993).

36. Sanji, T., Kawabata, K., and Sakurai, H., “Alkoxide initiation of anionic polymerization of masked disilenes to polysilanes”, Journal of Organometallic Chemistry 611, 32–35, (2000).

37. Suzuki, M., Kotani, J., Gyobu, S., Kaneko, T., and Saegusa, T., “Synthesis of sequence-ordered polysilane by anionic ring oppening polymerization of phenylnonamethyl cyclopentasilane”, Macromolecules, 27, 2360–2363, (1994).

38. Kashimura, S., Ishifune, M., Yamashita, N., Bu, H., Takebayashi, M., Kitajima, S., Yoshiwara, D., Kataoka, T., Nishida, R., Kawasaki, S., Murase, H. and Shono, T., “Electroreductive synthesis of polysilanes, polygermanes, and related Polymers with magnesium electrodes”, Journal of Organometallic Chemistry 64, 6615 (1999).

39. Wang, X., Yuan, Y., and Cabasso, I., “Cyclic voltammetric study of electroreduction of dichlorosilanes”, Journal of the Electrochemical Society 152, E259-E264 (2005).

40. West, R. J., “Polysilane High Polymers: An Overview, Chapter 2: Inorganic and Organometallic Polymers”, American Chemical Society (1988).

41. Hengge, E., and Litscher, G.K.J., “A new electrochemical method of forming Si-Si bonds”, Angewandte Chemie International Edition in English 15, 370, (1976).

42. Hengge, E.F., “New ways to polysilanes” Journal of Inorganic and Organometallic Polymers 3, 287-303, (2014).

43. Nonaka, T., Umezawa, M., Takeda, M., Ichikawa, H., Ishikawa, T., Koizumi, T. and Fuchigami, T. "Electroreductive polymerization of prganodichloromonosilanes", Electrochimica Acta 35, 1867-1872 (1990).

44. Sherman, C.-P., "Handbook of Instrumental Techniques for Analytical Chemistry, Infrared Spectroscopy", Prentice Hall PTR, New Jersey, (1997).

45. http://www.tutorvista.com/content/chemistry/chemistry-iii/atomic-structure/electromagnetic-nature-light.php], last accessible 16 December 2011

46. http://en.wikipedia.org/wiki/Infrared_spectroscopy, last accessible 16 December 2011

47. http://en.wikipedia.org/wiki/UV-visible_spectroscopy, last accessible 16 December 2011

48. http://en.wikipedia.org/wiki/NMR_spectroscopy, last accessible 16 December 2011

49. Polypropylene Chemical Fact Sheet, Copyright Orica Limited, ACN 004 145 868, (1992–1998)

50. Balow, M.-J., "Handbook of Polypropylene and Polypropylene Composites Chapter 1: Global Trends for Polypropylene", Marcel Dekker, Inc., New York (2003).

51. Introduction to polymer chemistry CHEM 421: Class notes http://chem.chem.rochester.edu/~chem421/tact1.htm, last accessible 16 December 2011

52. Balow, M.-J., “Handbook of Polypropylene and Polypropylene Composites Chapter 1: Global Trends for Polypropylene”, Marcel Dekker, Inc., New York (2003).

53. Pearce M.E. and Liepins R., “Flame retardants”, Environmental Health Perspectives 17, 55-63, (1976).

54. Horrocks, A.R. and Pierce D., “Fire Retardant Materials”, CRC Press LLC, (2000).

55. Ed. Grand, A.F., Author: Hirschler, M.M., “Fire Retardancy of Polymeric Materials, Chapter 2: Chemical Aspects of Thermal Decomposition of Polymeric Materials”, Marcel Dekker Inc., New York, (2000).

56. Gijsman, P., Hennekens, J., and Vincent, J., “The mechanism of the low-temperature oxidation of polypropylene”, Polymer Degradation and Stability 42, 95-105, (1993).

57. Zaikov, G.,E., and Lomakin, S.,M., “Ecological issue of polymer flame retardancy”, Journal of Applied Polymer Science 86, 2449–2462, (2002).

58. Ed: Hull, R.T., Kandola, B.K., Author: Hull, R.T. and Stec, A., A., “Fire Retardancy of Polymers: Polymers and Fire, Royal Society of Chemistry, UK, (2009).

59. Ed: Murphy, J., “Additives For Plastics Handbook: Modifying Specific Properties: Flammability-Flame Retardants”, Elsevier, (2001).

60. http://en.wikipedia.org/wiki/Flame_retardant, last accessible 16 December 2011

61. Titelman, G.I., Gonen, Y., Keidar, Y., and Bron S., “Discolouration of polypropylene-based compounds containing magnesium hydroxide.” Polymer Degradation and Stability 77, 345–352, (2002).

62. Ariagno, D., Barruel, P., and Viale, A., “Heat-vulcanisable organopolysiloxanes, intended for coating of electrical cables” European Patent 467800 (1992).

63. Hamdani, S., Longuet, C., Perrin, D., Lopez-cuesta, J-M. and Ganachaud F., “Flame retardancy of silicone-based materials” Polymer Degradation and Stability 94, 465–495, (2009).

64. Liu, Y.L., Chiu, Y.C. and Wu, C.S., “Preparation of silicon-/phosphorous-containing epoxy resins from the fusion process to bring a synergistic effect on improving the resins’ thermal stability and flame retardancy”, Journal of Applied Polymer Science 87, 404–411 (2003).

65. Wu, C.S., Liu, Y.L. and Chiu, Y.S., “Synthesis and Characterization of New Organosoluble Polyaspartimides Containing Phosphorus” Polymer 43, 4277, (2002).

66. Liu, Y.L. “Epoxy resins from novel monomers with bis-(9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl-)

substitiuent", Journal of Polymer Science Part A: Polymer Chemistry 40, 359, (2002).

67. Lu, S.Y. and Hamerton, I., "Recent developments in the chemistry of halogen-free flame retardant polymers", Progress in Polymer Science 27, 1661-1712, (2002).

68. Kandola, B.K. and Horrocks, A.R., Complex char formation in flame-retarded fibre-intumescent combinations—II. Thermal analytical studies, Polymer Degradation and Stability 54, 289, (1996).

69. Zaikov, G.E. and Lomakin, S.M., "Innovative type of low flammability varnish based on poly(viny1 alcohol)" Polymer Degradation and Stability 57, 279, (1997).

70. Kambour, R.P., Klopрer, H.J. and Smith, S.A. "Limiting Oxygen Indices of Silicone Block Polymers", Journal of Applied Polymer Science 26, 847, (1981).

71. Kambour, R.P., "Flammability resistance synergism in BPA polycarbonate-silicone block polymers" Journal of Applied Polymer Science 26, 861, (1981).

72. Masatoshi, I. and Shin, S., "Silicone Derivatives as New Flame Retardants for Aromatic Thermoplastics Used in Electronic Devices" Polymers for Advanced Technologies 9, 593, (1998).

73. Hsiue, G.H., Liu, Y.L. and Tsiao,J. "Phosphorus-containing epoxy resins for flame Retardancy V: Synergistic effect of phosphorus–silicon on flame retardancy, Journal of Applied Polymer Science, 78, 1-7, (2000).

74. Wang, W.J., Perng, L.H., Hsiue, G.H. and Chang, F.C. “Characterization and properties of new silicone-containing epoxy resin” Polymer 41, 6113, (2000).

75. Ebdon, J. R.; Hunt, B. J.; Jones, M. S.; Thorpe, F. G. “Chemical modification of polymers to improve flame retardance—II. The influence of silicon-containing groups” Polymer Degradation and Stability 54, 395-400, (1996).

76. Li, Q., Jiang, P., Su, Z., Wei, P., Wang, G., and Tang, X., “Synergistic effect of phosphorus, nitrogen, and silicon on flame-retardant properties and char yield in polypropylene” Journal of Applied Polymer Science 96, 854–860 (2005).

77. Istomin, E.I., Zubkova, N.S., Butylkina, N.G., Gordeev, S.A., Tjuganova M.A. and Khalturinsky N.A., “Lowering of polyethylene (PE) and polypropylene (PP) combustibility” Fire Safety Journal 26, 185. (1996).

78. Zhang, S., and Horrocks A.R., “A review of flame retardant polypropylene fibres”, Progress in Polymer Science 28, 1517–1538, (2003).

79. Lyons, J.W., “The Chemistry and Uses of Fire Retardants”, R.E. Krieger Publishing Company, (1987).

80. Eroğlu D., M.Sc. Dissertation, Middle East Technical University, 2008.

81. Lu, S.-Y. and Hamerton, I., "Recent developments in the chemistry of halogen-free flame retardant polymers", Progress in Polymer Science 27, 1661–1712, (2002).

82. Chen, Y., Liu, Y., Wang, Q., Yina, H., Aelmans, N. and Kierkels, R., "Performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology: effect of component ratio" Polymer Degradation and Stability 81, 215–224, (2003).

83. Li, Q., Zhong, H., Wei, P. and Jiang, P., "Thermal Degradation of polypropylene with Si-containing intumescent flame retardant", Journal of Applied Polymer Science 98, 2487–2492, (2005).

84. Dogan, M., Yılmaz, A. and Bayramlı, B., "Synergistic effect of boron containing substances on flame retardancy and thermal stability of intumescent polypropylene composites", Polymer Degradation and Stability 95, 2584-2588, (2010).

85. Zanetti, M., Kashiwagi, T., Falqui, L. and Camino, G., "Cone calorimeter combustion and gasification studies of polymer layered silicate nanocomposites", Chemistry of Materials 14, 881, (2002).

86. Song, R., Wang, Z., Meng, X., Zhang, B. and Tang, T., "Influences of catalysis and dispersion of organically modified montmorillonite on flame retardancy of polypropylene nanocomposites" Journal of Applied Polymer Science 106, 3488, (2007).

87. Jang, B.N., Costache, M. and Wilkie, C.A., "The relationship between thermal degradation behavior of polymer and the fire

retardancy of polymer/clay nanocomposites," Polymer 46, 10678-10687 (2005).

88. Isitman, N.,A. and Kaynak, C., "Nanoclay and carbon nanotubes as potential synergists of an organophosphorus flame-retardant in poly(methyl methacrylate)" Polymer Degradation and Stability 95, 1523-1532 (2010).

89. Tüzenli Z., M.Sc. Dissertation, Karadeniz Technical University, Trabzon, (2009).

90. Laachachi, A., Cochez, M., Ferriol, M., Lopez-Cuesta, J.M. and Leroy, E." Influence of TiO_2 and Fe_2O_3 fillers on the thermal properties of poly(methyl methacrylate) (PMMA)", Materials Letters 59, 36, (2005).

91. Baltaci, B., M.Sc. Dissertation, Middle East Technical University, (2011).

92. Einsele, U., Koch, W. and Herlinger, H., "Investigations into the development of heat when textiles burn in air", Melliand Textilberichte, 65, 200–6, (1984).

93. http://en.wikipedia.org/wiki/Flame_retardant, last accessible 16 December 2011

94. Chiu, S.-H. and Wang W.-K., "Dynamic flame retardancy of polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine additives" Polymer 39 , 1951-1955, (1998).

95. Marosi, G., Anna, P., Balogh, I., Bertalan, G., Tohl, A. and Maatong, M.A., “Thermoanalytical study of nucleating effects in polypropylene composites III. Intumescent flame retardant containing polypropylene” Journal of Thermal Analysis and Calorimetry 48, 717–726, (1997).

96. Zhang, S. and Wang, J., “Electron-beam irradiation initiated grafting to improve flame retardancy of polyethylene, Gaofenzi Cailiao Kexue Yu Gongcheng 16, 99–101, (2000).

97. Singh, U.P, Biswas, B.K, and Ray B.C. “Evaluation of mechanical properties of polypropylene filled with wollastonite and silicon rubber,” Materials Science and Engineering 501, 94–98, (2009).

98. F. W. Billmeyer, “Textbook of Polymer Science”, John Wiley & Sons, New York, (1984).

99. http://www.gcmachines.com/News/FISH-FEEDS-PROCESSING-AND-TECHNOLOGY.html, last accessible 16 December 2011.

100. Fenimore, C.P. and Martin, F.J., "Candle-Type Test for Flammability of Polymers," Modern Plastics 43, 141, (1966).

101. ASTM D 2863: Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index).

102. ASTM D 635 – 03: Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position

103. Vegt, A.K., “From Polymers to Plastics”, Delf Uni Pres, The Netherlands, (2002).

104. http://en.wikipedia.org/wiki/Tensile_test, last accessible 16 December 2011.

105. Özkan, N., PST 702 Characterization Techniques of Polymers, Lecture Notes: “Chapter: Mechanical Testing of Materials”, Ankara 2009.

106. http://en.wikipedia.org/wiki/Thermal_analysis, last accessible 16 December 2011.

107. http://www.npl.co.uk/advanced-materials/measurement techniques/thermal-analysis/differential-scanning-calorimetry, last accessible 16 December 2011.

108. http://en.wikipedia.org/wiki/Scanning_electron_microscope last accessible 16 December 2011.

109. http://www.petkim.com.tr/eng/Trade/Products/Products.aspx?urunId=51, last accessible 16 December 2011.

110. Watanabe, A., “Optical properties of polysilanes with various silicon skeletons”, Journal of Organometallic Chemistry 685, 122-133, (2003).

111. Li Q., Jiang P., Wei P., “Studies on the properties of polypropylene with a new silicon-containing intumescent flame retardant”, Journal of Polymer Science: Part B: Polymer Physics 43, 2548-2556, (2005).

112. S. Wlodek, A. Fox, and D. K. Bohme, Gas-Phase Reactions of Si+ and SiOH' with Molecules Containing Hydroxyl Groups: Possible Ion-Molecule Reaction Pathways toward Silicon Monoxide, Silanoic Acid, and Trihydroxy-, Trimethoxy-, and Triethoxysilane , Journal of American Chemical Society 109, 6663-6667, (1987).

113. Fenimore, C.P., Ed.s: Lewin, Atlas, S.M., and Pearce E.M., “Candle-type test for flammability of polymers” Flame-retardant polymeric materials Vol:1, New York: Plenum, 371-397 (1975).

114. Carr, C.N., “Chemistry of Textiles Industry”, Chapman&Hall, GB, (1995).

115. http://riodb01.ibase.aist.go.jp/sdbs/cgibin/direct_frame_top.cgi, last accessible 16 December 2011

APPENDIX A

FT-IR SPECTRA OF CHEMICALS

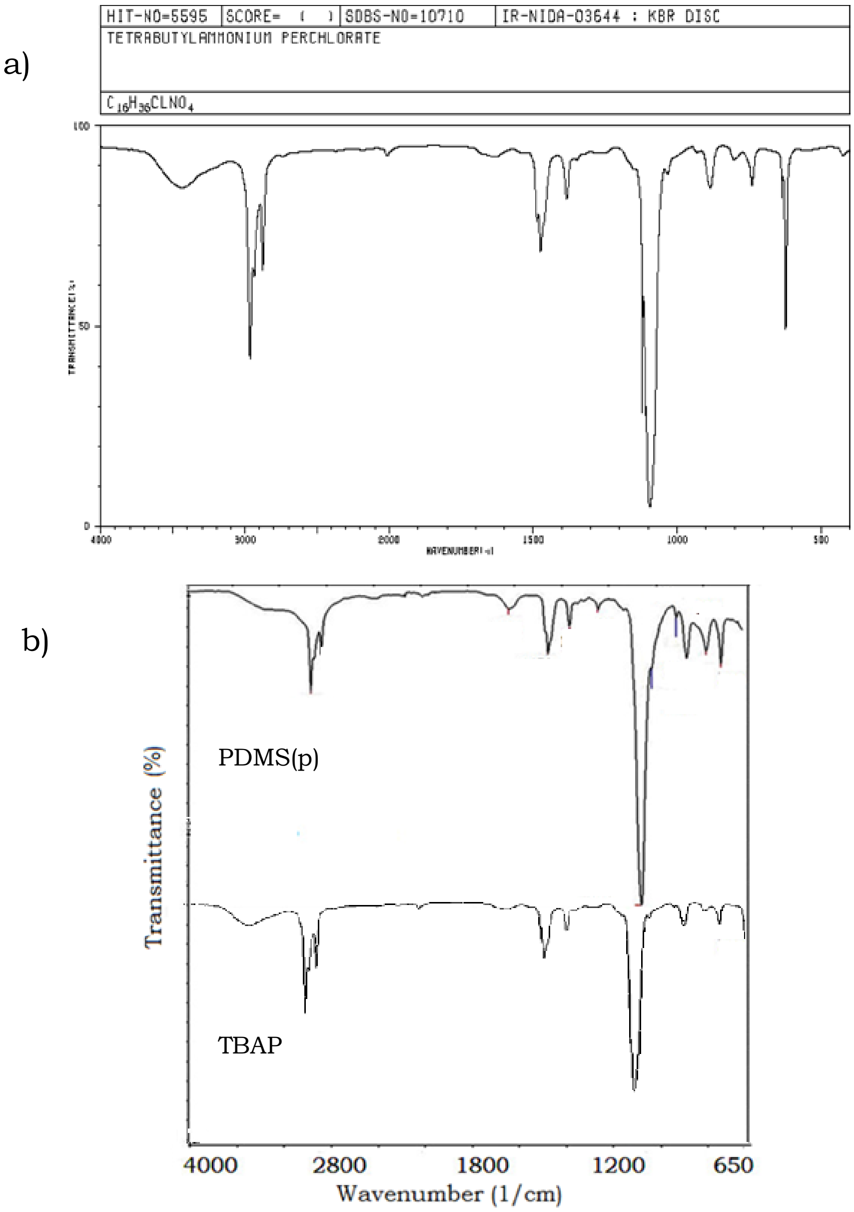
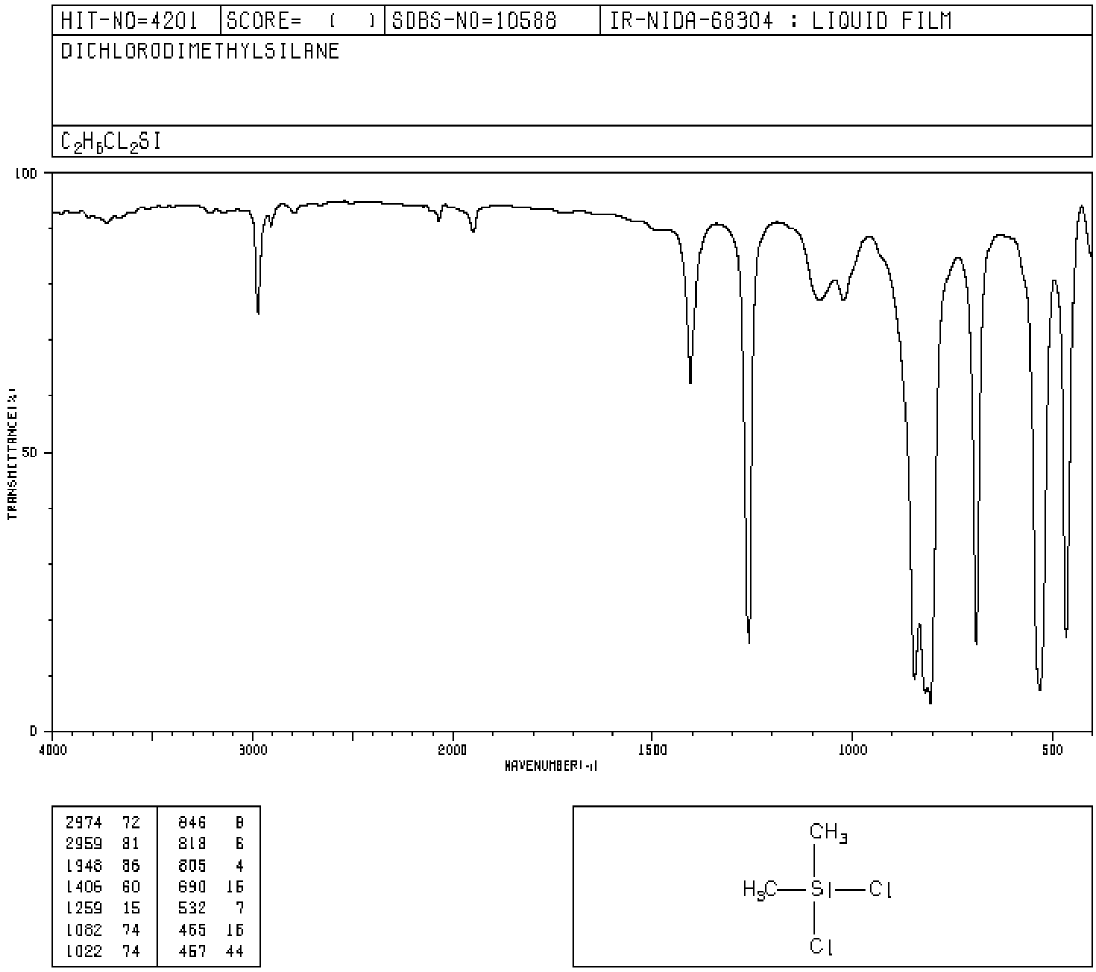


Figure A.1 (a) FT-IR spectrum of tetrabutyl ammonium perchlorate [115] and (b) FT-IR spectra of TBAP and PDMS(p)



HIT-NO=4201	SCORE= ( )	SDBS-NO=10588	IR-NIDA-68304 : LIQUID FILM

DICHLORODIMETHYLSILANE

$C_2H_6CL_2SI$

2974	72	846	8
2959	81	818	6
1948	86	805	4
1406	60	690	16
1259	15	532	7
1082	74	465	16
1022	74	467	44

Figure A.2 FT-IR spectrum of dichlorodimethylsilane [115]

APPENDIX B

TGA and DSC RESULTS OF PP AND ADDITIVES

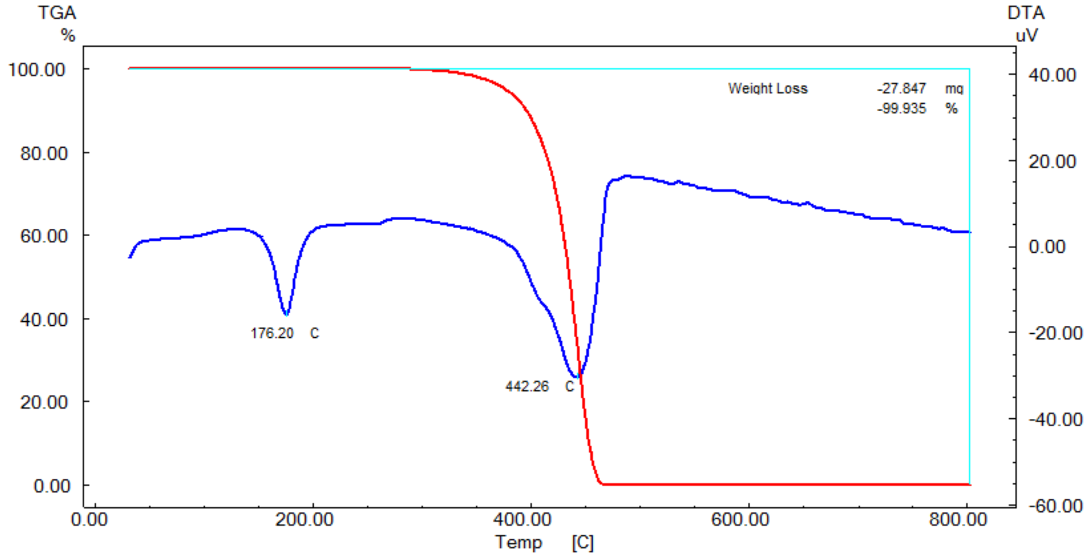


Figure B.1 TGA result of neat polypropylene (dark blue line: derivative of TGA curve)

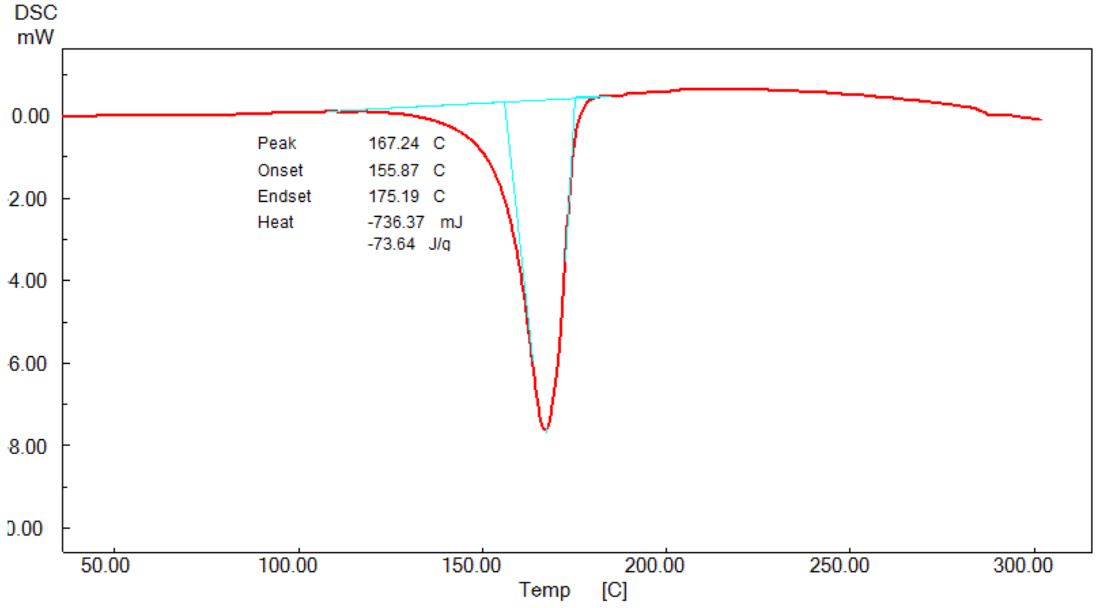


Figure B.2 DSC result of neat polypropylene

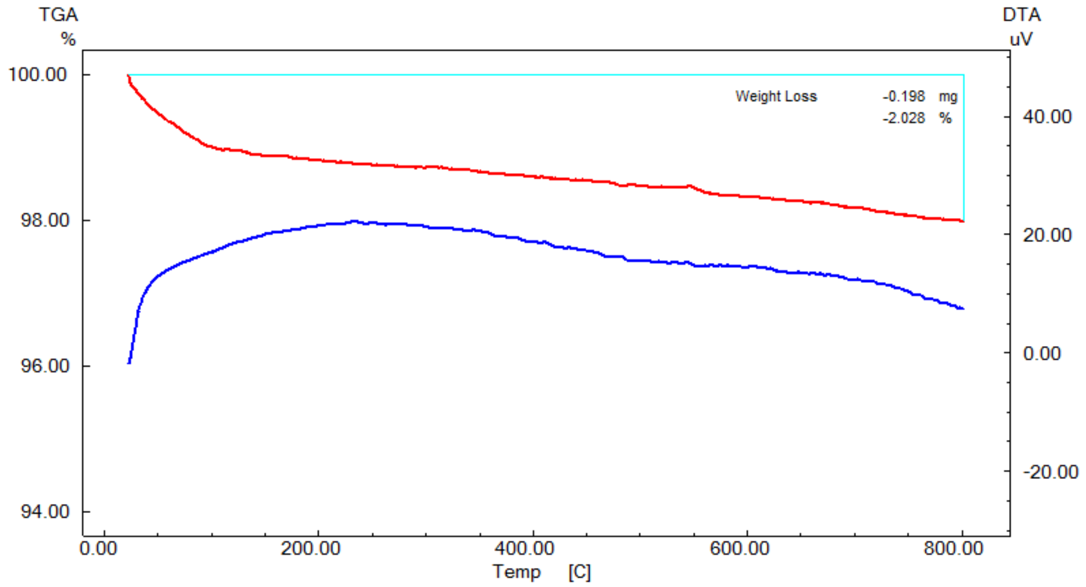


Figure B.3 TGA result of pure boron phosphate (dark blue line: derivative of TGA curve)

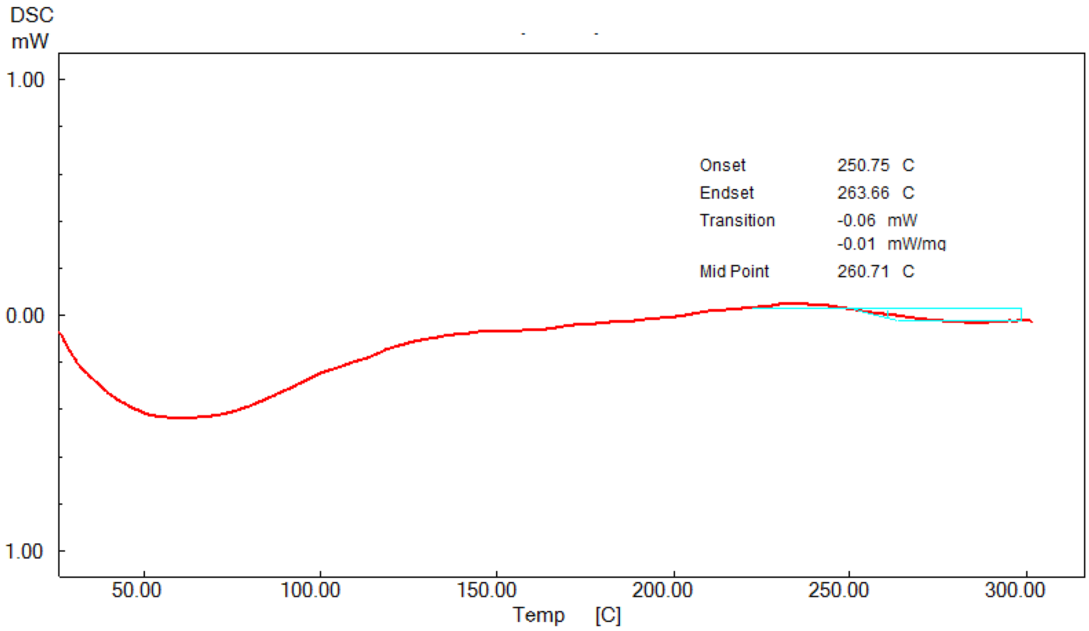


Figure B.4 DSC result of pure boron phosphate

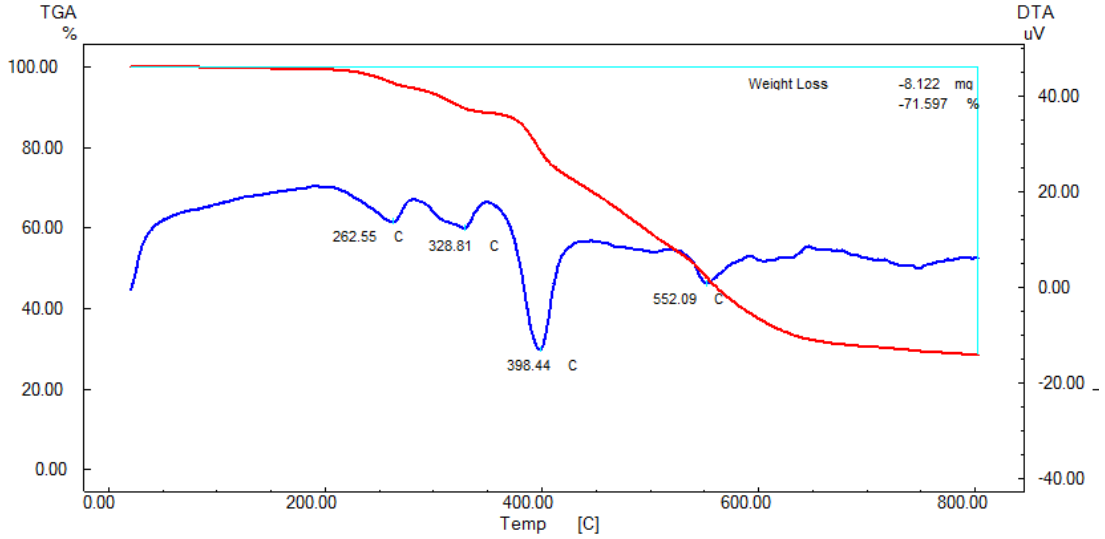


Figure B.5 TGA result of pure melamine phosphate (dark blue line: derivative of TGA curve)

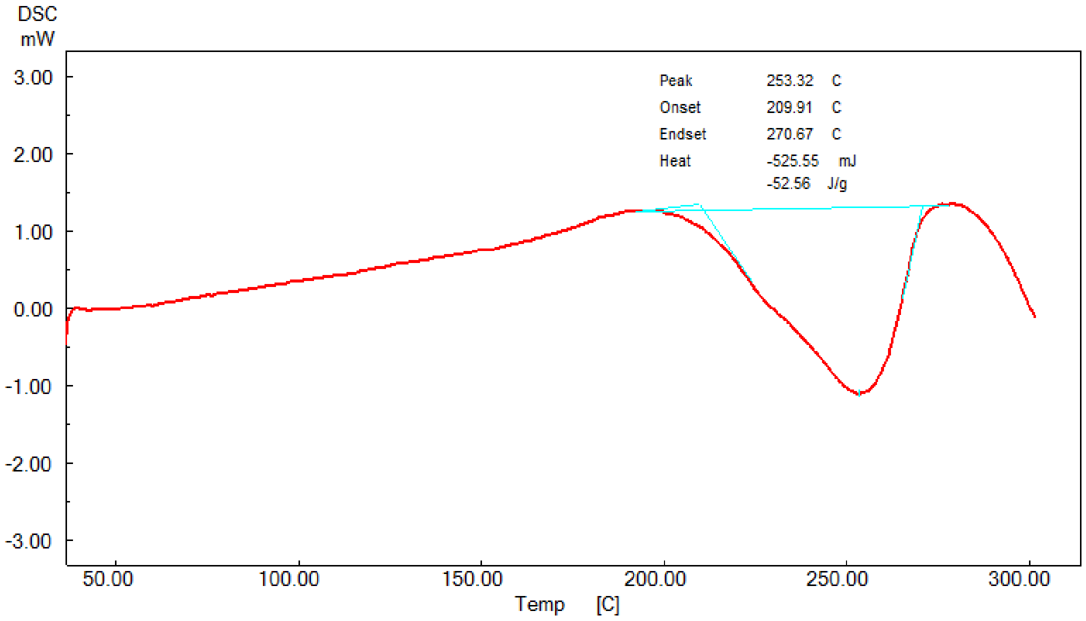


Figure B.6 DSC result of pure melamine phosphate

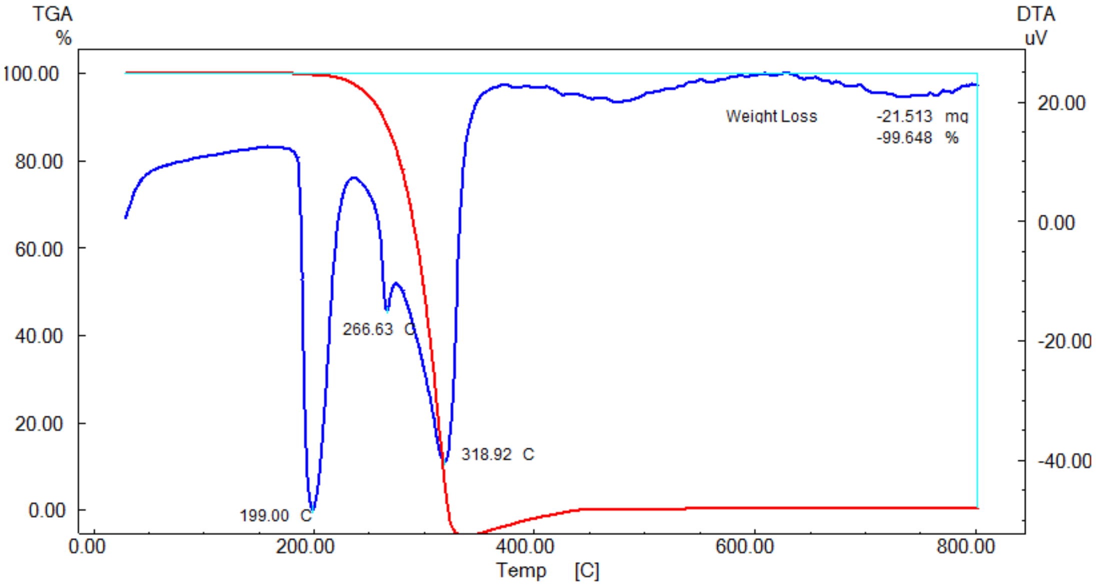


Figure B.7 TGA result of pure pentaerythritol (dark blue line: derivative of TGA curve)

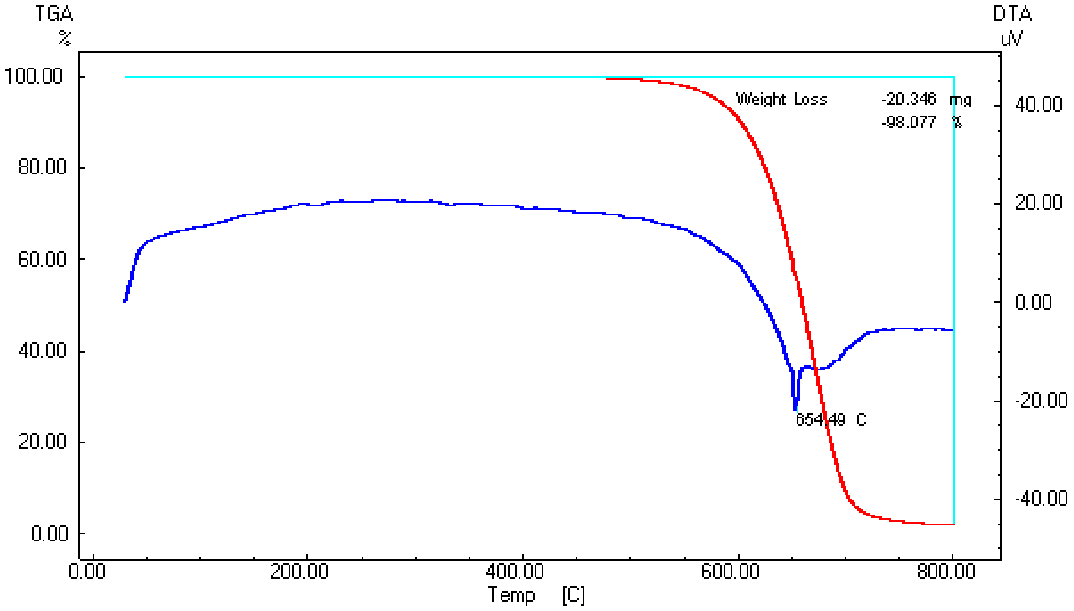


Figure B.8 TGA result of pure antimony trioxide (dark blue line: derivative of TGA curve)

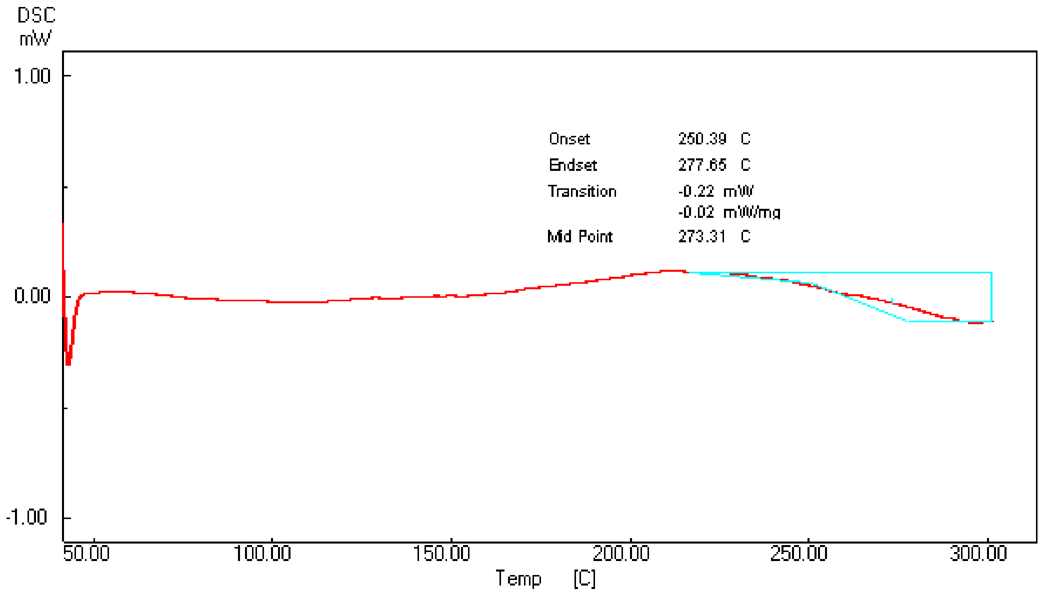


Figure B.9 DSC result of pure antimony trioxide

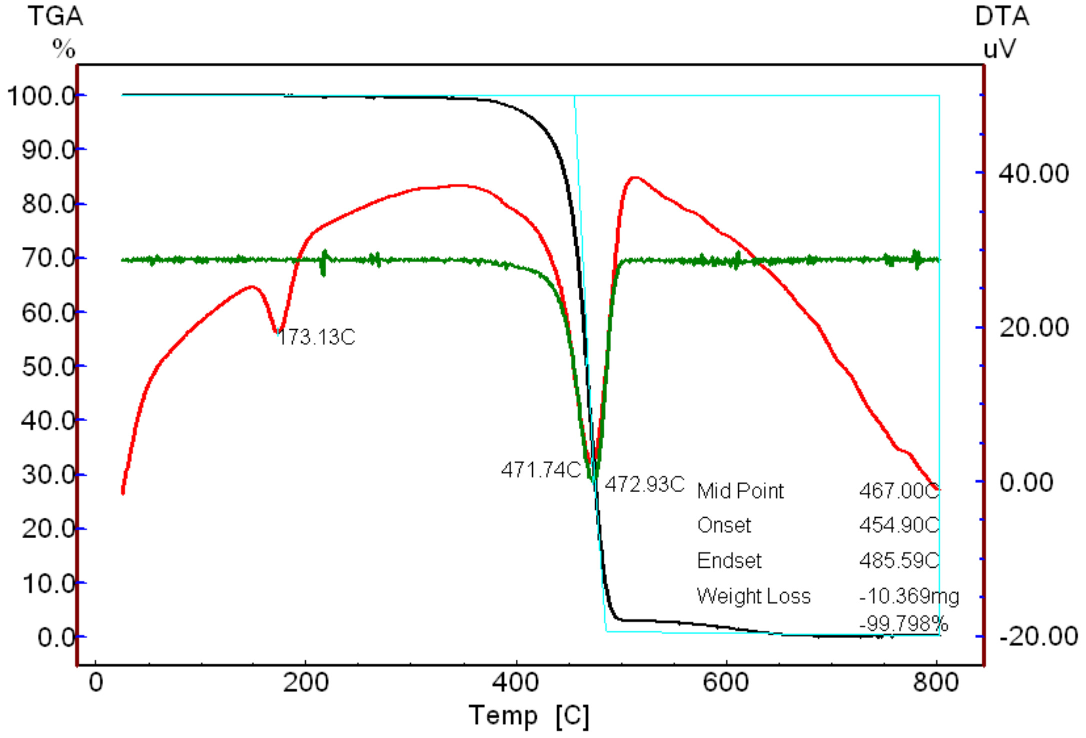


Figure B.10 The TGA curve of PP/10PDMS composite (red line: derivative of TGA curve, green line: second derivative of TGA curve)

APPENDIX C

SEM MICROGRAPHS OF ADDITIVES

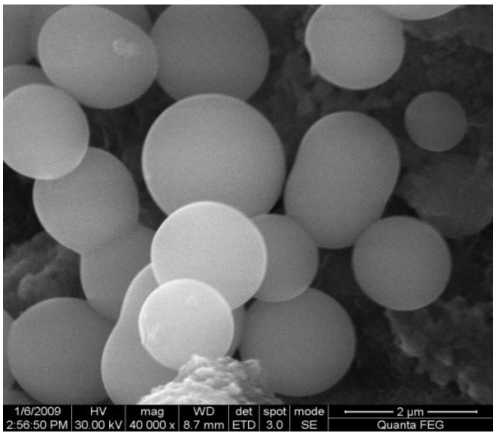


Figure C.1 SEM micrograph of poly(methylsilsesquioxane) at x40000 magnification (SEM machine: Quanta 400F Field Emission)

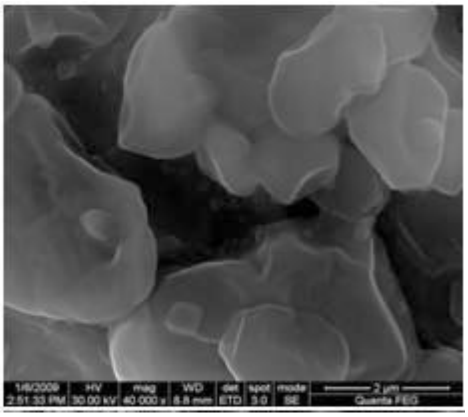


Figure C.2 SEM micrograph of poly(dimethylsilane) (powder) at x40000 magnification (SEM machine: Quanta 400F Field Emission)

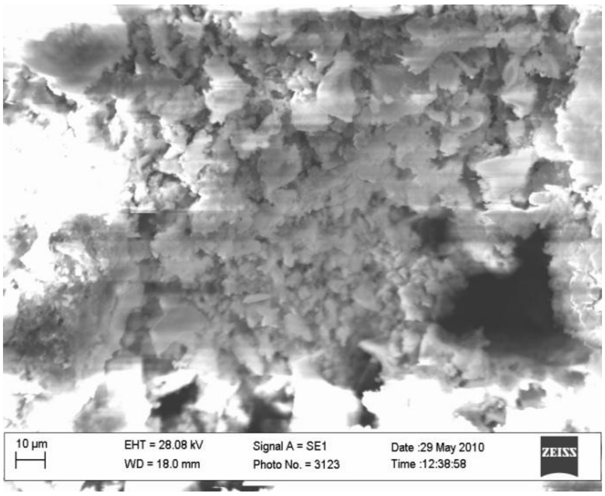


Figure C.3 SEM micrograph of boron phosphate with secondary electron beam (SEM machine: Zeiss EVO 40)

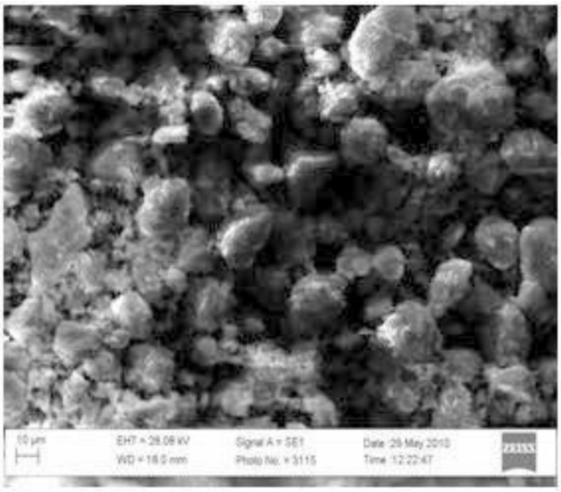


Figure C.4 SEM micrograph of melamine phosphate (SEM machine: Zeiss EVO 40)

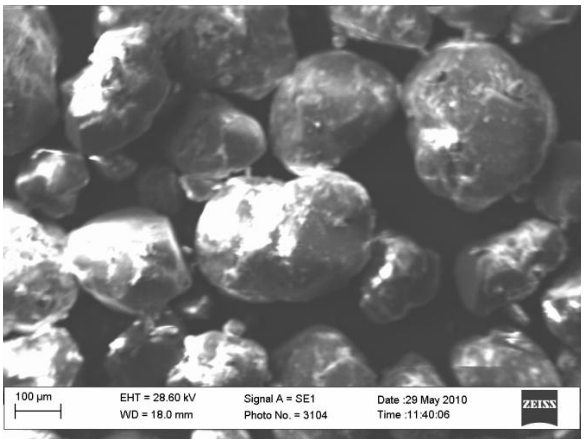


Figure C.5 SEM micrograph of pentaerythritol (SEM machine: Zeiss EVO 40)

APPENDIX D

EDX ANALYSES RESULTS OF PP-COMPOSITES

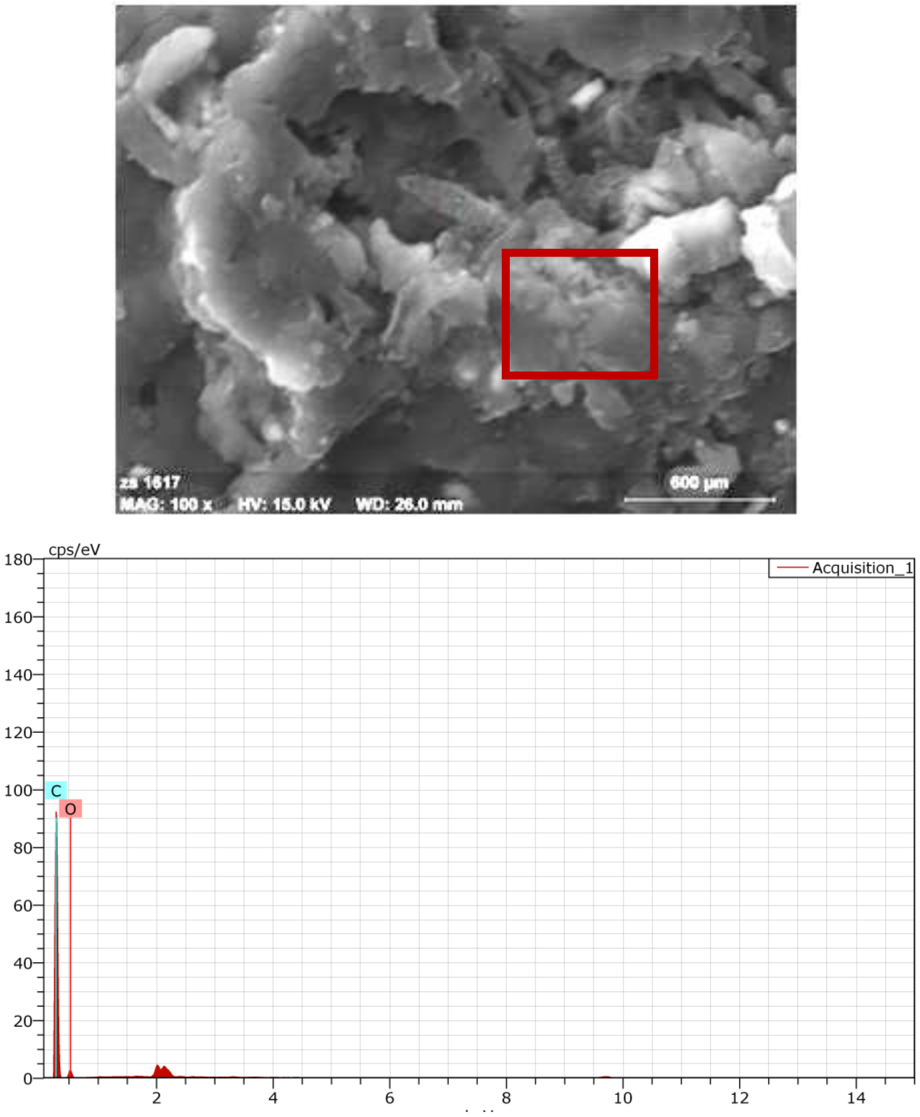
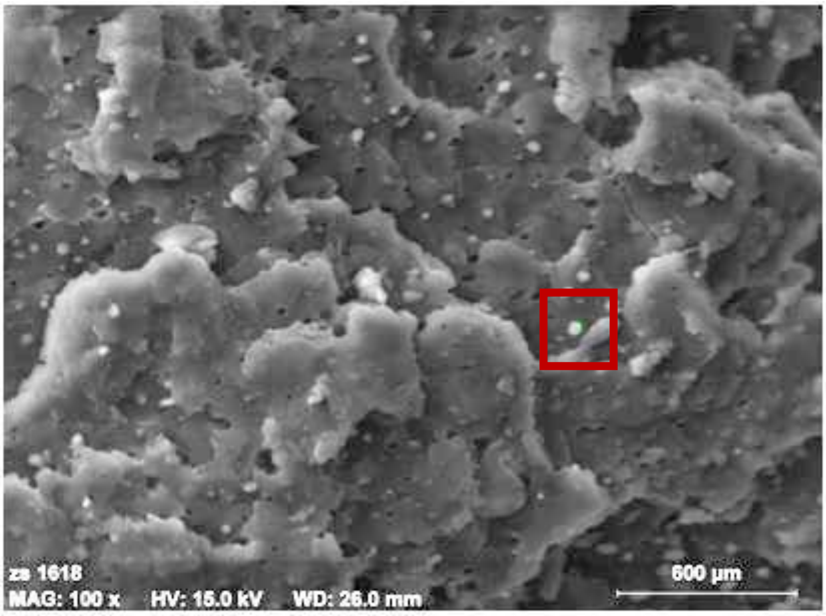


Figure D.1 EDX analysis result of composite PP/10MP/10PER



```
Spectrum: Acquisition_1

Element     Series    unn. C norm. C Atom. C Oxide Oxid. C Error
                      [wt.-%] [wt.-%] [at.-%]       [wt.-%]   [%]
----------------------------------------------------------------
Carbon     K-series    64.90   64.90   73.03 CO2     94.05  20.1
Phosphorus K-series     6.56    6.56    2.86 P2O5     5.95   0.3
Oxygen     K-series    28.54   28.54   24.11 O      -60.45   9.5
----------------------------------------------------------------
             Total:   100.00  100.00  100.00
```

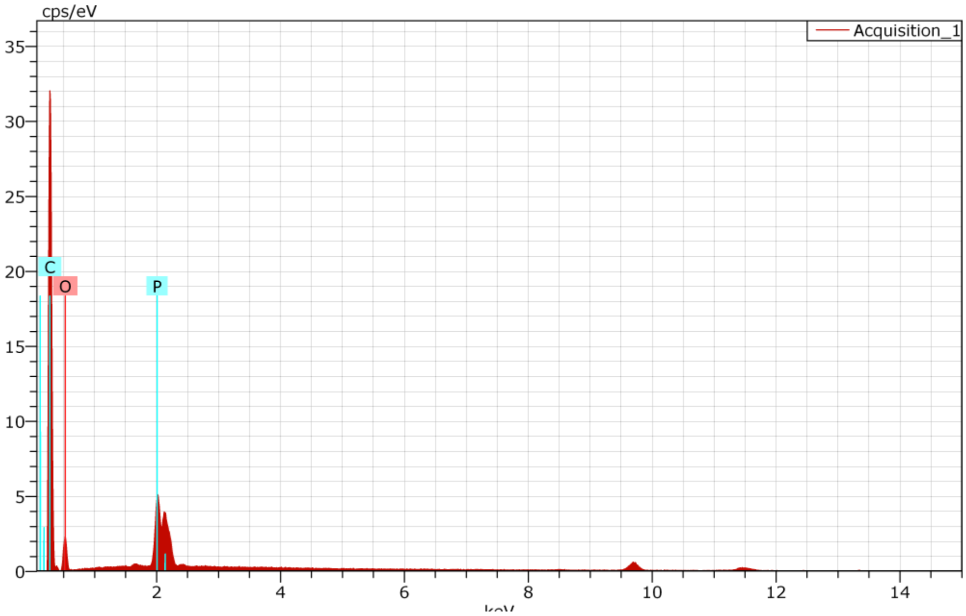
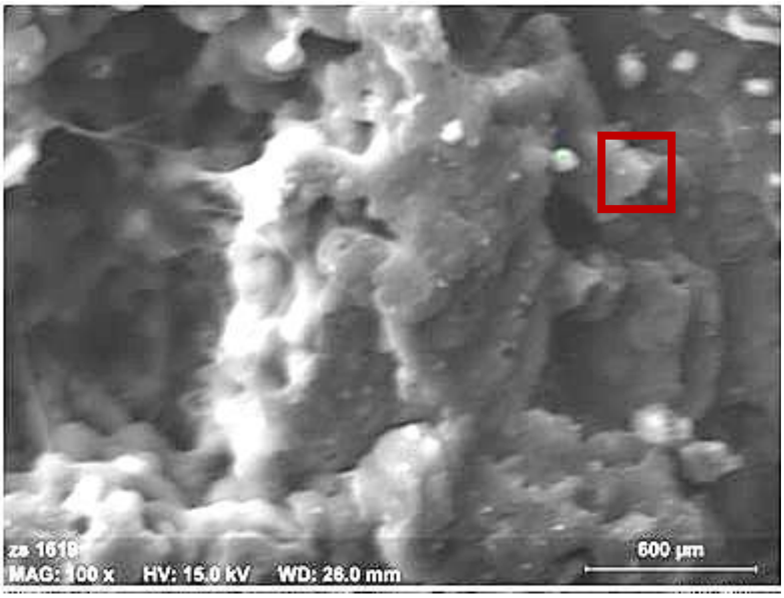


Figure D.2 EDX analysis result of composite of PP/15MP/5PER



```
Spectrum: Acquisition_1

Element    Series    unn. C norm. C Atom. C Oxide Oxid. C Error
                     [wt.-%] [wt.-%] [at.-%]        [wt.-%]   [%]
--------------------------------------------------------------
Carbon   K-series    68.22   68.22   85.66 CO2      93.22  28.5
Gold     M-series    15.19   15.20    1.16 Au        5.67   0.6
Antimony L-series     2.99    2.99    0.37 Sb        1.12   0.1
Oxygen   K-series    13.59   13.59   12.81 O       -62.71   9.9
--------------------------------------------------------------
           Total:   100.00  100.00  100.00
```

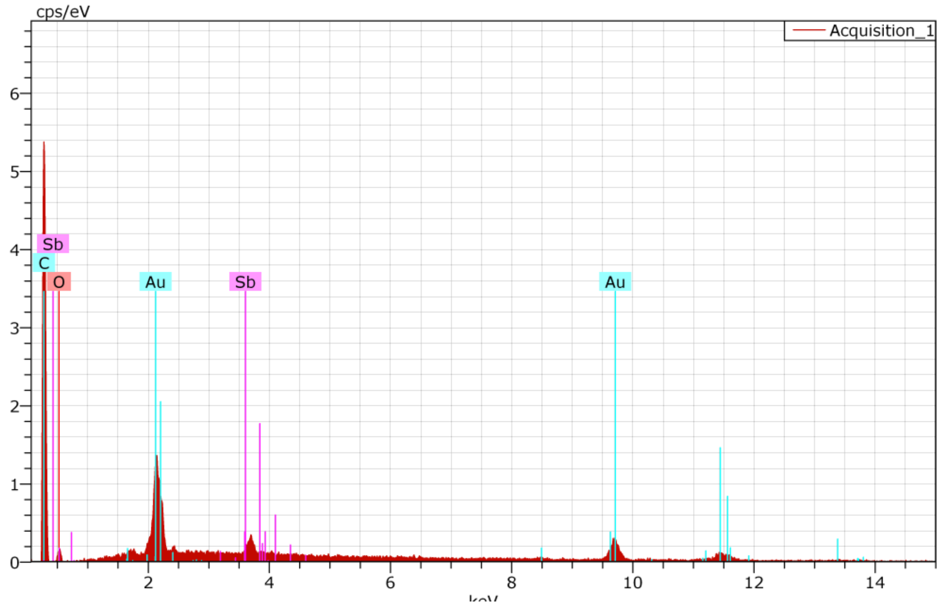
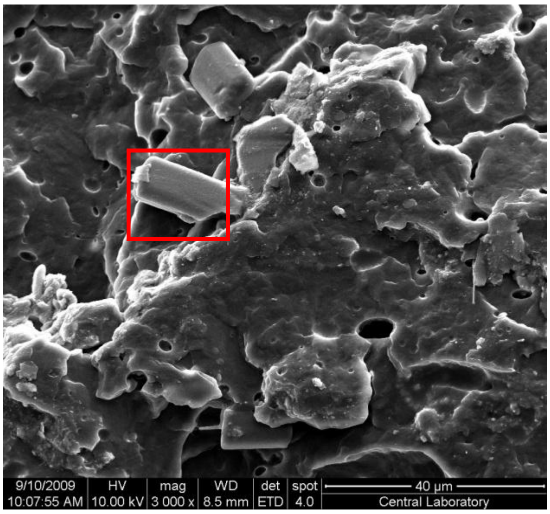


Figure D.3 EDX analysis result of composite of AO3



```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %    K-Ratio      Z         A         F

   C K     29.22    55.85    0.0562    1.1118    0.1730    1.0000
   SiK      1.67     1.36    0.0168    1.0259    0.9547    1.0305
   P K     53.06    39.32    0.5115    0.9887    0.9721    1.0030
   PdL     16.05     3.46    0.1186    0.7675    0.9625    1.0000
  Total   100.00   100.00

Element   Net Inte.     Bkgd Inte.    Inte. Error      P/B

  C K        7.25          0.25           7.91        28.50
  SiK        3.22          2.67          18.70         1.21
  P K       82.98          3.39           2.35        24.45
  PdL        6.41          3.27          11.57         1.96
```

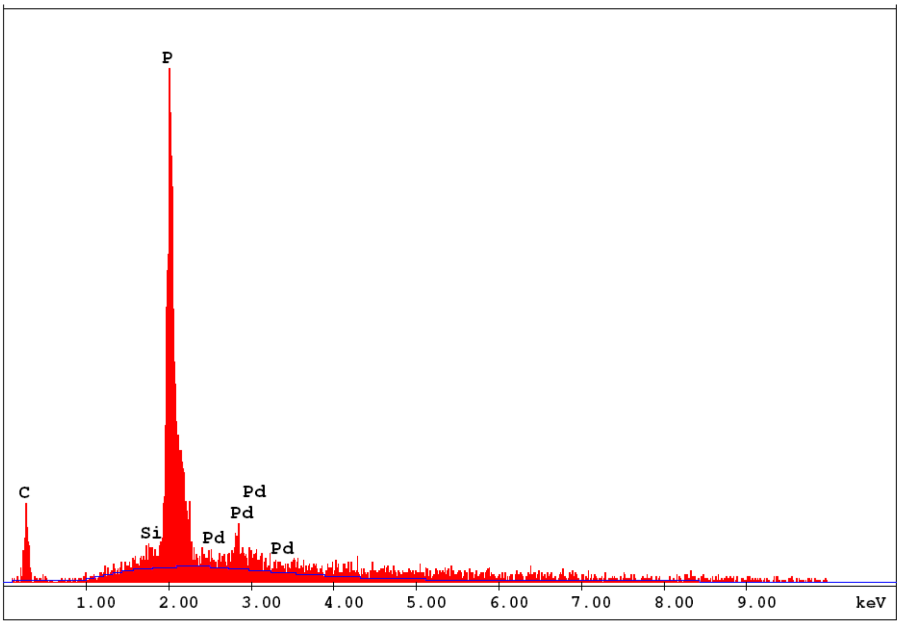


Figure D.4 EDX analysis result of composite of PP/5PDMS(p)/5TPP (TPP particles are marked with red square)

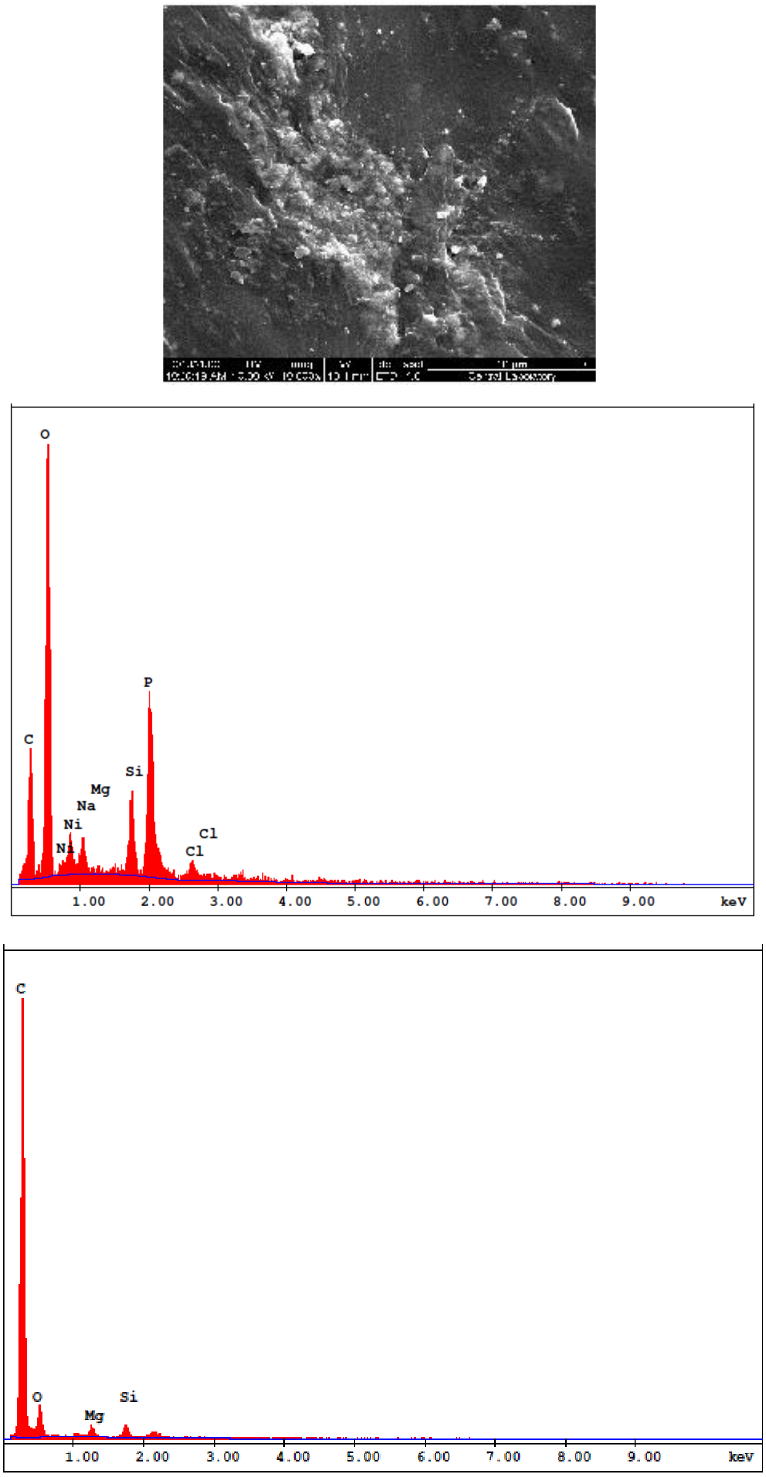


Figure D.5 EDX analysis result of composite of PP/10PDMS/5BP/5MH

APPENDIX E

MECHANICAL PROPERTIES OF COMPOSITES

Table E.1 Tensile strengths of composites

Composite	Tensile Strength (MPa)
PP	50.3 +/- 0.10
PP/1PDMS(p)	55.51 +/- 1.95
PP/5PDMS(p)	49.93 +/- 3.24
PP/5PDMS(p)/5TPP	37.56 +/- 6.61
PP/10PDMS	43.53 +/- 3.06
PP/10PDMS/5BP/5MH	39.94 +/- 0.89
PP/14.25MP/4.75PER/1BP (BP1)	38.59 +/- 1.01
PP/12.75MP/4.25PER/3BP (BP3)	40.03 +/- 2.09
PP/11.25MP/3.75PER/5BP (BP5)	37.08 +/- 1.33
PP/14.25MP/4.75PER/1AO (AO1)	39.75 +/- 2.74
PP/12.75MP/4.25PER/3AO (AO3)	39.69 +/- 2.02
PP/11.25MP/3.75PER/5AO (AO5)	36.43 +/- 1.29
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	36.02 +/- 1.96
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	36.56 +/- 1.18
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	35.18 +/- 1.47
PP/14.25MP/4.75PER/1PDMS (PDMS1)	35.62 +/- 0.90
PP/12.75MP/4.25PER/3PDMS (PDMS3)	24.12 +/- 2.05
PP/11.25MP/3.75PER/5PDMS (PDMS5)	36.21 +/- 1.38

Table E.2 Elastic modulus results of composites

Composite	Elastic Modulus (MPa)
PP	734.50 +/- 59.80
PP/1PDMS(p)	944.53+/-5.74
PP/5PDMS(p)	921.4+/-3.29
PP/5PDMS(p)/5TPP	819.78+/-4.38
PP/10PDMS	870.57+/-25.81
PP/10PDMS/5BP/5MH	1067.00+/-32.57
PP/14.25MP/4.75PER/1BP (BP1)	1443.50+/-162.49
PP/12.75MP/4.25PER/3BP (BP3)	1373.00+/-133.70
PP/11.25MP/3.75PER/5BP (BP5)	1254.40+/-103.08
PP/14.25MP/4.75PER/1AO (AO1)	1488.75+/-77.63
PP/12.75MP/4.25PER/3AO (AO3)	1356.40+/-78.19
PP/11.25MP/3.75PER/5AO (AO5)	1294.25+/-90.06
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	1390.33+/-92.93
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	1414.25+/-96.35
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	1184.25+/-93.98
PP/14.25MP/4.75PER/1PDMS (PDMS1)	1215.80+/-75.07
PP/12.75MP/4.25PER/3PDMS (PDMS3)	1093.40+/33.87
PP/11.25MP/3.75PER/5PDMS (PDMS5)	1040.00+/-71.74

Table E.3 Elongation at break values of composites

Composite	Elongation at Break (%)
PP	765.40 +/- 24.30
PP/1PDMS(p)	523.94 +/- 21.22
PP/5PDMS(p)	524.82 +/- 22.08
PP/5PDMS(p)/5TPP	513.57 +/- 12.12
PP/10PDMS	706.62 +/- 17.66
PP/10PDMS/5BP/5MH	476.46 +/- 14.64
PP/14.25MP/4.75PER/1BP (BP1)	164.99 +/- 67.24
PP/12.75MP/4.25PER/3BP (BP3)	290.50 +/- 59.29
PP/11.25MP/3.75PER/5BP (BP5)	293.18 +/- 56.03
PP/14.25MP/4.75PER/1AO (AO1)	52.52 +/- 19.52
PP/12.75MP/4.25PER/3AO (AO3)	64.55 +/- 22.79
PP/11.25MP/3.75PER/5AO (AO5)	47.56 +/- 14.67
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	309.81 +/- 29.09
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	298.97 +/- 30.81
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	197.24 +/- 10.07
PP/14.25MP/4.75PER/1PDMS (PDMS1)	242.47 +/- 45.91
PP/12.75MP/4.25PER/3PDMS (PDMS3)	243.45 +/- 46.01
PP/11.25MP/3.75PER/5PDMS (PDMS5)	499.08 +/- 46.23

Table E.4 Impact strengths of composites

Composite	Impact Strength (kj/m^2) with standard deviation
PP	23.52 +/- 3.50
PP/1PDMS(p)	23.08 +/- 2.19
PP/5PDMS(p)	28.71 +/- 1.78
PP/5PDMS(p)/5TPP	22.59 +/- 3.81
PP/10PDMS	67.24 +/- 6.81
PP/10PDMS/5BP/5MH	38.87 +/- 5.49
PP/14.25MP/4.75PER/1BP (BP1)	25.73 +/-3.05
PP/12.75MP/4.25PER/3BP (BP3)	23.09 +/- 1.49
PP/11.25MP/3.75PER/5BP (BP5)	23.40 +/- 1.64
PP/14.25MP/4.75PER/1AO (AO1)	23.34 +/- 1.80
PP/12.75MP/4.25PER/3AO (AO3)	25.20 +/- 1.09
PP/11.25MP/3.75PER/5AO (AO5)	21.61 +/- 1.16
PP/14.25MP/4.75PER/1PMSQ (PMSQ1)	27.03 +/- 1.49
PP/12.75MP/4.25PER/3PMSQ (PMSQ3)	25.52 +/- 2.49
PP/11.25MP/3.75PER/5PMSQ (PMSQ5)	25.91 +/- 2.55
PP/14.25MP/4.75PER/1PDMS (PDMS1)	29.14 +/- 1.59
PP/12.75MP/4.25PER/3PDMS (PDMS3)	23.69 +/- 2.82
PP/11.25MP/3.75PER/5PDMS (PDMS5)	45.21 +/- 1.61