

**Synergistic Effect of Natural Zeolites  
on Flame Retardant Additives**

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**A Dissertation Submitted to the  
Graduate School in Partial Fulfillment of the  
Requirements for the Degree of  
MASTER OF SCIENCE**

**Department: Chemical Engineering  
Major: Chemical Engineering**

**İzmir Institute of Technology  
Izmir, Turkey  
July, 2004**

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## ABSTRACT

Intumescent flame retardant systems were proposed to increase flame retardancy performance of polymers without environmental hazard. An intumescent system consisting of ammonium polyphosphate (APP) as an acid source and blowing agent, pentaerythritol (PER) as a carbonific agent and natural zeolite (clinoptilolite, G6) as a synergistic agent was used in this study for flame retardancy of polypropylene (PP). APP and PER combination were examined at different ratios (0.25, 0.33, 0.5, 1, 2, 3, and 4) for optimization of formulation of flame retardancy. The zeolite was incorporated into flame retardant formulation at four different concentrations (1, 2, 5, and 10wt%) to investigate synergism with the flame retardant materials. Filler content was fixed at 30wt% of total amounts of flame retardant PP composites. The zeolite and APP were treated with two different coupling agents namely, 3-(trimethoxysilyl)-1-propanethiol and (3-aminopropyl)-triethoxysilane for consideration influence of surface treatments on mechanical properties and flame retardant performance of composites.

To investigate thermal behaviour of flame retardant PP composites with and without zeolite, samples were heated on optic microscope hot stage. Both of the composites behaved similarly during heating from room temperature to 203°C. Molten pentaerythritol was observed as a second phase in molten polypropylene at 203 °C. Bubble formations were not observed. Flame retardants did not cause any foam formation during processing of mixture at 190°C in rheomixer and hot press. SEM pictures of non-burnt and burnt flame retardant (FR) PP composites with and without zeolites did not reveal significant difference considering foam size and shape compared to composites without zeolite. Zeolite crystals did not exhibit any deformation during burning of composite.

Flammability of FR-PP composites were determined by UL-94 flame test in air. Burning rate of composite was measured for flammable composite in atmospheric condition. The limiting oxygen index (LOI) test method provided measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports combustion of pure PP, zeolite reinforced PP and flame retardant PP composites. The best flame retardant performance was achieved with APP:PER(3:1)+PP+2% zeolite and APP:PER(2:1)+PP+5% zeolite formulations, exhibiting 37.4 and 38% LOI values respectively. LOI values reached maximum value 41% with mercapto silane treated APP:PER(2:1) at 5wt% Zeolite PP composite.

Young's modulus of composites decreased with increasing amounts of APP in composite on the contrary to their elongation at break properties.

## **ACKNOWLEDGMENTS**

I would like to thank to my advisors, Professor Semra ÜLKÜ and Professor Devrim BALKÖSE for their supervision, guidance, support and encouragement during my studies. I am also grateful to Dr. Esen ARKIŞ for proposal of this topic. I would also like to thank to İYTE-34-2002 fund for supporting my studies.

I would like to thank Research Specialists Burcu ALP and Filiz ÖZMIHÇI for the thermal analyses, Research Specialist Özlem ÇAĞLAR for the FTIR analyses, Research Specialists Gökhan ERDOĞAN, Duygu OĞUZ, Mine BAHÇECİ, and Evrim YAKUT for SEM analysis. I would like to express my sincere gratitude Feridun ŞENOL from PETKİM Petrochemicals Co. for providing mold of UL-94 test. I would like to appreciate deeply to my roommates, research assistants: Ayben TOP and Dildare METİN for their friendships and encouragement during my studies. I am also indebted to Ulaş ATIKLER and Gözde GENÇ for their helps.

## ÖZ

Polimerlerin ateşe dayanıklılığını arttırmak için kullanılan yanmayı önleyici sistemleri konu alan araştırmalarda özellikle çevreye zararsız sistemler tercih edilmektedir. Bu çalışmada, Polipropilenin yanmasını geciktirmek için asidik malzeme ve köpük yapıcı olarak amonyum polifosfat (APP), karbonlaştırıcı olarak Pentaeritritol (PER) ve sinerjik etki sağlayan doğal zeolitten (klinoptilolit, Gördes II) oluşan köpüren alev geciktirici sistem önerilmektedir. İdeal formülü belirlemek amacıyla farklı APP ve PER (0.25, 0.33, 0.5, 1, 2, 3, ve 4) oranları denenmiştir. Aleve dayanıklı formülün geliştirilmesi ve sinerji etkisi gözlenebilmesi için zeolit miktarı 1, 2, 5 ve 10% oranlarında katılmıştır. Toplam dolgu maddesi miktarı her denemede toplam PP kompozit ağırlığının 30%'u olarak sabit tutuldu. Zeolit ve APP katkı maddeleri iki çeşit yüzey geliştirici 3-(trimethoxysilyl)-1-Propanethiol ve (3-aminopropyl)-triethoxysilane modifiye edilerek, bu yüzey işlemlerinin mekanik özellikler ve alev geciktiricilik performansı üzerindeki etkileri incelendi.

Zeolit ilaveli ve zeolitsiz PP kompozit malzemelerin oda sıcaklığından 200°C'ye kadar olan sıcaklık aralığında gösterdikleri ısıl davranışlar optik mikroskop altında ısıl işlem uygulanarak gözlemlendi. Her iki malzeme ısıtma işlemi sırasında benzer davranış gösterdi. 203°C'de ikinci faz olarak pentaeritritol eriyiği meydana geldi ve kabarcık oluşumu gözlenmedi. Alev geciktirici malzemelerin 190°C'de reomixer ve sıcak preste işlemleri sırasında da köpük oluşturmadığı anlaşıldı. Yanmamış ve yanmış FR-PP kompozit malzemelerin SEM görüntülerinde zeolit ilaveli ve ilavesiz numunelerin köpük büyüklüğünde ve şeklinde belirgin bir farklılığa rastlanmadı ve zeolit ilaveli yanık numunelerde, zeolit kristalinin bozulmadığı görüldü.

FR-PP kompozit malzemelerin havada alev alma özelliklerini incelemek için UL-94 alev testi uygulandı ve atmosferik koşullarda numunelerin yanma hızları ölçüldü. Saf PP, zeolit katkılı PP ve alev geciktirici formül içeren PP kompozitlerin ayarlanabilir oksijen ve azot gaz karışımı altında yanmalarını sağlayan minimum oksijen konsantrasyonlarının belirlenmesi için sınırlı oksijen indisi (LOI) testi uygulandı.

Sonuç olarak en iyi alev geciktiricili kompozit malzemelerin APP:PER(3:1)+ PP +2% zeolit ve APP:PER(2:1)+ PP +5% zeolit formülleriyle elde edildiği gözlemlendi. Bu numunelerin sınırlı oksijen indisleri sırasıyla, 37.4 ve 38% olarak tayin edildi. Tüm deneyler sonucunda elde edilen en yüksek sınırlı oksijen indisi, merkaptosilan ile işleme tutulmuş APP:PER(2:1)+ PP +5% zeolit formülüyle 41% olarak bulundu. Hazırlanan

kompozit malzemelerin mekanik testleri sonucunda APP miktarı arttıkça elastik modülün düřtüęü, kırılma uzamalarınınsa arttıęı gözlemlendi.

# Chapter 1

## INTRODUCTION

The research and developments of new engineering materials belong to the important fields of material science. One can see the continuous competition between the traditional inorganic engineering materials and polymers. Since the polymeric materials (including composites) are promising, due to their economic versatile applicability, they are widely used in many applications, such as housing materials, transport and electrical engineering. These polyolefins are easily flammable due to their chemical constitutions. Due to increasing demand to polymers, the development of safe and environmental flame retarded polymers is a great importance. Many types of flame retardants are added to polymers to reduce their flammability. In recent years, intumescent technology has found a place in polymer science as method of providing flame retardance to polymeric materials. On heating, fire retardant intumescent material restricts the action of the heat flux or flame. The proposed mechanism is based on charred layer acting as physical barrier, which slows down heat and mass transfer between the gas and the condensed phases. (Bourbigot et al., 1996b)

The presence of non-flammable elements such as Cl, N, Si, and P in polymer chains reduces their flammability and their self-ignition (e.g. chlorinated PE, polyamide, polyacrylonitrile). Some polymers become completely flame resistant when their chains are made only of carbon and a non-flammable element i.e. is the case for poly (tetra fluoro ethylene) or poly (vinyl chloride), poly (vinylidene chloride) (PVDC), and chlorinated PVC (CPVC) which are extinguished immediately when taken out from the flame (Seymour, 1978)

Most of basic commercial polymers are easily flammable. For this reason, flame retardants are used. Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing down or by inhibiting them (Seymour, 1978). The flame retardant can act in various ways i.e. physically or chemically. They do not occur in one stage but should be considered as complex processes in which many individual stages occur simultaneously with one dominating. In addition to an endothermic reaction, dilution of ignitable gas mixture due to the formation of

inert gases may also occur (Troitzsch, 1990). In spite of the few thousands of references on flame retardants, only a small number of compounds are commercially produced as such. They are mainly phosphorus, antimony, aluminium and boron-containing compounds, chlorides and bromides. Flame retardants containing lead, zinc, silicon, zirconium, tin, bismuth, sulphur, and selenium are less common (Seymour, 1978). It is almost accepted that flame retardant can inhibit combustion process of polymers. For example, department of trade and industry consumer safety unit (DTI) reported the fire statistics caused by TV fires from 1974 to 1994 in UK. Reported TV fires are 2356 in 1974 and this reduced to around 430 fires per year between 1984 and 1994. Reduction is 79%. These improvements were obtained as a result of improved the use of flame retardants in circuit boards, components and cabinet panels (DTI report, 2002).

Many types of flame retardants are used in consumer products. Phosphorus-containing flame retardant compounds are family of promising flame retardants as they release less toxic gases and smoke during combustion compared with conventional halogen-based compounds (Zhu and Shi, 2003). Aluminium and magnesium hydroxides are increasingly being incorporated in polypropylene due to its flame retardancy and smoke suppressing effect (Velsco et al., 2002).

In recent years, two or more flame retardants are used for obtaining synergism. A synergist may be defined as a case which the effect of two components taken together is greater than the sum of their effects taken separately (Lyons, 1987). Chigwada and Wilkie (2003) studied synergy between conventional phosphorus fire retardants and organically modified clays. The presence of clay along with phosphate provides fire retardancy for styrenic polymer. The adding of zeolites in thermoplastic polymers with combination ammonium polyphosphate and pentaerythritol, leads to significant improvement of their fire retardant performance. Thermo gravimetric analysis reveals that the zeolite may act as a catalyst for development of the intumescent carbonaceous material and stabilise that carbonaceous residue resulting to the degradation of the intumescent shield (Bourbigot et al., 1996c).

Additives play an important role in different application fields in polymer systems. The interface of the surface of particle inclusion plays a key role in the

structure-property relationship. Surfactants and elastomers are used for developing interface surface of filler particle. Bertalan et al., (2001) synthesised and applied reactive surfactants and synergistic reactive surfactants, containing reactive groups and longer unsaturated apolar hydrocarbon chains, respectively, in filled and flame retarded polymer systems. The reaction of these compounds with polyolefins is proven on model system by surface analysis, while their reactions with fillers are demonstrated by DSC. The interface modification in filled/reinforced polymer systems improves mechanical properties. Furthermore, the efficiency of intumescent flame retardant additives in polyolefin could be enhanced (Bertalan et al., 2001). Ravadits et al., (2001) treated surface of polyethylene with vinyltriethoxysilane and with organoboraxo-siloxane (OBSi) and an OBSi-containing intumescent flame retardant compound based on polypropylene, ammonium polyphosphate and pentaerythritol are prepared and investigated. Radio-frequency plasma treatment is applied on samples. Oxygen permeability of samples decreased with modification of surface of polyethylene. Marosi et al., (1998) studied with talc,  $\text{CaCO}_3$ , and modified surface of fillers with reactive and non-reactive surfactants, dicarboni-anhydride containing long unsaturated hydrocarbon and glycerol-monostearate respectively. Higher tensile strength and best flame retardant performance are achieved with employment of surface treatment (Almeras et al., 2003; Marosi et al., 2003).

The effect of flame retardants was to reduce the yields of the organic irritants, acrolein and formaldehyde at test temperatures, 400 and 700°C, under non-flaming conditions. The toxic potency caused by flame retardants under non-flaming conditions is not great enough to outweigh the advantage of reducing the rate of growth of fires (DTI report, 2002). Hardy et al., (2003) reported that flame retardants prevent or delay ignition, reduce the rate of heat release, reduce the quantity of toxic gases generated, and increase the time available for escape.

In this study, the goal was to increase flame resistance of polypropylene. For this purpose, intumescent flame retardant system was selected. Intumescent system requires three different functions of compounds, acid source, blowing agent and carbonific compounds. Ammonium polyphosphate (APP) was used as acid source and blowing agents. Pentaerythritol (PER) was used as carbonific compounds. Natural zeolite, clinoptilolite, was used for synergistic agents with intumescent flame retardant materials. For best flame retardant performance,



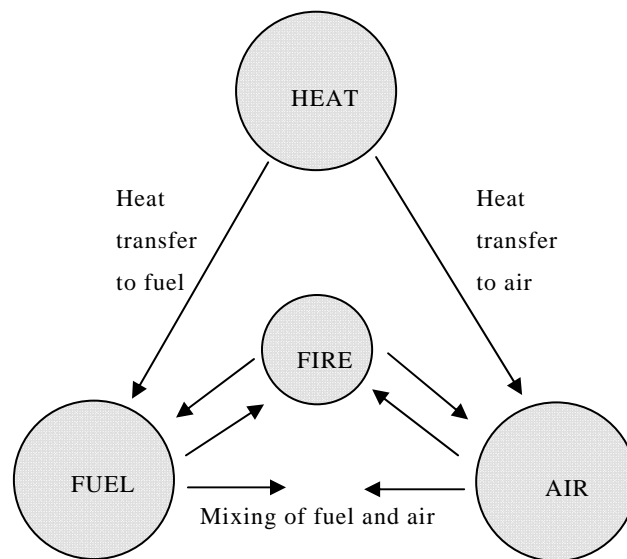
optimum APP/PER ratio and zeolite loading were investigated. Flammability of samples were characterized with standard burning test (UL-94), limiting oxygen index (LOI), and thermal gravimetric analysis (TGA). For improving adhesion between fillers and polymeric matrix, coupling agents 3-(trimethoxysilyl)-1-Propanethiol (MS), (3-aminopropyl)-triethoxysilane (AS) were employed onto surface of APP and natural zeolite. Influence of surface treatments on mechanical properties and flame retardant performance was investigated.

## Chapter 2

### BURNING OF PLASTICS AND FLAME RETARDANTS

#### 2.1 Fire

In order to start a fire, three components, fuel, oxygen and energy, are necessary. The combustion process can not take place without them. The relationship between these three components is illustrated in Figure 2.1.



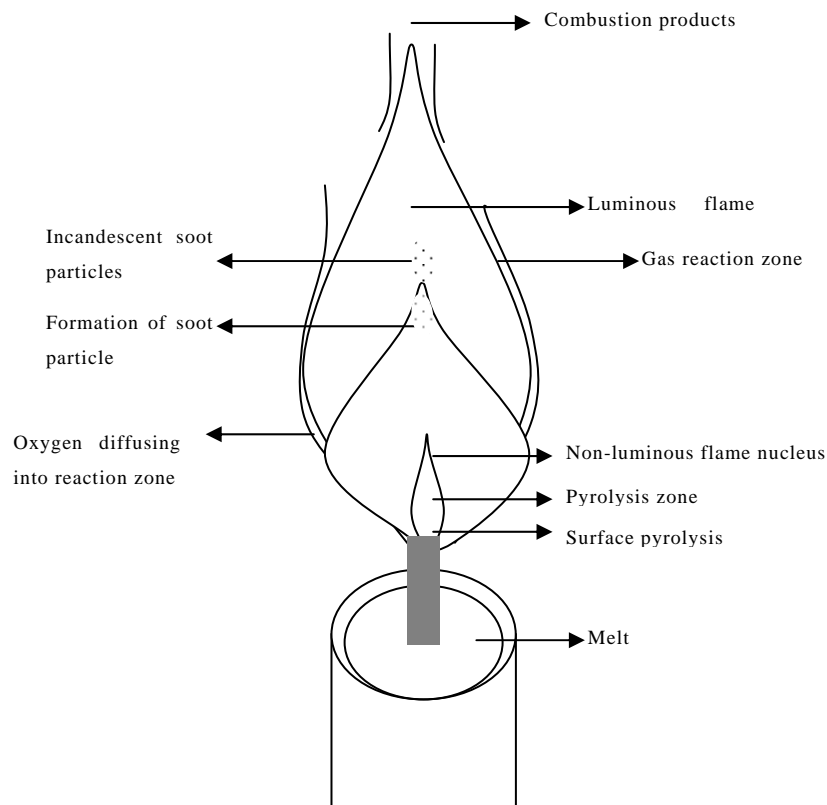
**Figure 2.1:** Fire triangle (Troitzsch, 1990)

Properties of these three components are important for developing or spreading of fire.

- Energy can be transferred to the fuel by radiation, sparks, and flames.
- Oxygen is necessary for the actual burning process, i.e. for chemical reaction of the fuel. It must be present in sufficient quantities at the site of the fire.
- The fuel itself influences fire situations in several ways. Parameters of primary importance affecting the behaviour of fuel in a fire include position in the fire room, “built-in” state, form and physical and chemical properties (Troitzsch, 1990).

## 2.2 The Flame

The flame is combustion process which takes place exclusively in the gas phase. Basically, two types of flame exist: **the premixed** in which the gas composition is fixed prior to combustion (e.g. as in the Bunsen burner) and **the diffusion flame** so-called because the oxygen necessary for combustion diffuses into the gas mixture from the surrounding atmosphere. The best known example of a diffusion flame is the candle flame.



**Figure 2.2:** Candle flame (Troitzsch, 1990)

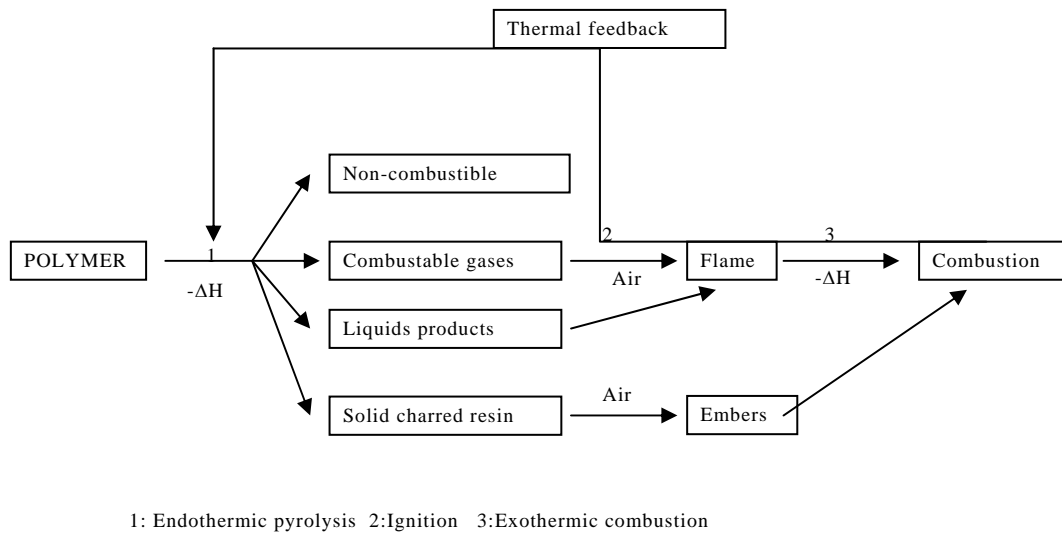
An illustration detailing the individual phenomena of the combustion process in such a flame is shown in Figure 2.2. A reducing atmosphere exists in the flame nucleus owing to the lack of oxygen. The hydrocarbon fragments from pyrolysis migrate to regions in which temperatures reach  $1000^{\circ}\text{C}$ . Generation of conjugated double bonds followed by cyclisation and aromatisation leads to the formation of soot particle. The latter are transported further and start to glow, causing luminescence of the flame. They are consumed in the luminescent region of the flame by reaction with water and carbon dioxide to form carbon monoxide.

The pyrolysis gases are carried to the exterior and encounter oxygen diffusing inwards. In this flame mantle reaction zone, high energy, primarily oxygen-containing radicals are generated at temperature around 1400°C. These maintain the combustion reaction. If the process is uninterrupted and an adequate supply of oxygen is maintained, the end products of combustion of the candle flame are carbon dioxide and water. The processes which take place during the combustion of plastics are, in principle, similar to those of the candle flame (Troitzsch, 1990).

### 2.3 Burning of Plastics

There are several distinct stages in the burning process of plastics: heating, degradation and decomposition, volatilisation and oxidation (Lyons, 1987). To understand the burning of polymers better combustion processes are illustrated in Figure 2.3.

In the first stage, a source of energy (radiative, convective or conductive) causes thermal degradation (pyrolysis) of the polymer resulting in breakage of covalent bonds and formation of a range of intermediate products.



**Figure 2.3:** Polymer combustion process (DTI report, 2002)

The precise degradation mechanism also depends on the nature of the atmosphere and environment in which the polymer substrate degrades. Under reduced oxygen conditions the pyrolysis is endothermic but in the presence of oxygen, oxidative pyrolysis occurs which is generally exothermic.

The initial pyrolysis products consist of complex mixture of combustible and non-combustible gases, liquids, which may subsequently volatilize and solid carbonaceous chars, together with highly reactive species such as free radicals. The free radicals formed at different stages of the combustion process play a key role in determining the course of this process, the rate and magnitude of heat release and the consequential rate of flame spread.

When the initial combustible products in an admixture with atmospheric oxygen reach the lower ignition limit, they ignite producing the flame. These reactions with oxygen are generally exothermic. The energy released by these processes can initiate further thermal degradation reactions promulgating the fuel source to sustain combustion, thus leading to flame spread. The reactions which take place in the flame are radical chain branching reactions which lead to the production of highly energetic hydrogen and hydroxyl radicals (H- and –OH respectively) which propagate the overall combustion process (Troitzsch, 1990; DTI report, 2002).

Table 2.1 shows the resistance to flammability of well-known commercial polymers having different chemical structure. Obviously, the resistance to flammability decreases when the hydrogen and the oxygen contents increase in the polymeric chain. The increase of C/O ratio cause to decrease flammability of polymer (Seymour, 1978).

**Table 2.1:** Relative resistance of burning of polymers which having different chemical structures (Seymour, 1978)

<b>Polymer</b>	<b>Relative resistance</b>
Poly (methyl methacrylate)	1.13
Polyethylene	1.13
Polystyrene	1.20
Poly(ethylene terephthalate)	1.40
Polycarbonate	1.93
Polyamides	2.00
Phenolic resins	2.40

### 2.3.1 Polypropylene

The most important polyolefins used as standard plastics are low density polyethylene (PE, LD), high density polyethylene (PE,HD), and polypropylene (PP).

Polyolefins burn hesitatingly at first with a small bright blue flame (PE,LD; PE,HD) and subsequently with a bright yellow flame which continues to burn after removal of the ignition source. The fire gases and smoke vapours smell of wax and paraffins; this odour is pungent in the case of polypropylene.

The degradation of polyolefins involves statistical chain rupture, resulting in multitude short, and medium and long chain fragments. These consist mainly of olefins, paraffins and cyclic hydrocarbons. The long chain fragments and the soot-like products formed by cyclisation and dehydrogenation contribute to smoke development. Carbon oxides and water are also formed during combustion. Thermal characteristics of various thermoplastics are shown in Table 2.2 (Troitzsch, 1990).

Polypropylene is the lightest major plastic, with a density of 0.905 kg/cm<sup>3</sup>. It is high crystallinity imparts to it high tensile strength, stiffness and hardness. Polypropylene can be made in isotactic or atactic form. Polypropylene has excellent electrical properties and the chemical inertness and moisture typically of hydrocarbon polymer. It is completely free from environmental stress cracking. However, it is inherently less stable than polyethylene to heat, light and oxidative attack (presumably because of the presence of tertiary hydrogens) and must be stabilized with oxidants and ultraviolet light absorbers for satisfactory processing and weathering. The crystallizability of isotactic polypropylene makes it the sole form with properties of commercial interest. Isotactic polypropylene is an essentially linear, high crystalline polymer, with a melting point of 165°C.

Further comparison to HDPE, commercially grades of isotactic-PP have a higher T<sub>m</sub>, slightly lower crystallinity, and better crack resistance. Unlike polyethylene, whose lowest-energy conformation is the extended planar zig zag the pendant methyl groups of PP requires more complicated conformation whereby three monomer units constitute a single turn in a helix. Its higher T<sub>m</sub> allows PP to be used in products that must be steam sterilized. One disadvantage of PP is the susceptibility of its methyl groups to thermooxidative degradation (Fried, 1995).

**Table 2.2:** Thermal characteristics of various thermoplastics (Troitzsch, 1990)

Polymer	Temperature resistance		Vicat-softening point B (°C)	Decomposition temperature (°C)	Flash-ignition temp. (°C)	Self-ignition temp. (°C)	Heat of combustion $\Delta H$ (kJ/kg)
	short term (°C)	Long term (°C)					
Polyethylene LD	100	80	-	340-440	340	350	46500
Polyethylene HD	125	100	75				
Polypropylene	140	100	145	330-410	350-370	390-410	46000
Polystyrene	90	80	88	300-400	345-360	490	42000
PVC rigid	75	60	70-80	200-300	390	455	20000
Polyamide 6	150	80-120	200	300-350	420	450	32000
Poly carbonate	140	100	150-155	350-400	520	No ignition	31000

The oxidative processes of PP are rather complex. The oxidative and degradation products formed are dependent on a variety of factors, including oxygen availability, impurities, residual catalyst form, physical form (molten solid), crystallinity, storage temperature, air pollutants, radiation exposure, metal exposure, chemical exposure, part thickness, stress in the part, co monomer content, and other additives present. The traditional description of oxidation and degradation of PP shows the initiation, propagation, branching and termination steps:

RH: polypropylene

RO-: alkoxy radical

R-: alkyl radical

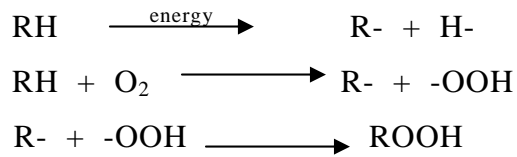
ROO-: peroxy radical

HO-: hydroxy radical

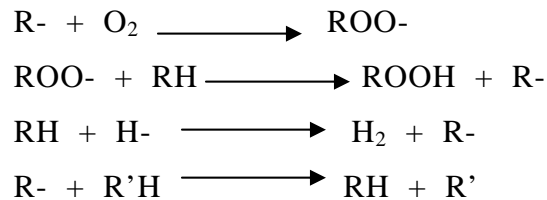
ROH-: alcohol

ROOH-: hydroperoxide

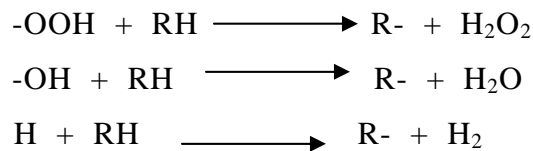
Initiation:



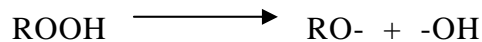
Propagation:



contribution of small free radical fragments

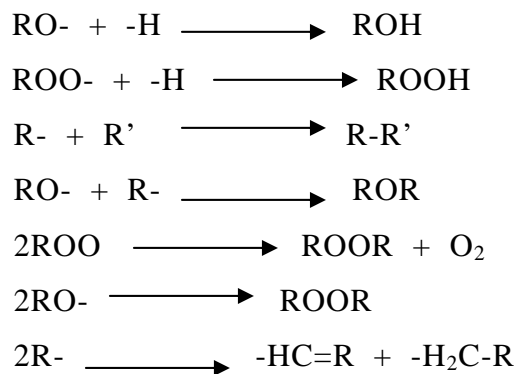


Branching:



This step can be considered a secondary initiation.

Termination:



The viscous environment provided by the PP relative to other non-polymer hydrocarbons affects the radical pair formed in the initiation. The high viscosity should make recombination to the hydro peroxide. If the radicals combine, the propagation is delayed until enough energy is available to cause homolytic cleavage of the hydro peroxide. These reactions do not occur haphazardly. In propagation step, carbon-based radical is formed. If a peroxy radical is formed



in propagation step then the next step can be the intramolecular abstraction of hydrogen atoms. The act of intramolecular abstraction will cause the radical site to migrate down the polymer chain. This migration provides a mechanism for radicals to “find” another radical or antioxidant molecule that can terminate the chain reaction. If termination does not occur, then a mechanism exists for the build up of hydroperoxide concentration in the polymer (Moore, 1996).

## 2.4 Flame Retardants

Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing them down or by inhibiting them (Seymour, 1978). Flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread (Troitzsch, 1990). The various ways in which a flame retardant can act physically or chemically are described below.

### Physical Action

There are several ways in which the combustion process can be retarded by physical action:

- **By cooling:** Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.
- **By formation of a protective layer (coating):** The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cooled, smaller of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded.
- **By addition:** The incorporation inert substances (e.g. fillers) and additives which evolve inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded (Troitzsch, 1990).

## **Chemical Action**

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases.

- **Reaction in the gas phase:** The radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant. The exothermic processes are thus stopped, the system cools down and supply of flammable gases is reduced and eventually completely suppressed.
- **Reaction in the solid phases:** Here two types of reaction can take place. Firstly, breakdown of the polymer can be accelerated by the flame retardant causing pronounced flow of the polymer and, hence, its withdrawal from the sphere of influence of the flame which breaks away. Secondly, the flame retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These form the carbonaceous layer by cyclising and cross-linking (Troitzsch, 1990).

### **2.4.1 Types of Flame Retardants**

The selection of flame retardants is very important, since they often affect polymer properties such as melt viscosity, light stability, heat stability, mechanical and other physical properties. Their choice is also affected by the processing temperature of polymers. They must stand high temperatures without being seriously affected (Seymour, 1978). Additionally, toxicity of flame retardants and of their combustion products is major factor in their selection.

A distinction is made between reactive and additive flame retardants. Combinations of flame retardants may produce a synergistic effect of great importance for practical use.

**Reactive flame retardants** serving as the reactive component are built chemically into the polymer molecule, together with the other starting components. This prevents them from bleeding out of the polymer and volatilising and their flame retardance is thus retained. In addition, they have no plasticizing effect and do not affect the thermal stability of the polymer. They are

used mainly in thermosets (especially polyesters, epoxy resins and polyurethane) in which they can be easily incorporated.

**Additive flame retardants** are incorporated in the plastic either prior, or, more frequently, following polymerisation. They are used specially in thermoplastics. If they are compatible with the plastic they act as plasticizers, otherwise they are considered as fillers. They are sometimes volatile or tend to bleed so their flame retardance may be gradually lost.

Combination of additive or reactive flame retardants with further additives can produce synergistic or antagonistic effect. The synergistic effect occurs when they are used together with specific flame retardants. Synergistic have achieved great importance in practical use because they are less expensive than the actual flame retardants and the additions of the latter can be greatly reduced in the presence of the synergist, without any reduction of the flame retardant effect (Troitzsch, 1990).

#### **2.4.1.1 Halogen-Containing Flame Retardants**

Halogen atoms can be bound aliphatically or aromatically in the flame retardants. The more effective aliphatic halogen compounds are easier to break down and hence are less temperature resistant than aromatic retardants. Their suitability depends on the plastic and the method of incorporation.

The effectiveness of halogen-containing flame retardants increase in the order of  $F \ll Cl < Br < I$ . Fluorine and Iodine-based flame retardants are not used in practice because neither type interferes with the combustion process at the right phase because of its strong bond to carbon. Iodine in contrast is attached to carbon so loosely that it is liberated by even a negligible energy supply; as a result, the polymer properties (e.g. light stability) are affected and the flame retardant effect is already lost in the temperature range of pyrolysis.

Of the two remaining halogens, bromine is the more effective since its weaker bonding carbon enables it to interface at a more favourable point in the combustion process. It is assumed, moreover, that the effective agent, HBr, is liberated over a narrow temperature range so that it is available at high concentration in the flame zone. HCl, which is formed over a wider temperature range and is present at lower concentrations, is thus less effective (Troitzsch, 1990).

### 2.4.1.2 Phosphorus-Containing Flame Retardants

Phosphorus has the most complex and perhaps the most fully developed chemistry. In all cases phosphorus is the central element in a compound; there may be an almost infinite variety of substituents in several oxidation states. In contrast to P, the halogens are not found as central atoms in fire retardants compounds. Rather they are substituents primarily on organic compounds (Lyons, 1987).

Phosphorus-containing flame retardants mainly influence the reactions taking place in the condensed phase. The following processes probably take place in the condensed phase:

- The non-volatile, polymeric phosphoric acids just formed inhibit the pyrolysis reactions by providing the simultaneously forming carbonaceous layer with a glassy coating. The protective layer is resistant to even high temperatures and shields the underlying polymer from attack by oxygen and radiant heat.
- Compounds such as phosphine, some of which are highly reducing that have been formed in addition to the phosphoric acid in the pyrolysis zone promote pronounced charring. The phosphines reduce the formation of CO and CO<sub>2</sub> in favour of C. They probably also suppress after glow in the solid phase because this phenomenon is caused by the oxidation of carbon to CO and CO<sub>2</sub> (Troitzsch, 1990).

### 2.4.1.3 Inorganic Flame Retardants

Few inorganic compounds are suitable for use as flame retardants in plastics, since such compounds must be effective in the range of decomposition temperatures of plastic. This range lies between 150 and 400°C.

Apart from antimony trioxide, which interferes with the combustion process chemically in combination with halogen-containing flame retardants, the most widely used inorganic flame retardants such as aluminium hydroxide and boron-containing compounds affect the combustion process via physical means.

Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, HCl etc., mostly in endothermic reactions. In the gas

phase, these act by diluting the mixture of flammable gases and by shielding the surface of the polymer against oxygen attack (Troitzsch, 1990).

#### **2.4.1.4 Intumescent Coating as Flame Retardants**

Intumescent agents are available commercially for 30 years and used foremost as fire protective coatings. In recent years, they have been used as “flame retardants” for plastics by incorporating the intumescent components in the polymer matrix (Troitzsch, 1990). The intumescent coating must have ingredients which will react on heating to form large amounts of an incombustible, or nearly so, residue. At the same time this residue must be expanded to cellular foam with good insulating properties. And the foam must be tough and adherent so as to resist violent drafts and other forces arising from the fire (Lyons, 1987).

Intumescent coatings are always formulated according to same principles whether they are used as coating or as flame retardants. The intumescent effect is achieved by using the following components.

**Acid source:** This usually consists of the salt of an inorganic non-volatile acid such as boric, sulphuric or phosphoric acid. Salts of phosphoric acid like ammonium poly phosphate which liberate the acid at temperature above 150°C are mostly used. The acid generated initiates the first of a series of reactions, which begins with the dehydration of the carbonific compound and its subsequent charring.

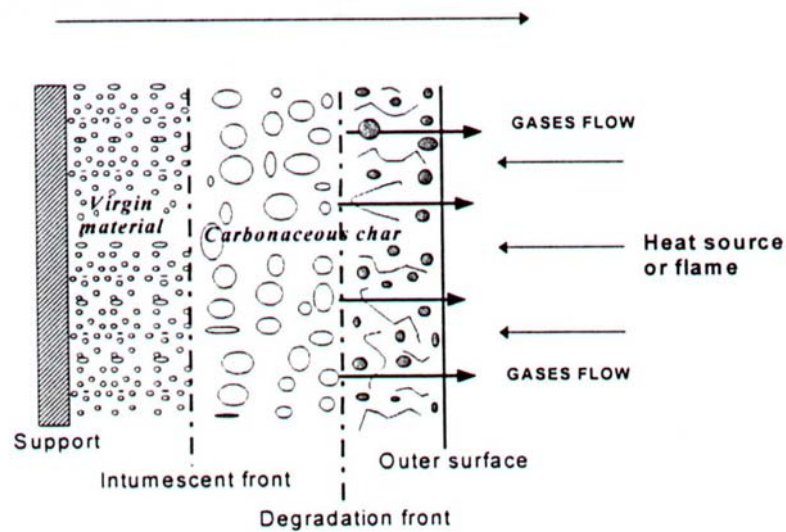
**Carbonific compounds:** They are polyhydroxy compounds which dehydrate and char due to acid attack. These compounds proceed via an esterification reaction. Compounds frequently used include pentaerythritol, starch and phenolic or urea resins.

**Spumific compounds:** Compounds such as chloroparaffins, melamine and guanidine are used as spumific compounds. Under the effect of temperature they liberate large quantities of non-combustible gas such as HCl, NH<sub>3</sub>, CO<sub>2</sub> and ensure the formation of the carbonaceous foam layer over substrate. The

decomposition products of the blowing agent (e.g. chloroparaffin residue) frequently assist charring.

**Resin binders:** These cover the foam with a skin which prevents gas release. They should not harden but remain thermoplastic in order to have an optimum effect. Chlorinated rubbers, for example, are highly suitable since they soften and melt at low temperatures, act as blowing agents via formation of HCl, and contribute to charring with their residue (Troitzsch, 1990).

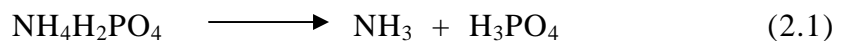
Bourbigot et al.,(1996d) illustrated intumescent coating schematically as shown in Figure 2.4.



**Figure 2.4:** Scheme of intumescent system. (Bourbigot et al., 1996d)

Intumescent coatings act as follows:

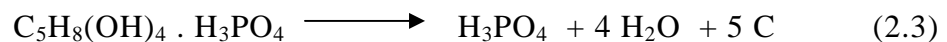
In the first stage the effect of intense heat causes the inorganic salt to decompose to the acid (e.g. ammonium dihydrogen phosphate):



The components of the intumescent mixture start to soften. The acid esterifies the polyhydroxy compound to give the polyol ester (e.g. penta erythritol):



The mixture melts and decomposes; the polyol ester breaks down to acid, water and a carbonaceous residue:



Simultaneously, the compound supplying the blowing agent decomposes and the gases generated expand the molten mass (e.g. chloro paraffin):



The softened resin binder forms a skin over the foam and prevents gas release to the atmosphere. The viscosity of the frothy mass increases and the foam solidifies completely by cross-linking and charring. The foam is some 50 to 100 times as thick as the original intumescent layer resulting in good thermal insulation thus protecting the substrate from the effect of heat and decomposition (Troitzsch, 1990).

#### **2.4.1.4.1 Ammonium Polyphosphate**

The generally accepted explanation of the flame-retarding action of phosphorus-containing substances is that the very stable poly (metaphosphoric acid) formed during the thermal decomposition of the plastic material creates an insulating and protecting surface layer between the polymer and the flame. It has been found that the flame retardancy effect of these compounds depends not only on their concentration but on the heat of their decomposition reaction, which depends on their chemical structure. Compounds containing phosphorus in the lowest oxidation state are the most efficient (Seymour, 1987).

$(\text{NH}_4\text{PO}_3)_n$  is a crystalline compound. It is relatively insoluble in water. The commercial products contain about 85% material that is insoluble in water. It is essentially neutral in pH. When heated, it gradually gives off  $\text{NH}_3$ , the evolution becoming rapid at  $250^\circ\text{C}$  (Lyons, 1987). Properties of ammonium polyphosphate are summarized in Table 2.3.

The synergistic effect of phosphorus and nitrogen compounds has been definitely proven for their use in cellulose. Nitrogen compounds, such as urea, added together with phosphorus compounds are assumed to facilitate the phosphorylation of cellulose with phosphoric acid. They accelerate the formation of phosphoric acid, which is considered the actual dehydrating agent. Dehydration then leads to charring of the substrate.

**Table 2.3:** Properties of ammonium polyphosphate (Clariant Co.)

<b>Features</b>	<b>Data</b>
% N	14-15 % (w/w)
%P	31-32 % (w/w)
Water	Max 0.25
PH value	5.5 – 7.5
10% aqueous solution	
Solubility in water	Max 0.5
At 25°C in 10% suspension	
Decomposition T (°C)	>275°C
Density at 25°C	1.9 g/cm <sup>3</sup>

It is further assumed that the charred zone can be covered.

- By a layer of liquid phosphoric acid,
- By a glassy, temperature-resistant layer of polymeric PNO,
- By a layer of cross-linked polyphosphazenes.

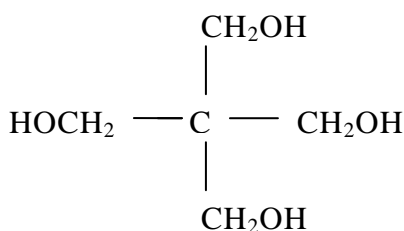
The nitrogen compounds prevent the phosphorus compounds from escaping by pyrolysis into the molten phase, where they are less effective than in the condensed phase (Troitzsch, 1990).

#### **2.4.1.4.2 Pentaerythritol**

Pentaerythritol, 2,2-bis(hydroxymethyl)-1,3 propanediol or tetramethylol methane, is a tetrahydric neopentyl alcohol discovered accidentally by Tollens in 1882 as the by product of the reaction between impure formaldehyde and barium hydroxide.

Pentaerythritol usually crystallizes in the tetragonal shape. Pentaerythritol is an odorless, white compound. It is non-hygroscopic, practically non-volatile and stable in air. Pure pentaerythritol melts at 170°C sublimes slowly on heating and boils at 276°C at 4 kPa.





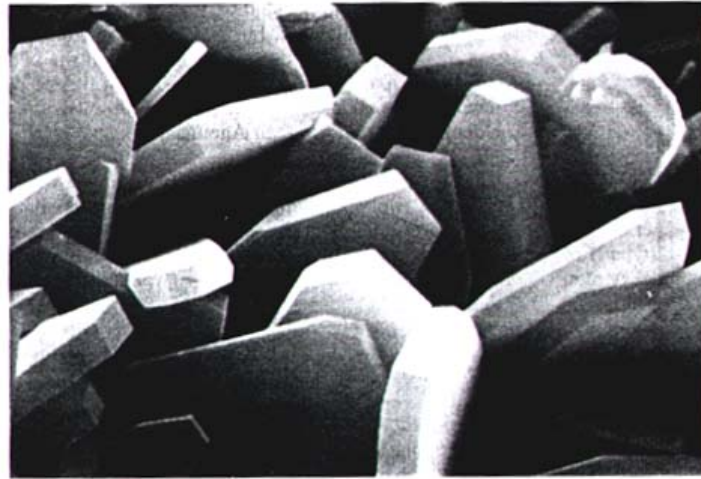
Its density is 1.396g/ml. Pentaerythritol is moderately soluble in cold water and quite soluble in hot water. Solubility of pentaerythritol at different temperatures and solvents are shown in Table 2.4 (Webber et al, 1980).

**Table 2.4:** Solubility of pentaerythritol (Webber et al, 1980)

Solvent	Temperature (°C)	Solubility (g/100g solvent)	Temperature (°C)	Solubility (g/100g solvent)
Water	25	7.23	97	77.2
Methanol, 100%	25	0.75	50	2.1
Methanol 65%	25	3.0	50	8.1
Ethanol 100%	25	0.33	50	1.0
Ethanol 65%	25	3.1	50	8.0
Acetone	56	<1.0		
Benzene	80	<1.0		

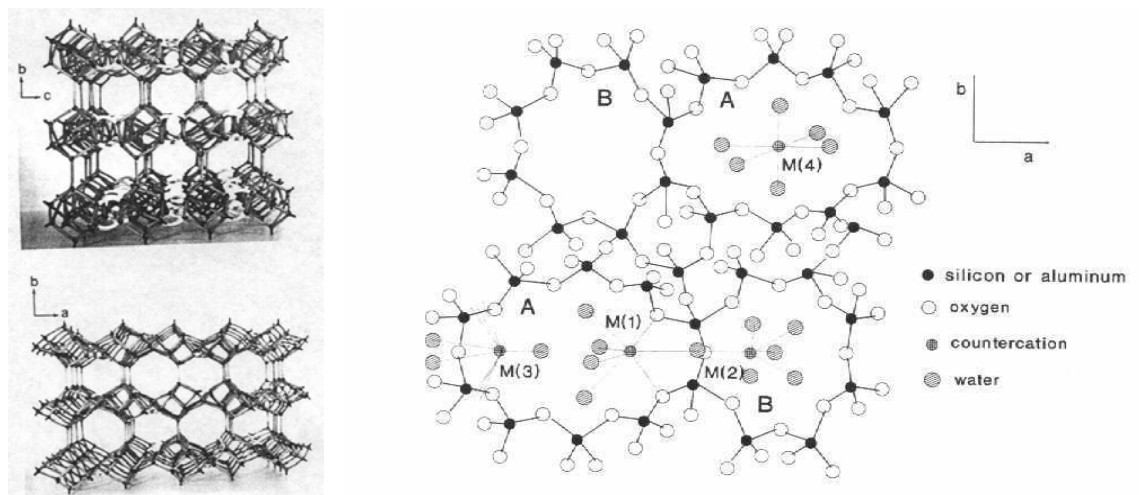
#### 2.4.1.4.3 Synergistic Agent: Natural Zeolite

Zeolites are tectosilicate characterized by three-dimensional framework of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra as shown in Figure 2.5. The framework contains channels and inter-connected voids, which are occupied by the cation and waste molecules as show in Figure 2.6. The size of the voids or the channels is approximately the size of the usual organic molecules. The chemical ideal formula is  $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]_2\text{H}_2\text{O}$ . The part into brackets is the framework of the zeolite with ratio  $y/x \geq 1$  (Lowenstein rule) and  $\text{M}^{n+}$  is the balance cation (Bourbigot, 1996a).



**Figure 2.5:** SEM picture of clinoptilolite (Gottardi and Galli, 1985)

Table 2.5 summarised channel characteristics and cation sites in clinoptilolite. According to literature, the structure of clinoptilolite consists of a two dimensional system of three types of channels. A (10 member ring) and B (8 member ring), perpendicular intersected by channels C (8 member ring) are shown in Figure 2.6.



**Figure 2.6:** Model framework of structural clinoptilolite (Gottardi and Galli, 1985)

Clinoptilolite does not suffer any contraction, nor is the lattice destroyed below 750°C. Clinoptilolite is undestroyed and stable after the overnight heating

at 450°C (Gottardi and Galli, 1985). Clinoptilolite shows three different thermal behaviors.

**Thermal behavior of type I:** If heated up 200°C, the zeolite losses up to 12 H<sub>2</sub>O with a small contraction of the lattice. After that:

Phase A: lattice returns to the original cell dimensions readsorbing its water when cooled to room conditions. It is called phase A.

Phase B: If lattice returns shorter dimensions than the original cell and does not rehydrate immediately. It is called phase B.

Phase I: After months the crystals invert to heulandite I (for intermediate) very close both in water content and cell dimensions to the original phase I.

**Thermal behavior of type II:** the crystals show the reversible dehydration with a corresponding very small contraction of part of the sample, so that after cooling the three phases. A,B and I are all present, even if the original sample is chemically quite homogeneous; the lattice resists without destruction up to 550°C and over.

**Thermal behavior of type III:** The sample undergoes continuous reversible dehydration with only a very small lattice contraction and the lattice is not destroyed if not over 750°C (Gottardi and Galli, 1985)

**Table 2.5:** Channel characteristic and cation sites in clinoptilolite (Top, 2001)

Channel	Tetrahedral ring size/channel axis	Cation site	Major cations	Approx. channel dim. (nm x nm)
A	10/c	M(1)	Na, Ca	0.72x0.44
B	8/c	M(2)	Na, Ca	0.47x0.41
C	8/a	M(3)	K	0.55x0.40
A	10/c	M(4)	Mg	0.72x0.44

Akdeniz (1999) investigated thermal behaviour of clinoptilolite, which was obtained from Gördes II region by DSC. Gördes II clinoptilolite shows three different dehydration behaviors in ambient air. External, loosely bound and

tightly bound water vaporize at three different temperature ranges. External water content of clinoptilolite is 2.27% and vaporizes below temperature 85°C. Loosely bound water of Gördes II is 6.07% and vaporizes between temperature 85°C and 285°C. Tightly bound water is 3.22% of sample and vaporizes above temperature 285°C (Akdeniz, 1999).

## **2.5 Flammability Test Methods**

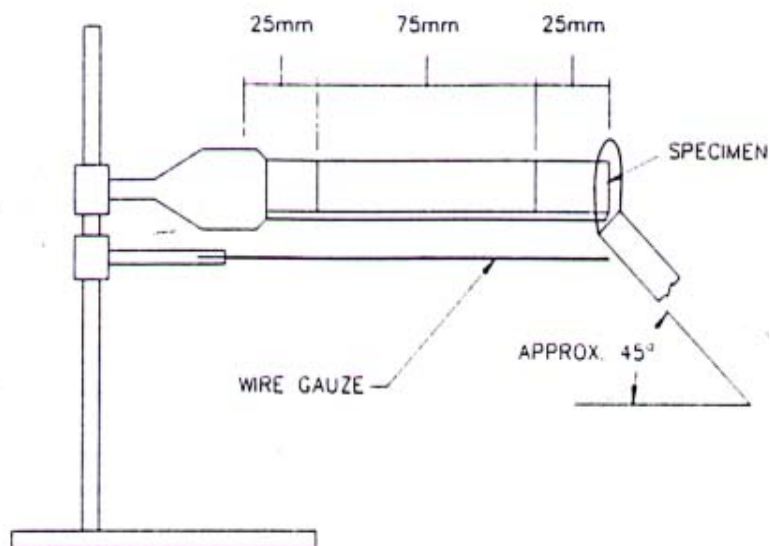
Combustibility tests on materials are used mainly in product development and quality control. The results enable chemists working on improving the fire safety of plastics to compare the combustibility of modifications of chemically similar polymers. And also, data from combustibility tests assist the development of engineering to select materials when designing new products. The results of material tests can, however, give only limited prediction of the fire performance of the plastic in the finished product (Troitzsch, 1990).

### **2.5.1 Standard Flame Test (UL-94)**

UL-94 is one of the most important UL standards to fire safety methods and requirements and contains several fire tests of plastics. UL-94 applies not only to the electrical industry but also to all areas of application except the use of plastics in building (Troitzsch, 1990).

This test method covers a small-scale laboratory screening procedure for comparing the relative rate of burning and/or extent and time of burning of self supporting plastics in the form of bars, molded or cut from sheets, plates or panels and tested in the horizontal position as shown in Figure 2.7. This test method should be used to establish relative burning characteristics of plastic materials and should not be used as a fire hazard test method.

Tests made on a material under conditions herein prescribed can be of considerable value in comparing the rate of burning and/or extent and time of burning characteristics of different materials in controlling manufacturing processes or as a measure of deterioration or change in these burning characteristics prior to or during use correlation with flammability under use conditions is not implied (ASTM D-635, 1994).



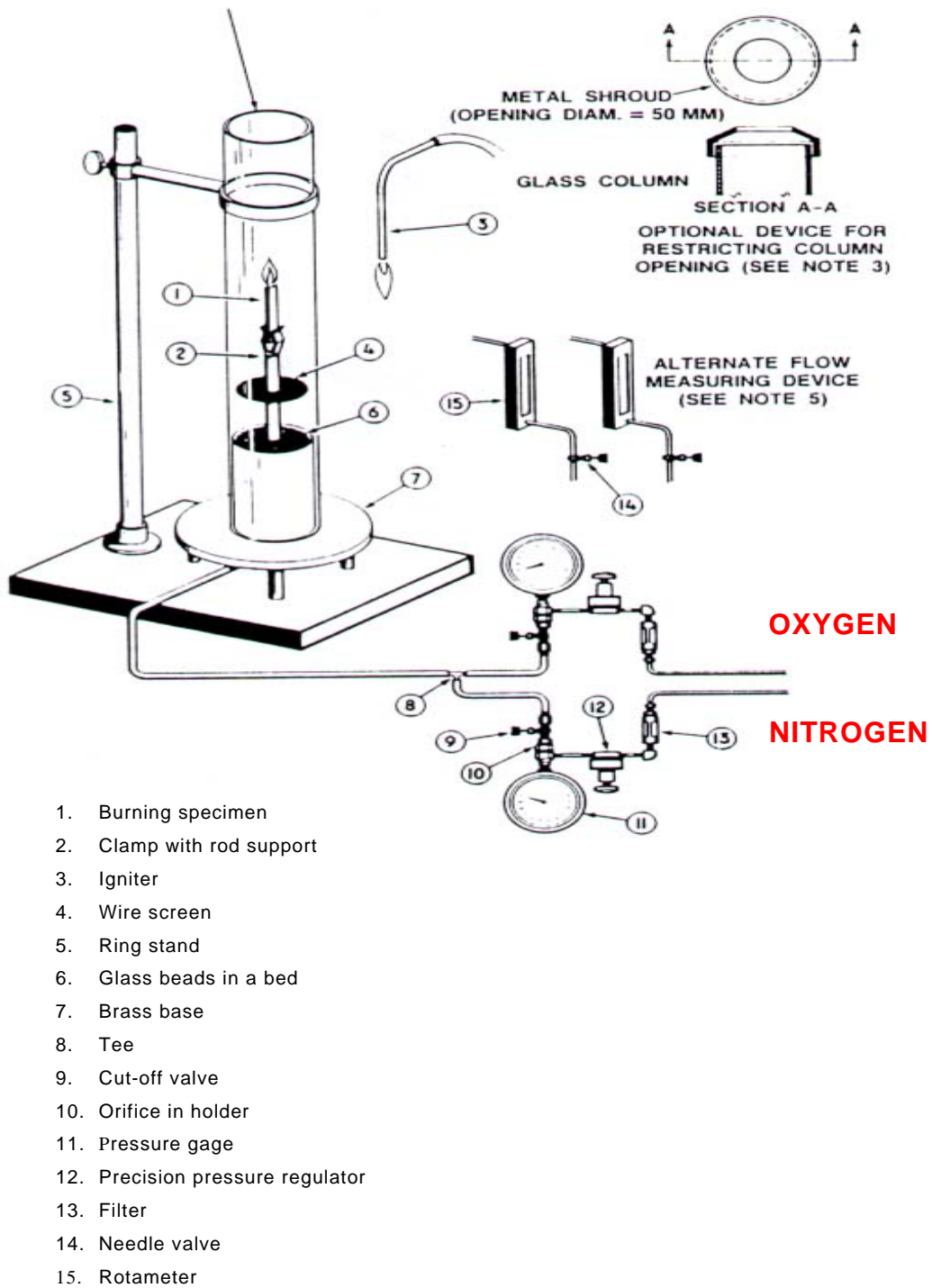
**Figure 2.7:** Schematic illustration of UL-94 test apparatus (ASTM D-635, 1994)

### 2.5.2 Limiting Oxygen Index (LOI)

The oxygen index test is certainly a valuable aid in the development of materials particularly when plastics with the same chemical basis are being compared. Difficulties occur when different types of polymer are being compared, e.g. a poly carbonate which tends to char and polymethyl methacrylate which is non-charring, since carbon formation in the vicinity of the flame can affect the oxygen index.

The test conditions such as burning from top to bottom in an artificially enriched oxygen atmosphere do not reflect a real situation. It is thus incorrect to assume that material with an oxygen index of over 21% can not burn in practice because air contains only 21% oxygen. Such an assumption disregards the fact that burning actually proceeds upwards causing preheating, so that materials with oxygen indexes over 21% can burn in air (Troitzsch, 1990).

Figure 2.8 shows typically scheme of test apparatus. The tubing is connected to flowmeters and the minimum volume of oxygen mixed with a given volume of nitrogen necessary to maintain the combustion of the sample is determined.



**Figure 2.8:** Schematic illustration of Limiting Oxygen Index (LOI) test apparatus (ASTM D-2863, 1994)

### 2.5.3 Thermal Gravimetric Analysis

In thermogravimetric analysis, the weight of a substance is measured as a function of its temperatures. Marosi et al, (1999) summarised the advantages and limitation of thermal analysis at this area:

- The development of new intumescent FR formulations are based generally on the results of thermal analysis as the reduced mass loss (that means the increased char formation) and the endothermic reactions (that cool the systems) can be studied this way.
- TG is powerful method not only to evaluate the residue char, but also to measure the thermo-oxidative resistance of the char and to study the mechanism of action of spumific agents.

These thermal analytical methods promote the conscious choice or new FR additives but in some cases do not allow predicting the efficiency of certain additives. The reason for it is the lack of information about the

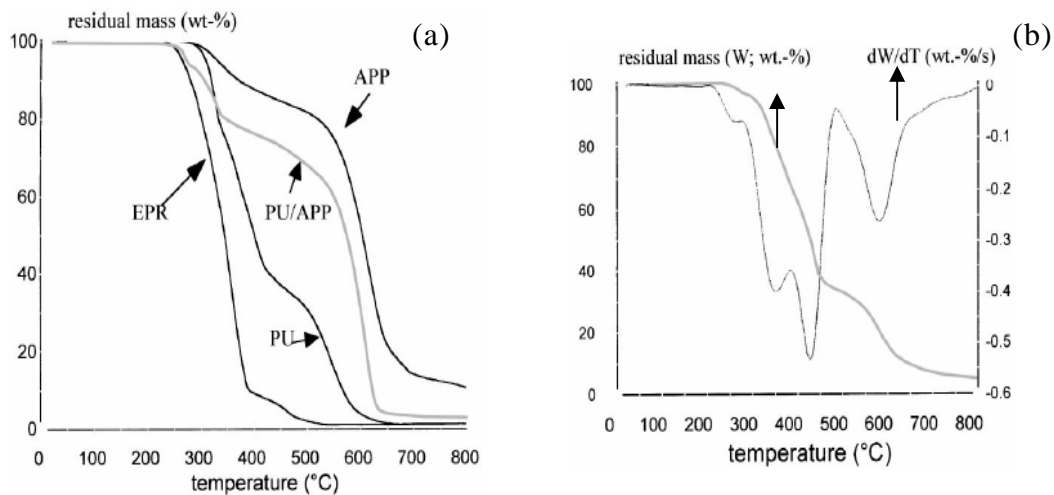
- Interaction between the components
- The rate of charring and
- The changes of surface composition

All of the three mentioned parameter may play determining role in the FR process.

### 2.6 Thermal Behaviour of FR Composites

Bugajny et al, (1999) used TG for determining thermal behaviour of ethylene-propylene rubber (EPR) / polyurethane (PU) / ammonium polyphosphate (APP) intumescent formulations. Analysis was carried out at 7.5 °C/min heating rate under synthetic air flow with a  $5 \times 10^{-7}$  m<sup>3</sup>/s flowrate. EPR decomposed via a two step process: formation of a relatively stable residue at about 375°C which is completely degraded in air at temperatures higher than 550°C as shown in Figure 2.9a. The degradations of PU and APP begin at approximately 300°C whereas the degradation of the PU/APP (1:3) system begins at comparatively low temperature about 270°C. It has been suggested that PU and APP react first at this temperature. The TG and DTG curves of intumescent material (Figure 2.9b) shows four significant change in the slopes, which prove that its degradations is a four steps process. The first one at about 260°C, is

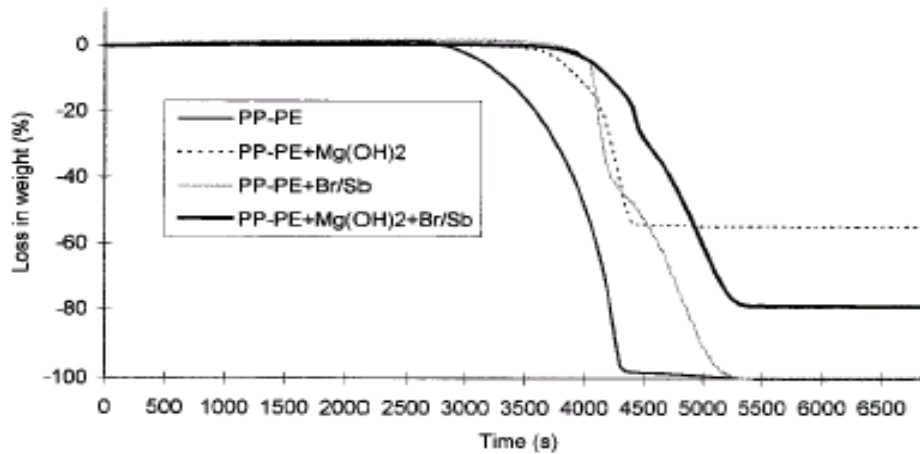
assigned to reaction between the additives. A carbonaceous materials formed in a two step processes in the temperature range 300-430°C. These materials show low rate degradation between 430 and 530°C and finally a rapid degradation in the higher temperature range with formation of residue (about 7w% at 800°C) is observed. Hence, TG curves revealed that degradation of the additives mixture begins at the same temperature in comparison with the virgin polymer, so the intumescent process starts as soon as polymer needs a protection against heating.



**Figure 2.9:** (a) TG curves of EPR, PU, PU/APP(1:3) and APP; (b) TG and DTG curves of EPR/PU/APP (air flow, heating rate 7.5°C/min) (Bugajny et al, 1999)

Flame retardant material (brominated trimethylphenyl indane), antimony and magnesium hydroxide have been used in PP/PE copolymer matrix composite for the determination of effect of flammability by Gibert et al, (2000). TGA curves of PP/PE copolymer and polymer containing additive are illustrated in Figure 2.10. The brominated compound / antimony mixture and virgin polymer are completely decomposed. In samples containing magnesium hydroxide, the calcinated residue contains mainly magnesium hydroxide. The relative location of TGA curves indicates that the brominated flame retardant is more efficient than magnesium hydroxide.





**Figure 2.10:** TGA curves of PP/PE copolymer containing flame retardants (air flow, heating rate 7.5°C/min) (Gibert et al, 2000)

### 2.7 Influence of Fillers

Almeras et al, (2003) investigated effects of fillers (talc, calcium carbonate) on the fire retardancy of intumescent polypropylene compounds. The LOI values of various FR compounds are given in Table 2.6. They found that CaCO<sub>3</sub> decreases flame retardancy of polymers slightly, while the talc has insignificant effect. Almeras et al. researched effect of filler on mechanical properties. The mechanical properties of PP and intumescent FR additives system (APP/PA6/EVA) containing PP (reference) are compared to the compounds loaded with fillers CaCO<sub>3</sub> (PPcarb), talc included as pure filler (PPtalc), and commercial talc (PPtalcom). Table 2.7 shows that the incorporation of intumescent FR additive in the PP and fillers reinforced materials leads to an increase of the Young's modulus and to a decrease of the elongation at break as expected.

**Table 2.6:** Flammability characteristics of various FR compounds (Almeras et al, 2003)

For compounds	Flammability LOI (%)
Reference	32±0.5
PP carb	29±0.5
PP talc	31±0.5
PP talcom	32±0.5

**Table 2.7:** Mechanical properties of various FR compounds (Almeras et al, 2003)

<b>Properties</b>	<b>PP</b>	<b>Reference</b>	<b>PP carb</b>	<b>PP talc</b>	<b>PP talcum</b>
Young's Modulus (MPa)	1340±50	1730±90	1750±100	2200±200	2400±130
Stress max (MPa)	33±1	21.8±0.3	15±0.5	19.7±0.5	35±0.5
Elongation at break (MPa)	14±0.5	10±0.5	4±0.5	4±0.5	7±0.2

Chigwada and Wilkie (2003) studied synergy between conventional phosphorus fire retardants and organically-modified clays and they found organically-modified clays can lead to fire retardancy of styrenics. Polystyrene-clay nano-composites are combined with phosphorus-containing fire retardants, tricresylphosphate (TCP), trixylylphosphate (TXP) and resorcinoldiphosphate (RDP). The TGA data for all of the nano-composites are shown in Table 2.8. The addition of clay to PS caused an increase in the degradation temperatures however the addition of phosphate causes to small decrease in the mid-point temperature of the degradation.

Combination of clay with TCP and TXP phosphorus compounds increases the onset temperature. In the particular case of RDP, the onset temperature is actually decreases with clay combination. RDP has a better thermal stability than other phosphates (TCP and TXP).

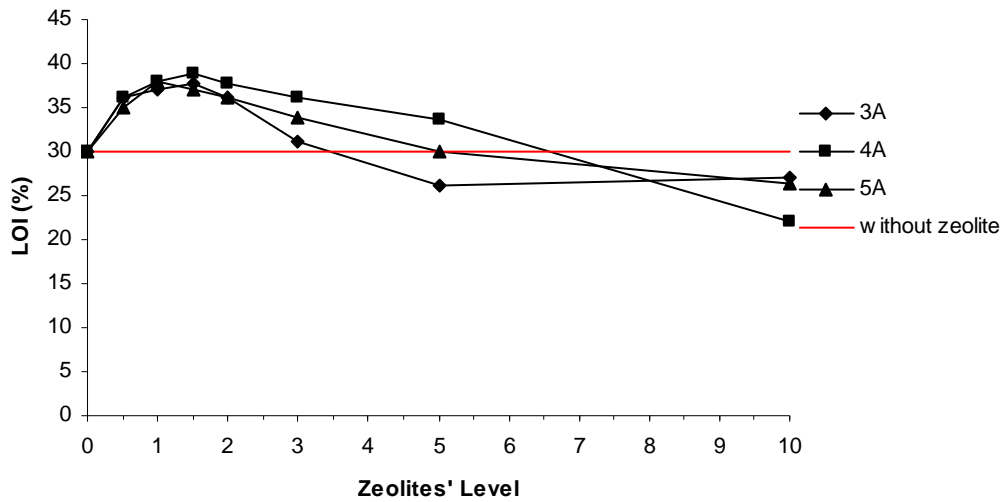
Zeolites are used as synergistic agents for intumescent fire retardant formulations. Zeolites act as a catalyst for the development of the intumescent carbonaceous material and stabilize the carbonaceous residue resulting to the degradation of the intumescent shield (Bourbigot et al, 1996a)

During thermal degradation of intumescent formulation zeolite may adsorb some volatile components. The adsorption influence in the zeolites depends thus on the size of the apertures and the dipolar moment of the fixed molecule. The size of the apertures depends on the zeolite structure and on the number and the size of cations.

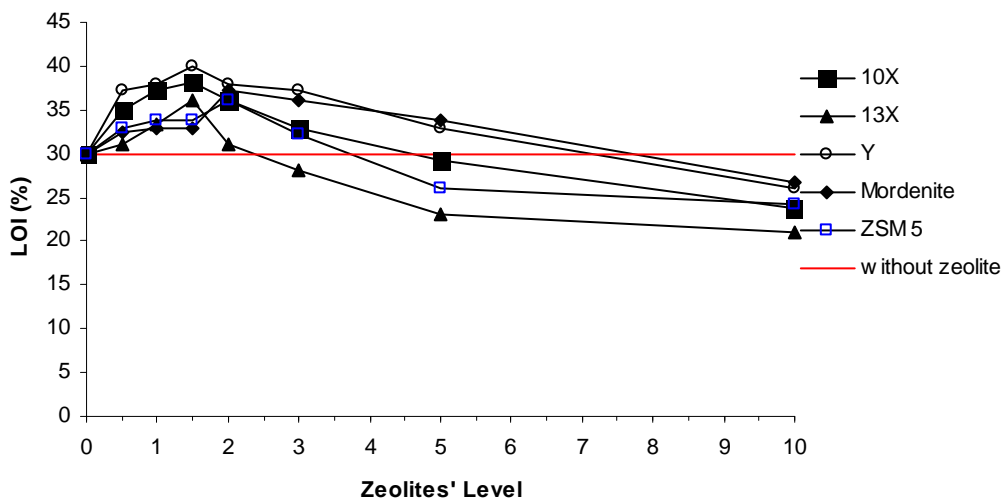
Bourbigot et al, (1996a) studied effects of apertures' size, cation and cavities' diameter of zeolite on flammability of PP containing 30%. The curves of the LOI values versus zeolites' level are shown in Figures 2.11 and 2.12. Synergistic effect is observed for all zeolites and that the LOI maxima are at about 1.5wt% of zeolite. For a type of zeolite the maxima of the LOI values are very close and there is therefore no significant influence of the alkali cation on the maximum performance. In the case of a X type zeolite, a calcium compensation cation seems favourable whereas in the case of a A type zeolite the contrary is observed. Bourbigot et al, (1996a) found no relation between the compensation cation or the apertures' size of the zeolites and the flame retardance performance. Zeolite delays the oxidation of the char and turns the degradation of the material to the formation of phosphocarbonaceous structure covered by a carbonaceous coating constituted mainly in polyaromatic species (Bourbigot et al, 1997). Among the possible alumino-silicate fillers, Bourbigot et al, (1997) proved that zeolites present a potential application as FR material; the combination of zeolites and conventional heat insulating materials ensures an enhancement of the protective effect.

**Table 2.8:** TGA data for polystyrene nano-composites containing various phosphates (Chigwada and Wilkie, 2003)

Sample	T <sub>10% mass loss</sub>	T <sub>50% mass loss</sub>	Char (%)
PS	351	404	0
PS+3% clay	401	454	4
10% TCP+PS	353	419	2
15% TCP+3% clay	374	439	6
15% TCP+5% clay	332	428	11
15% TXP+PS	370	437	3
15% TXP+3% clay	376	443	6
15% TXP+5% clay	371	439	6
15% RDP+PS	417	447	2
15% RDP+3% clay	387	438	8
15% RDP+5% clay	404	446	8



**Figure 2.11:** LOI values of polymer + APP/PER vs A types of zeolites' level (additives' level is remained constant equalling 30wt%) (Bourbigot et al, 1996a)

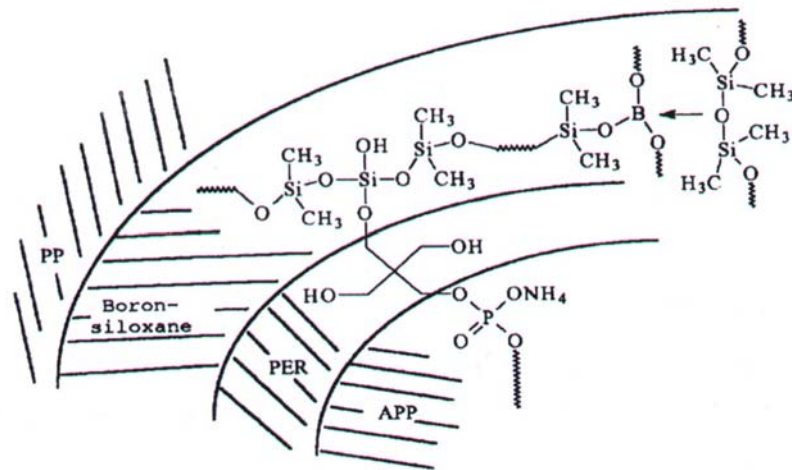


**Figure 2.12:** LOI values polymer + APP/PER synergistic agents' level (additives' level is remained constant equalling 30wt%) (Bourbigot et al, 1996a)

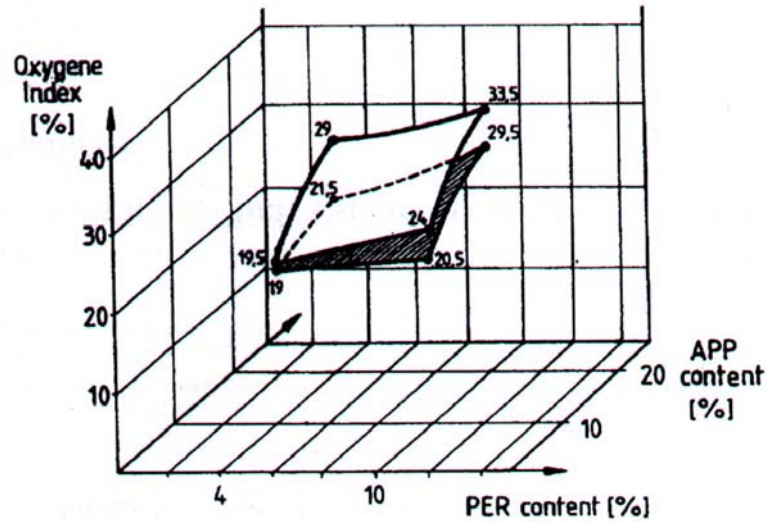
## 2.8 Role of Interface Modification

Surface modification of additives is employed for improving compatibility of filler with polymer matrix. The particulate additives are incorporated at low concentration. However, they cause to decrease mechanical properties. Surface modifiers such as silanes etc. promote adhesion between filler and matrix by either physical or chemical bonding. Enhanced interface of additives and polymeric matrix provide to increase mechanical properties of composite.

Marosi et al. (1998) improved mechanical properties and stability of the products by modification of the interphase using a boron siloxane-elastomer as shown in Figure 2.13. The treatment was proved to be quite effective not only for improving the mechanical properties, but also for developing flame retardant efficiency as shown in Figure 2.14.

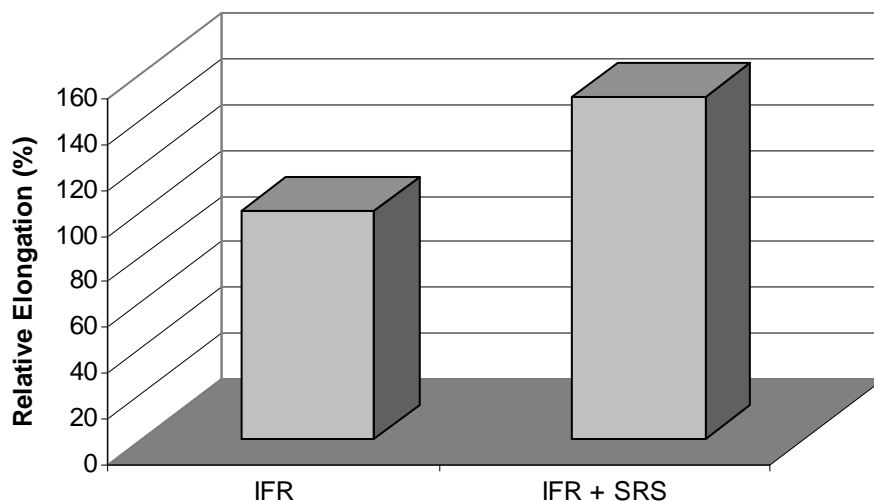


**Figure 2.13:** The schematic structure of interphase formed around APP flame retardant particles (Marosi et al, 1998)

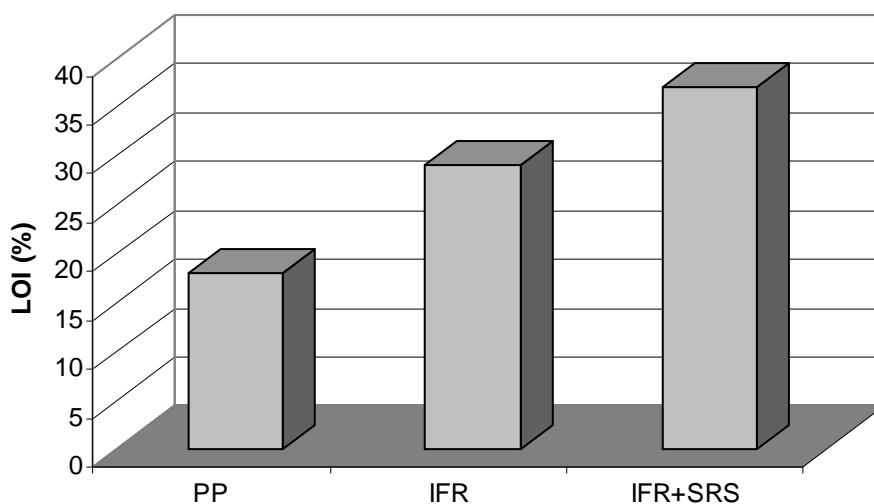


**Figure 2.14:** Oxygen index of PP containing 34% flame retardant additive without (shaded) and with 9.7% boron siloxane (clear) interlayer (Marosi et al, 1998)

Bertalan et al. (2001) used synergistic reactive surfactant (SRS), capable of reaction with the ammonium polyphosphate, for interfacial modifier improving not only the mechanical properties but also the flame retardancy. In the presence of synergistic reactive surfactants, including low molecular boron silicone segment, the elastic elongation at breaks improves markedly as shown in Figure 2.15. The LOI of PP and intumescent system without and with SRS are shown in Figure 2.16. The considerable enhancement of LOI shows the improved flame resistance in presence of a small amount of SRS. The simultaneous improvement of elongation at break and flame retardancy could be explained with formation of a flexible interface that transforms to an oxygen barrier surface layer under the effect of flame.



**Figure 2.15:** Influence of SRS on the relative elongation at break (Bertalan et al, 2001)



**Figure 2.16:** Influence of SRS on the Limiting Oxygen Index (LOI) of PP (Bertalan et al, 2001)

Table 2.9 illustrates some previous studies on flame retardancy of polymers. Different types of polymers were investigated for improving flame resistant performance. For this purpose, several flame retardants and additives were added into polymer. Composites were characterized mainly by FTIR, UL-94, LOI, TGA, GC-MS, NMR, Cone Calorimetry and XPS etc. Henrist et al. (2000) investigated thermal degradation of commercial fire-resistant cable. Cable

made from silicone-ethylene propylene diene monomer (EPDM) blend containing alumina trihydrate and hydrated zinc borate as flame retardants. Jurs and Tour (2003) synthesized new flame resistant polymers (polyarylethers A-C) which do not require the use of any flame retardant synergist. Residue of Polyarylethers A-C was found 55%, 42.5% and 30% with TG analysis.



**Table 2.9:** Review of previous studies on flame retardancy of polymers

References	Polymers	Flame Retardants	Additives	Characterization Method	Scope
Anna et al., 2001	PP	APP, PER	Borax siloxane elastomer	FTIR	Coupling agent effect on flammability
Balabanovich and Engelmann, 2003	Polybutylene terephthalate (PBT)	poly(sulfonyldiphenylene phenyl phosphate (PSPPP)		UI-94, LOI, TGA, GC-MS	Obtaining good flame retardant properties with addition PSPPP in PBT
Bertalan et al., 2001	PP, Poly amide	APP, PER	Coupling agent	DSc, SEM, Mechanic test	Effects of coupling agent to flammability
Beyer et al., 1989	Mineral wool	Stainless steel, 13X, gibbsite		TGA	Temperature profile of fillers
Bourbigot et al., 1996	PE, PP, Ethylene butyl acrylate, Maleic anhydride terpolymer	APP, PER	Zeolite 3A, 4A, 5A, 10X, 13X, Y, mordenite, ZSM5	LOI, TGA	Effect of Si/Al ratio of zeolite to flame retardant properties of composites
Bourbigot et al., 1996	PE, PP, Ethylene butyl acrylate, Maleic anhydride terpolymer	APP, PER	Zeolite 4A	NMR, TGA	Effects of zeolite concentration
Bourbigot et al., 1996	PE, PP, (Ethylene co/terpolymer)	APP, PER	Zeolite 4A	LOI, UL 94, TGA, Cone calorimetry	Effect of filler concentration to LOI Effect of molecular weight of polymer on LOI value
Bourbigot et al., 1996	Ethylene butylacrylate	APP, PER	Zeolite 4A	TGA	Chemical and structural characterization of composites at different temperature
Bourbigot et al., 1997	Ethylene butylacrylate maleicanhydride	APP, PER	Zeolite 4A	XPS	Investigate chemical reactions during heating
Bras and Bourbigot, 1996	LDPE, PP	diammonium diphosphate, d-sorbital, $\beta$ -cyclodextrine, APP, PER	-	LOI, NMR	review
Bras et al., 2000	Polyamide 6, ethylene vinyl acetate	APP		UL-94, LOI, cone calorimeter	Characterization of PA6 and EVA based intumescent additive for thermoplastic formulation
Bugajny et al., 1999	Ethylene Propylene Rubber, Polyurethane	APP	-	TGA, LOI, Cone calorimetry	Research APP loading on flammability
Chiu and Wang 1997	PP	APP, PER, Melamine	-	LOI, cone calorimetry	Effect of APP concentration on flammability of polymer

**Table 2.9:** continued

References	Polymers	Flame Retardants	Additives	Characterization Method	Scope
Dvir et al., 2003	Polypropylene	penta bromobenzyl acrylate (PBBMA)	magnesium hydroxide, glass	UL-94, LOI, izod impact test, ASTM D-638 test	Effect of additives on mechanical and flammability properties of propylene matrix composites
Henrist et al., 2000	Electrical cable	Zinc borate, aluminium trihydrate		SEM	Effect of the addition of zinc borate and aluminium trihydrate on physical properties of commercial cables
Jeng et al., 2002	bis(3-t-butyl-4-glycidyloxyphenyl 2,4-di-t-butylphenyl) resorcinol diphosphate			TGA,NMR, FTIR, LOI	Synthesised the flame retardant epoxy polymer
Jurs and Tour, 2003	Polyethers			TGA, DSC, UL-94 rating	Synthesised flame retardant polymers, polyethers, without needing synergist agent
Kandola et al., 2002	Polyester	Antiblaze NW , Antiblaze NH		LOI, cone calorimetry	Investigate flame retardant properties of coated Polyester
Lee et al., 2000			zeolite		Surface tension of silane treated natural zeolite
Marosi et al., 1999	PP, Ethylene-PP copolymer	APP, PER, Melamine	-	TGA, Charring test, FTIR	Research coupling agent affect on flammability of polymers
Marosi et al., 2003	Polypropylene	APP, PER	Montmorillonite, poly borosiloxane	XRD, TGA, FTIR	Effect of montmorillonite nanoparticles on flame retardant properties of polypropylene
Mequanint et al., 2002	Phosphated polyurethane	Phosphated macroglycol		TGA	Thermal stability of phosphated polymethane dispersions is investigated
Ohlemiller et al., 1998	Brominated vinyl ester		glass	Cone calorimeter	Effect of ignition conditions on flame spread on a composite material
Price et al., 2001	Methylmethacrylate (MMA), Poly(methyl methacrylate) (PMMA)	diethyl ethyl phosphonate (DEEP)		TGA, LOI, cone calorimeter	Improve flame retardansy property of PMMA with phosphorus containing additives
Quedo et al., 2002	Polyamide 6	1.1,3.3 tetramethyl disiloxane (TMDS)		cold plasma, LOI, cone calorimeter	Investigate flame retardant properties of coated PA6
Ravadits et al., 2001	PP, PE	APP, PER	Poly dimethyl siloxane, Dihydroxy oligodimethyl siloxane, boric acid	XPS	Coupling agent effect on flammability

**Table 2.9:** continued

References	Polymers	Flame Retardants	Additives	Characterization Method	Scope
Riva et al., In press 2003	Poly amide 6, poly(ethylene co-vinyl acetate)	APP	magnesium hydroxide	TGA, FTIR, UL_94	The thermal and combustion behaviour of an intumescent FR system based on P6 and EVA
Spirckel et al., 2002	Phosphonate polyurethane			TGA, LOI	Research the thermal degradation and fire behaviour of phosphonates
Velasco et al., 2002	Polypropylene		Aluminium hydroxide, magnesium hydroxide	DSC, Melt flow index, DMTA	Thermal and dynamic mechanical characteristics of injection-moulded discs of polypropylene filled with MOH and AOH
Wang, 2000	Polybutylene terephthalate (PBT), Acrylonitrile-butadiene styrene (ABS), Polycarbonate-ABS blend	Halogenated organics antimony		Pyrolysis GC	Investigated behaviour of different flame retardants in different polymer matrix by characterization py-GC
Zaharescu 2001	Ethylene propylene elastomers	Deca bromodiphenyl oxide, tetra brombisphenol A		Oxygen uptake measurements	Investigate the degradation of polymers by oxygen consumption
Zhu and Shi 2003	Poly phosphate methacrylate	Phosphoruscontaining polymer		FTIR, XRD, XPS	Investigate thermal behaviour of phosphorus containing polymers

## Chapter 3

### EXPERIMENTAL

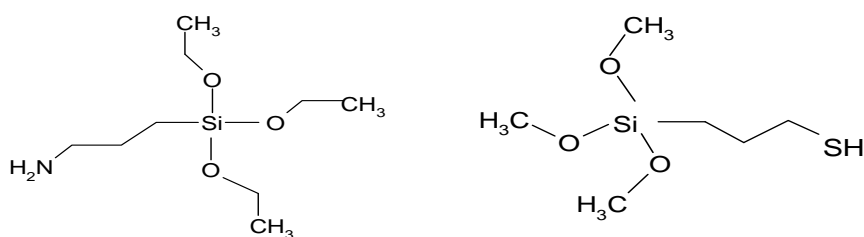
#### 3.1 Materials

In this study, Gördes clinoptilolite mineral, supplied from Enli Madencilik Company, was used. Clinoptilolite was characterised by Top (2001) in previous study. 95.5% of Clinoptilolite particles size are below 50 $\mu$ m as shown by the cumulative particle size distribution determined by using Micromeritic Sedigraph 5100 in Figure A1 in the Appendix. Exolit 422 is ammonium polyphosphate (APP) ( $n > 1000$ ), soluble fraction in water below 1%, supplied by Clariant. Average particle size of APP is 15 $\mu$ m. Pentaerythritol (PER) is supplied by MKS Marmara Kimya Sanayi A.Ş. Particle size of pentaerythritol is below 75 $\mu$ m. Pentaerythritol starts to melt at 170°C and peak maximum of the DSC curve is at 190°C as seen in Figure A2 in the Appendix. Polypropylene (PP) is MH 418 supplied by PETKİM A.Ş. Antioxidant, butylated hydroxy toluene, is supplied by Sigma Co.

#### 3.2 Methods

##### 3.2.1 Surface Treatments of Fillers

Coupling agents were used for surface modification of APP and natural zeolite. 3-(trimethoxysilyl)-1-Propanethiol (Mercapto silane, MS) have molecular formula  $C_6H_{16}O_3SSi$ , supplied by Merck Co. and (3-aminopropyl)-triethoxysilane (Amino silane, AS) have molecular formula  $C_9H_{23}NO_3Si$ , supplied by Fluka Co. Chemical structure of (3-aminopropyl)-triethoxysilane and 3-(trimethoxysilyl)-Propanethiol are shown in Figure 3.1.

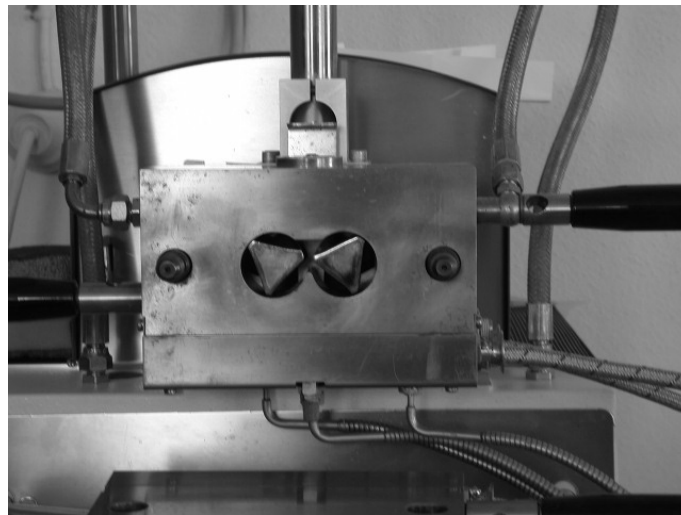


**Figure 3.1:** Chemical structure of (3-aminopropyl)-triethoxysilane and 3-(trimethoxysilyl)-1-Propanethiol, respectively.

Coupling agents, amino or mercapto silane, 1w% of fillers was added to 95wt% ethanol solution and mixed for 15 minutes to let silane hydrolysis. Then fillers (APP or Zeolite) were added to mixture and mixed for 45 minutes for condensation and chemical bonding of silanes and particles. Treated fillers were washed with ethanol to remove excess of coupling agents and dried in a oven 70°C for overnight.

### 3.2.2 Preparation of Flame Retardant Composites

Polypropylene matrix composites were prepared by blending of PP pellets, flame retardant materials (APP and PER), antioxidant (0.5w%) and treated or untreated clinoptilolite. Materials were mixed by using Haake polydrive mixer as shown in Figure 3.2.

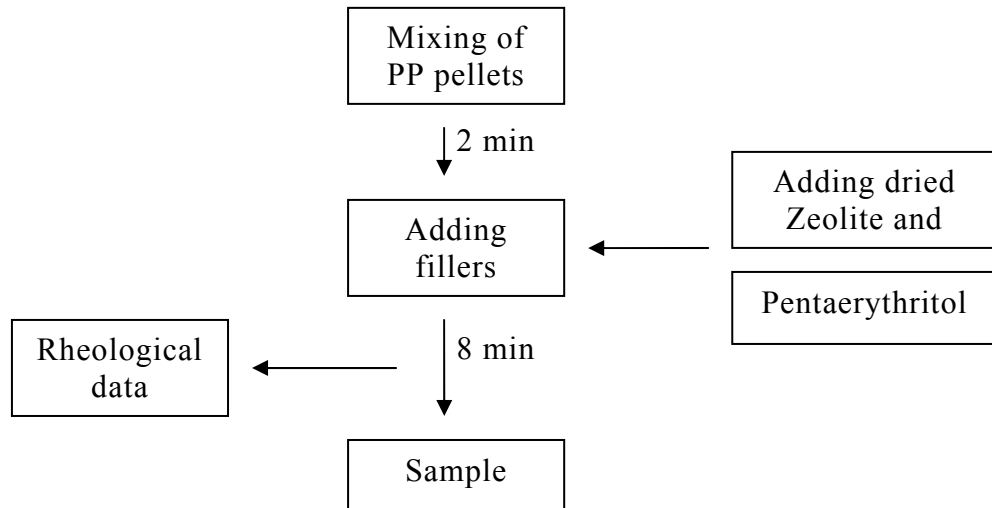


**Figure 3.2:** Thermo Haake polydrive mixer.

Concentration of fillers was fixed at 30% weight of total amounts of composite. Amounts of APP was changed in proportion to amounts of pentaerythritol. Zeolite was added with weight fractions of 1,2,5 and 10%.

Clinoptilolite and APP were dried in oven at 120°C for over night. First, polypropylene was melted in plastograph for 2 min. Antioxidant was added to molten PP. Afterwards, clinoptilolite, APP and PER were added respectively. Flowsheet of processing was shown in Figure 3.3. and experimental conditions of mixing process was given in Table 3.1. Amounts of sample, feeded in to

plastograph, were adjusted according to optimum mixing volume advised by company. The plastograph is capable of receiving Torque data during mixing wrt time which is valuable information about rheological properties of the mixture. Torque is an indicator of viscosity. Hence, rheological properties of composites can be examined.



**Figure 3.3:** Flowsheet of mixing process

**Table 3.1:** Operation conditions of mixing process

Screw speed (rpm)	Temperature (°C)	Mixing time (min)
60	190	10

Mixed materials were pressed by Carver hot press as shown in Figure 3.4. First, hot press was heated at 190°C. Samples was put in a mold, dimensions is 15x15 cm and 3 mm in thickness. Sample was melt in mold for 4 min without pressure. Afterwards, pressure was applied gradually until 2000 psi pressure in 6 minutes. Samples were cooled to room temperature at the same pressure.



**Figure 3.4:** Carver hot press

Composites were cut by bar shaped hollow die punch, with dimensions 125x12.5mm according to UL-94 test standard as shown in Figure 3.5.



**Figure 3.5:** Hollow die punch for flammability test

### **3.2.3 Characterization**

Materials and FR-PP composites were characterized by Fourier Transfer Infrared (FTIR) analysis, Thermal Gravimetric analysis (TG), Scanning Electron Microscope (SEM) and Optical Microscope.

### **3.2.3.1 Characterization by FTIR Analysis**

FTIR analysis can give information about the chemical structure of ammonium polyphosphate and pentaerythritol. APP and PER were analyzed by preparing KBr pellets. The pellets, containing 2% wt sample in KBr, were prepared by mixing of 0.004gr APP or PER with 0,2 gr of KBr. IR spectra were made up of 20 scans from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  with a Shimadzu FTIR 8201 model instrument.

### **3.2.3.2 Scanning Electron Microscope and Optical Microscope**

Scanning electron microscopy (SEM) was used to examine the morphology of the burnt and non-burnt FR-PP composites. Fracture surfaces of tensile tested specimens, untreated and treated with amino silane and mercapto silane were also observed with a Philips XL-305 FEG – SEM to investigate the interface between filler and matrix and dispersion of filler in the matrix.

Surface compositions of burnt and non-burnt FR-PP composites were determined with EDX elemental analysis method. Analysis data were taken from 5 points to cover whole surface of samples.

Thin film samples, containing APP:PER(2:1)+PP with and without zeolite, were laminated onto microscope slides and heated with INSTEC hot plate up to  $200\text{ }^{\circ}\text{C}$ . Behaviour of samples was observed by Olympus CH40 type optical microscope with changing temperature.

### **3.2.3.3 Characterization by Thermal Analysis**

TGA of APP and PER and composites were carried out using SETERAM Thermal Gravimetric Analyzer from room temperature to  $600^{\circ}\text{C}$  at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . Nitrogen was used as a carrier gas with a constant flow rate during analysis.

Differential scanning calorimetric analysis of PER was carried out using Shimadzu 50 from room temperature to  $250^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . Flow rate of Nitrogen was  $40\text{ml}/\text{min}$ .



### 3.2.3.4 UL-94 Test

Standard test method for rate of burning and extent and time of burning of self supporting plastics in a horizontal position was constructed according to ASTM D-635. A bar of the material to be tested was exposed to gas flame for 30s. Time and extent of burning were measured and reported if the specimen does not burn 100mm. An average burning rate was reported for a material if it burns to the 100mm mark from the ignited end.

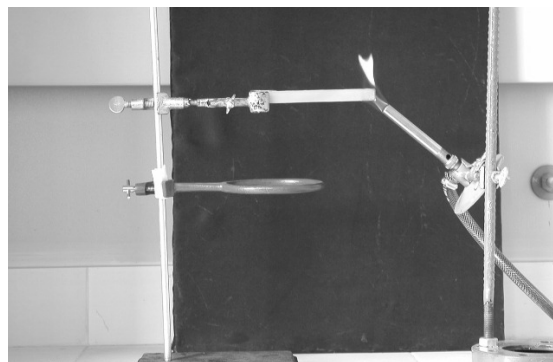
Specimen were clamped at the end nearest 100mm mark. Burner was placed 45° to the horizontal and remote from the specimen, ignited, and adjusted it to produce a blue flame 20 mm high as shown in Figure 3.6. Flame was contacted the end of the test specimen and the stop watch was started simultaneously. Flame was applied for 30s. When burning or glowing combustion ceases, the watch was stopped. The time was recorded in seconds as burning time and unburned length of specimen was measured to the nearest 1 mm along the lower edge of specimen from the mark.

Average burning rate was reported as the average of the burning rates of all specimens which have burned to the mark in cm/min. Average time of burning (ATB) and average extent of burning (AEB) were calculated according to Equations 3.1 and 3.2, respectively.

$$ATB = \sum(t-30s) / \text{number of specimen} \quad (3.1)$$

$$AEB \text{ (mm)} = \sum(100\text{mm} - \text{unburned length}) / \text{number of specimen} \quad (3.2)$$

If burning or glowing continued less than 3s after removal of flame average time of burning was recorded less than 5s. In the case of average extent of burning, specimen was burned less than 3mm, reported as less than 5mm.



**Figure 3.6:** Apparatus of UL-94 test

### 3.2.3.5 LOI Test

Standard test method for measuring the minimum oxygen concentration to support candle-like composition of composites was constructed according to ASTM D-2863 as shown in Figure 3.7. The minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that was support combustion was measured under equilibrium conditions of candle-like burning.

Test column was composed of heat resistant glass tube of 75mm inside diameter and 450mm heights. The bottom of the column or the base to which the tube was attached shall contain non-combustible material to mix and distribute evenly the gas mixture entering at this base. The igniter was a tube with a small orifice, 1 to 3mm in diameter. The flame was 25mm long inserted into the open end of the column to ignite the specimen. The gas flow rate in the column must be  $4 \pm 1$  cm/s, adjusted by Cole Parmer flowmeter (A-3227-30).

Initial concentration of oxygen was determined arbitrarily. If the specimen burns rapidly, concentration of oxygen reduces below the oxygen concentration of air. When the specimen was not burnt at selected a concentration, concentration of oxygen was increased gradually.

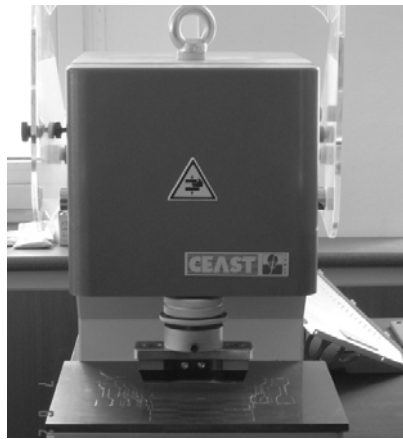


**Figure 3.7:** Apparatus of limiting oxygen index test.

### 3.2.3.6 Mechanical Properties of FR PP Composites

ASTM D638 standard test method covers the determination of the tensile properties of unreinforced and reinforced plastics in the form of standard dog bone-shaped test specimens.

The test samples for mechanical properties of composites were cut with a Ceast pneumatic hollow die punch according to ASTM D-638 procedure as shown in Figure 3.8. A minimum of five specimens for each composition were tested. The full-scale load of mechanical test machine (Testometric instrument) was 100kN and the cross head speed was 50mm/min. The test results were taken from WINTEST software program supplied from Testometric Co.



**Figure 3.8:** Ceast pneumatic hollow die punch for mechanical test

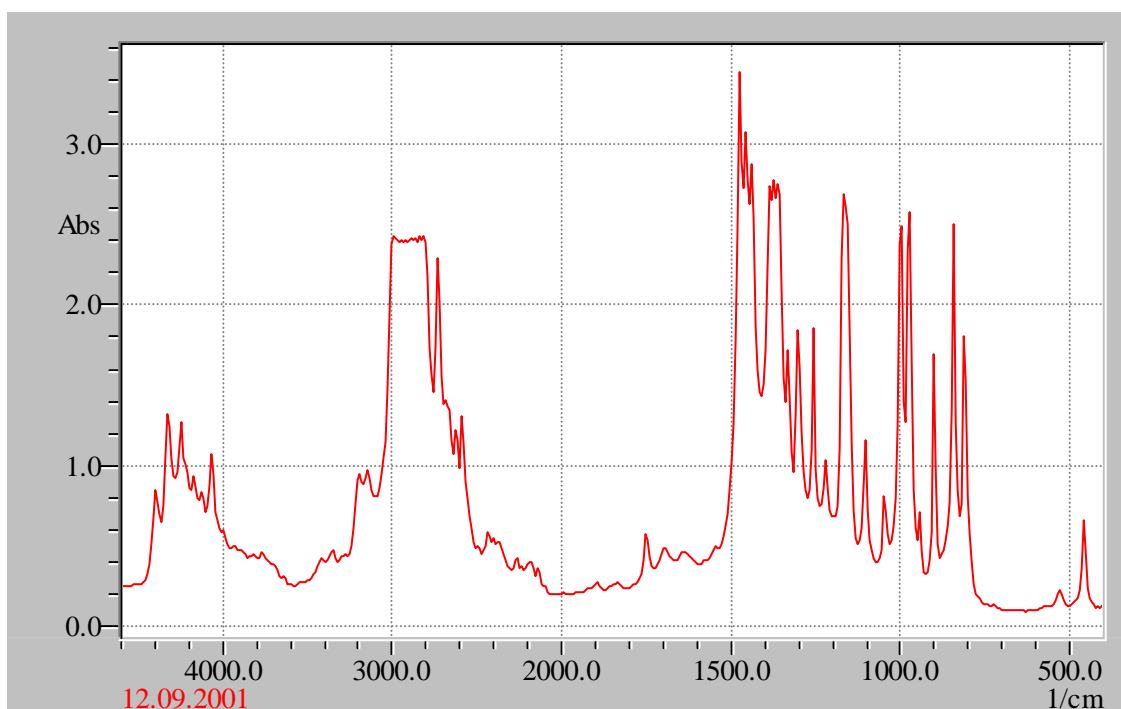
## Chapter 4

### RESULTS AND DISCUSSION

#### 4.1 Characterization of Materials by FTIR Spectroscopy

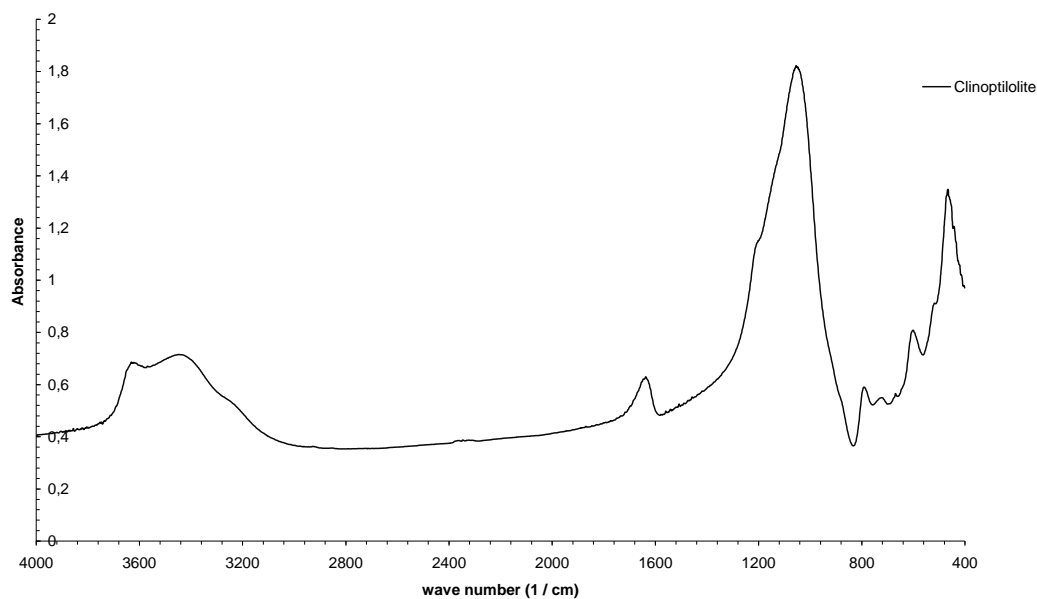
FTIR spectroscopy was used for determining the chemical composition and structure of materials i.e. chain structure, degrees of branching, geometric isomerization and functional groups present in the material. In this study, IR spectra were characterized for raw materials of flame retarded polypropylene matrix composites. The structural and characteristic groups of materials were determined.

Characteristic peaks of isotactic polypropylene are observed at 790 and 1158  $\text{cm}^{-1}$  as shown in Figure 4.1. The 1470  $\text{cm}^{-1}$  peak indicates deformation of  $-\text{CH}_2$ . The symmetric and asymmetric stretching vibrations of bonds are observed at peaks 2860 and 2930  $\text{cm}^{-1}$  respectively. The 2870  $\text{cm}^{-1}$  peak refers to symmetric stretching of  $-\text{CH}_3$  and peak at 2970  $\text{cm}^{-1}$  shows asymmetric stretching of  $-\text{CH}_3$ . The symmetric deformation of  $-\text{CH}_3$  observes at 1375  $\text{cm}^{-1}$  band and 1460  $\text{cm}^{-1}$  band illustrates asymmetric deformation of  $-\text{CH}_3$  bond.



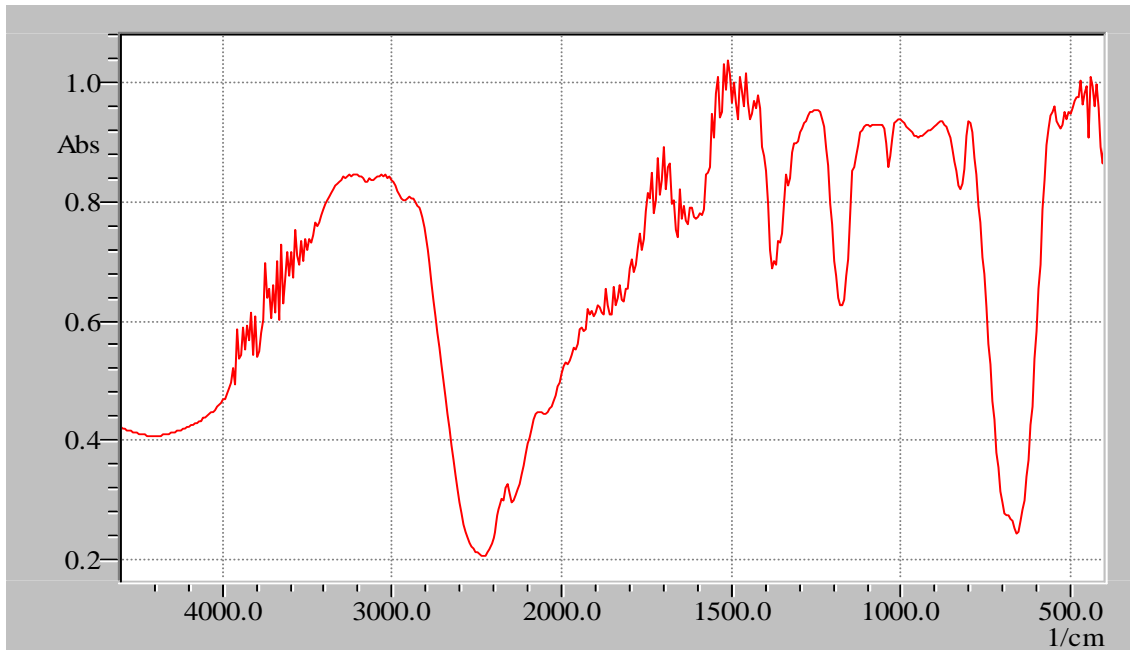
**Figure 4.1:** Infrared spectrum of MH 418 Polypropylene

Top (2001) characterized clinoptilolite by FTIR spectroscopy as shown in Figure 4.2. The internal T-O bending was observed at  $468.7\text{ cm}^{-1}$ . The internal symmetric and asymmetric stretching vibration peaks were found at  $721.3$  and  $1215\text{ cm}^{-1}$  respectively. The band at  $792.7\text{ cm}^{-1}$  indicated external asymmetric stretching and  $1050\text{ cm}^{-1}$  band refers to external symmetric stretching. The OH bending was observed at  $1639.4\text{ cm}^{-1}$  band. The H-bonded OH stretching and isolated OH stretching peaks were found at  $3460$  and  $3633.6\text{ cm}^{-1}$  respectively.



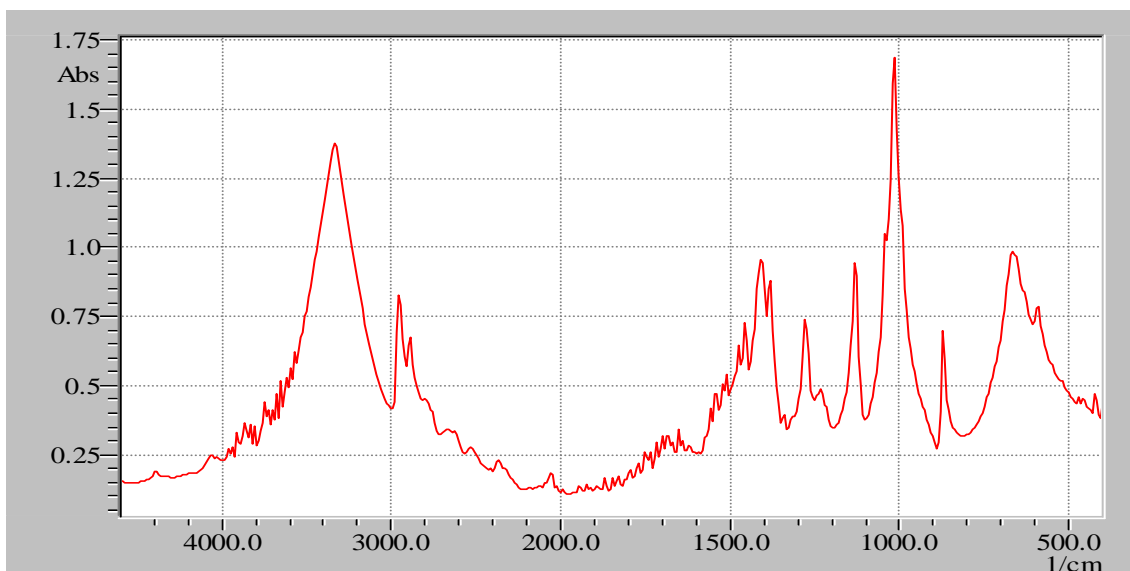
**Figure 4.2:** Infrared spectrum of natural zeolite clinoptilolite (Top, 2001)

FTIR spectrum of ammonium poly phosphate was shown in Figure 4.3. The peak at  $3050\text{ cm}^{-1}$  indicates  $\text{NH}_4$  stretching vibration. The  $1373$  and  $1489\text{ cm}^{-1}$  bands belong to  $\text{NH}_4$  deformation. The peak P=O bond was found at  $1260\text{ cm}^{-1}$  wave number. The asymmetric stretching of P-O-P band was observed at  $1016$  and  $880\text{ cm}^{-1}$ . The peak at  $530\text{ cm}^{-1}$  refers to bending vibration of  $\text{PO}_4$ .



**Figure 4.3:** Infrared spectrum of APP422 Ammonium polyphosphate

The chemical structure of Pentaerythritol was characterized by using FTIR spectroscopy as shown in Figure 4.4. The C-O bonds give a peak at  $1015\text{ cm}^{-1}$ . The  $1405$  and  $1465\text{ cm}^{-1}$  indicate  $\text{CH}_2$  bending. The stretching vibration of  $\text{CH}_2$  was observed at  $2882$  and  $1962\text{ cm}^{-1}$ .



**Figure 4.4:** Infrared spectrum of Pentaerythritol

The  $3330\text{ cm}^{-1}$  refers to stretching of OH bonds. The  $1140\text{ cm}^{-1}$  band illustrates the tertiary alcohol. The deformation of O-CH<sub>2</sub> bonds was found as peak at  $1450$  and  $1490\text{ cm}^{-1}$ .

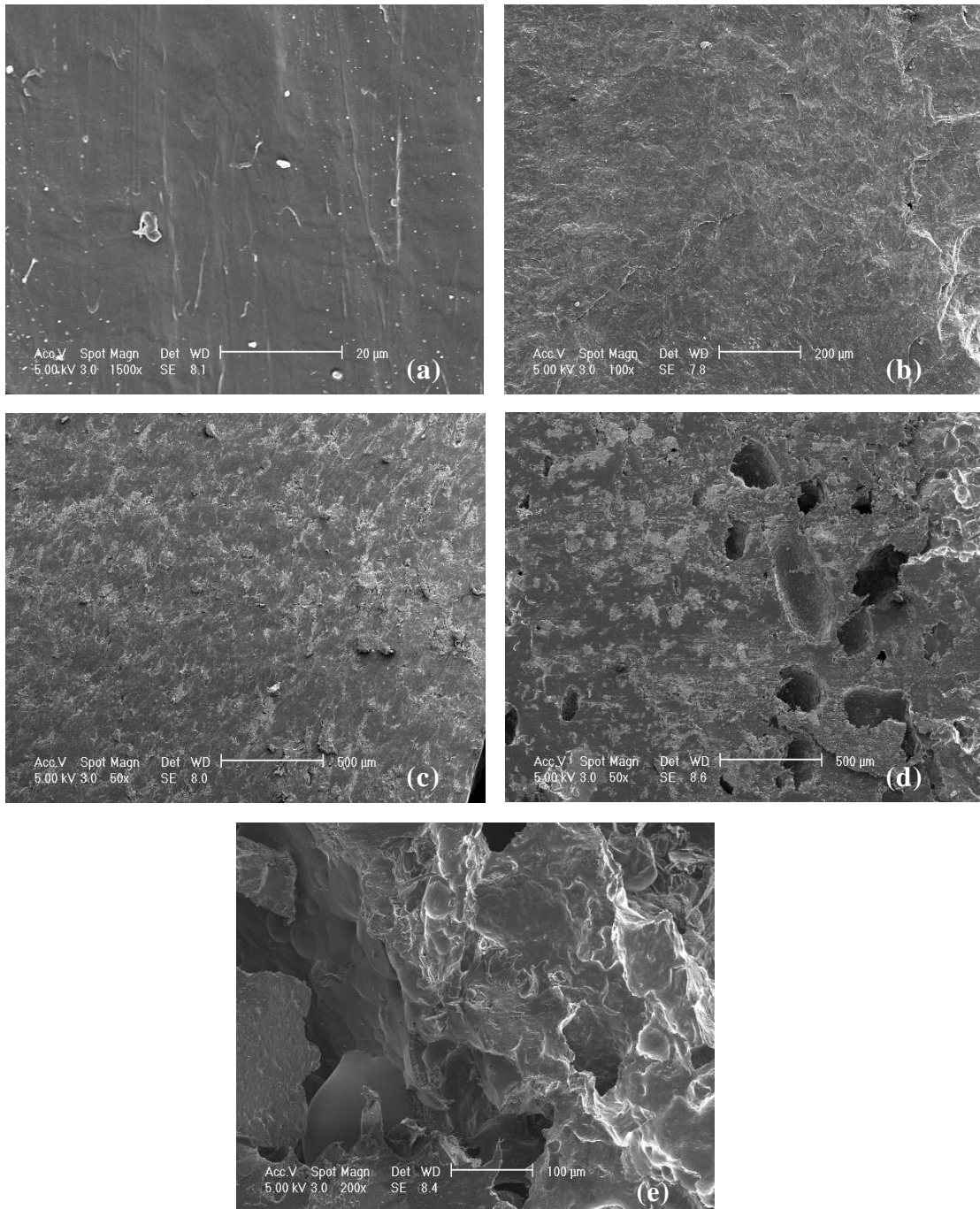
## 4.2 Morphology of Composites

Figure 4.5 shows SEM pictures of non-burnt and burnt PP, APP-PER(3:1)+PP composites. Polypropylene exhibited homogeneous structure and bubbles do not form during processing as shown in Figure 4.5a. Burnt polypropylene also showed homogeneous structure and all polymers consumed as shown in Figure 4.5b. Flame retardant materials (APP and PER) were well distributed in polypropylene matrix and bubble formation on surface of composites was not observed as shown in Figure 4.5c. Bubble formation on surface of burnt flame retardant polypropylene near the edge and non-burnt zone can be easily observed at the middle of the sample as shown in Figure 4.5d. Bubbles distributed randomly and have different size and shapes. Figure 4.5e was taken from the edge of burnt sample. Micro bubbles can be observed.

Figure 4.6 shows SEM pictures of non-burnt and burnt APP-PER(3:1) + 1%Zeolite +PP composites. Flame retardant materials and zeolite were distributed homogeneously in the polymer matrix as shown in Figure 4.6a. Bubble formation was not observed on surface of sample. Figure 4.6b exhibits the bubbles on surface of sample. Bubbles distributed arbitrarily on the surface and had different size and shapes. The foam size increased 2 or 3 times with incorporation of zeolite in composites. Micro bubbles were also illustrated with 500x magnification. The sizes of micro bubbles were approximately 50 micron. Figure 4.6d shows zeolite crystal on surface of burnt part of the sample. Zeolite crystal did not exhibit any deformation during burning of composite.

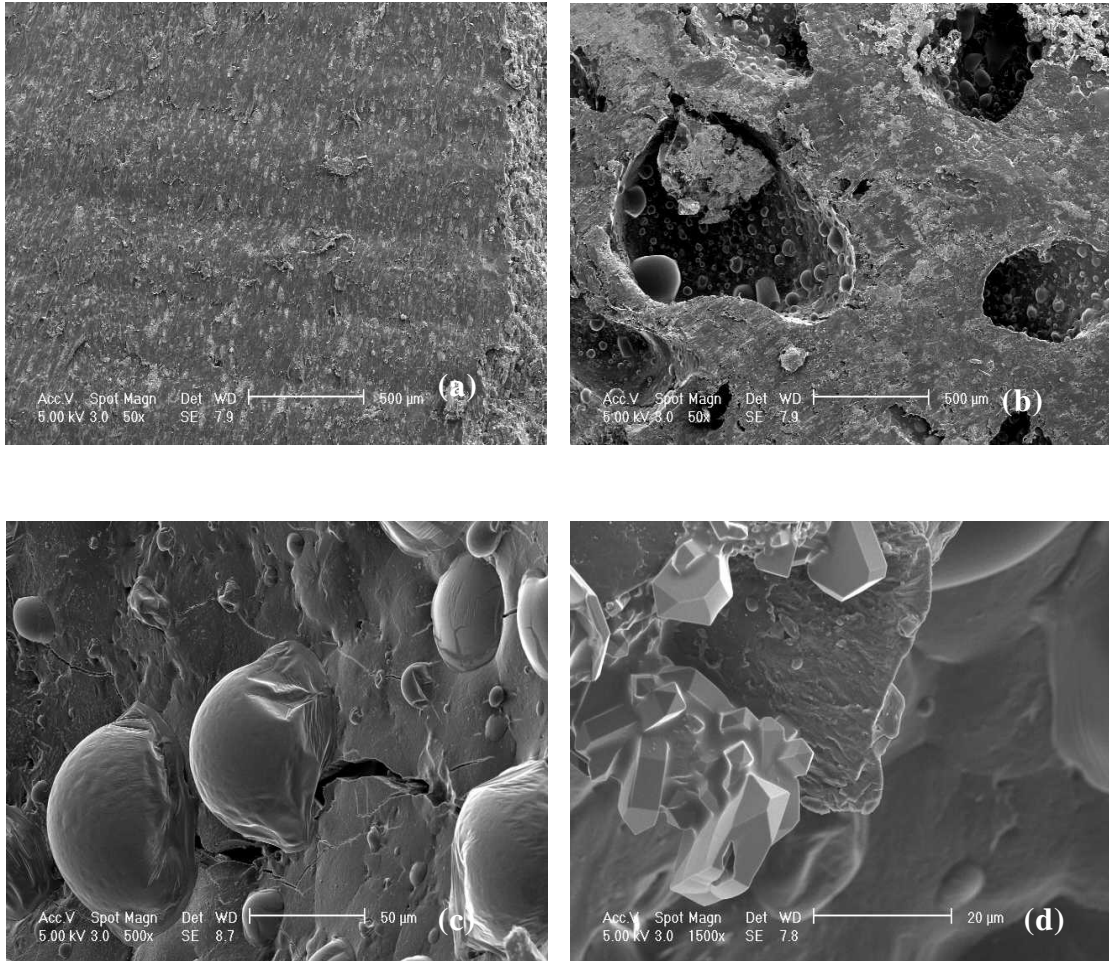
Figure 4.7 (a-c) shows fracture surface of untreated and silane treated APP:PER (2:1) 5% zeolite PP composites. The micrographs were taken in 200x magnification. In untreated sample, fillers did not adhere to polymeric matrix and ductile fracture of PP phase was observed in Figure 4.7. Amino and mercapto silane surface treatments of APP and zeolite did not improve interface between fillers and polymeric matrix sufficiently as shown in Figure 4.7 b-c. Particles did

not adhere to surface of polymeric matrix and cracks and voids were observed around the particles clearly.

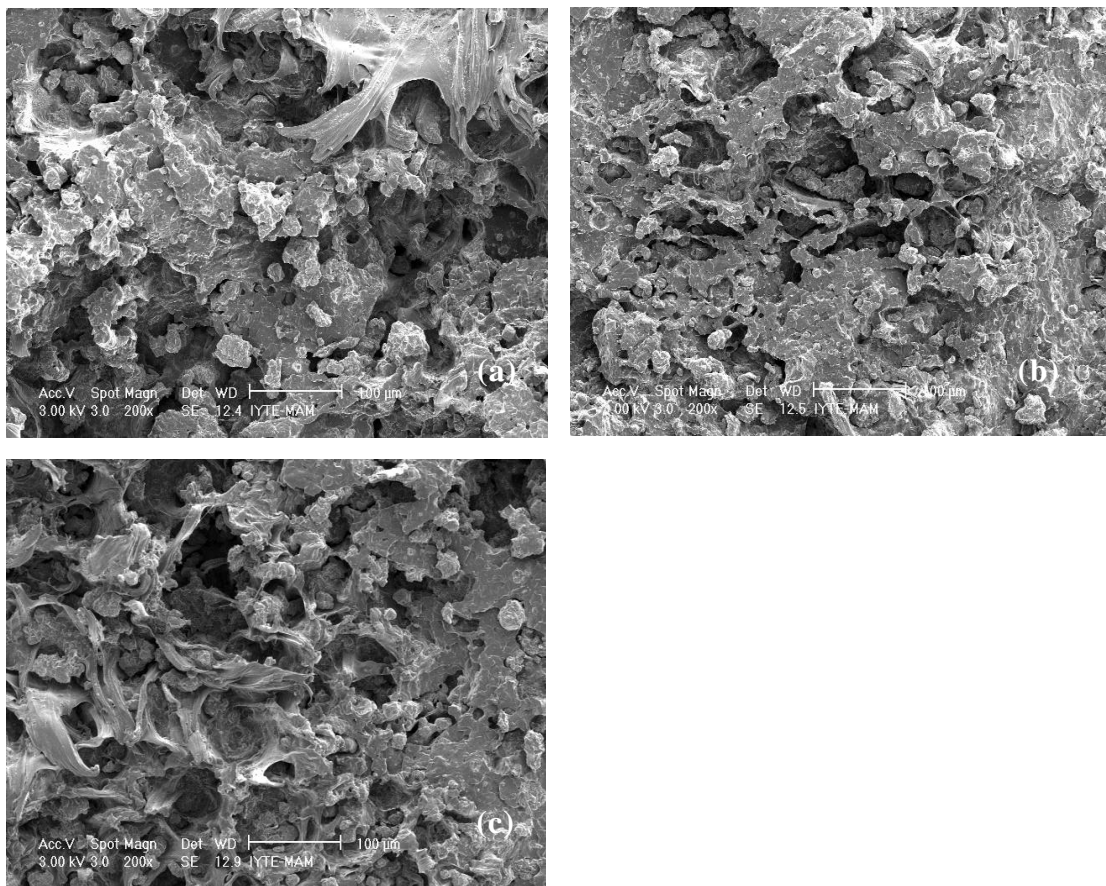


**Figure 4.5:** SEM micrograph of cross-section of non-burnt pure PP (a), burnt PP (b), non-burnt APP-PER(3:1)+PP composite (c) and burnt APP-PER(3:1)+PP composite (d,e).





**Figure 4.6:** SEM micrograph of cross-section of non-burnt APP-PER (3:1) + 1% Zeolite + PP composite (a) and burnt APP-PER (3:1) + 1% Zeolite + PP composite (b,c,d).



**Figure 4.7:** SEM micrograph of fracture surface of tensile tested untreated (a), amino silane (b), and mercapto silane (c) treated APP:PER (2:1) 5% Zeolite PP composites.

### 4.3 Elemental Analysis by EDX

EDX elemental analysis results of burnt and non-burnt PP, APP-PER(3:1)+PP, and APP-PER(3:1)+1%Zeolite+PP composites were shown in Table 4.1. An oxygen element was observed on surface of non-burnt PP. Since, polypropylene is a commercial product containing several additives such as stabilizer, anti-oxidants etc. and monomers which could be oxidized during processing. This can be reason for the presence of oxygen on the non-burnt PP. EDX analysis does not provide confidential data below 5% of results. For this reason, elemental analysis results are not reliable for N, Al, Si and P elements. Oxygen elements increase in burnt part of sample as expected because of oxidation reactions during burning. Carbon element concentration decreased in burnt part of flame retardant polypropylene composites compared to non-burnt

part. Carbon concentration decrease can be explained by the increase in oxygen concentration during burning.

**Table 4.1:** EDX data of burnt and non-burnt of PP, APP:PER (3:1)+PP and APP:PER (3:1)+1%Zeolite+PP composites

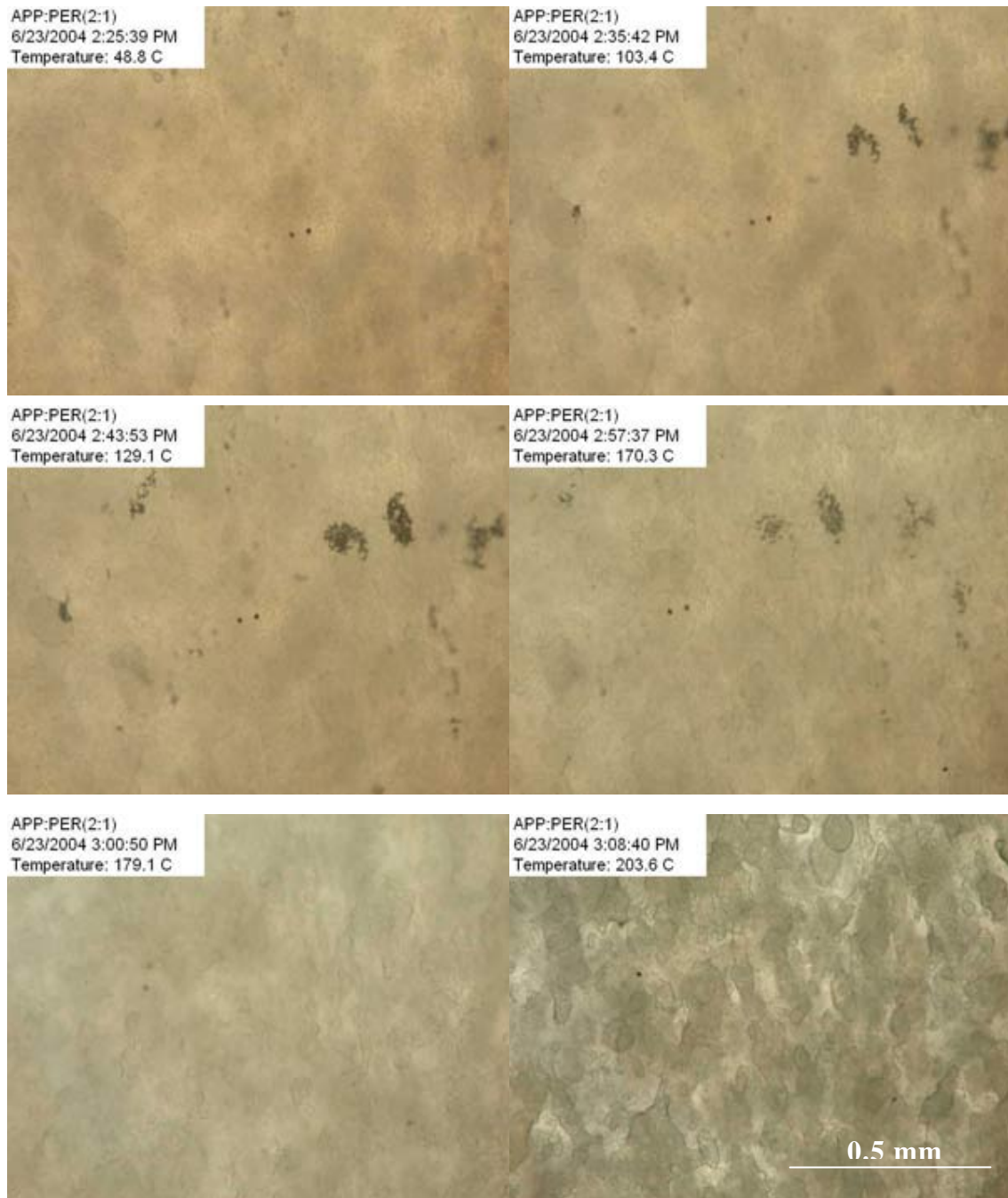
Elements	PP		APP:PER (3:1) + PP		APP:PER (3:1) + 1% Zeolite + PP	
	Non-burnt	Burnt	Non-burnt	Burnt	Non-burnt	Burnt
<b>C</b>	92.8±1.28	93.14±0.78	88.57±0.87	79.2±5.92	85.05±0.73	78.65±2.67
<b>O</b>	7.38±1.28	9.2±0.78	6.39±0.35	13.18±4.27	9.62±0.28	13.27±1.34
<b>N</b>			2.93±0.71	3.52±0.91	5.19±0.48	6.69±0.98
<b>Al</b>			0.27±0.07	0.13±0.07	0.07±0.12	0.01±0.03
<b>Si</b>			0.22±0.06	0.12±0.16	0.04±0.08	0.02±0.03
<b>P</b>			1.63±0.018	3.86±1.48	0.03±0.08	1.35±0.75

#### 4.4 Behaviour of Composites on Heating

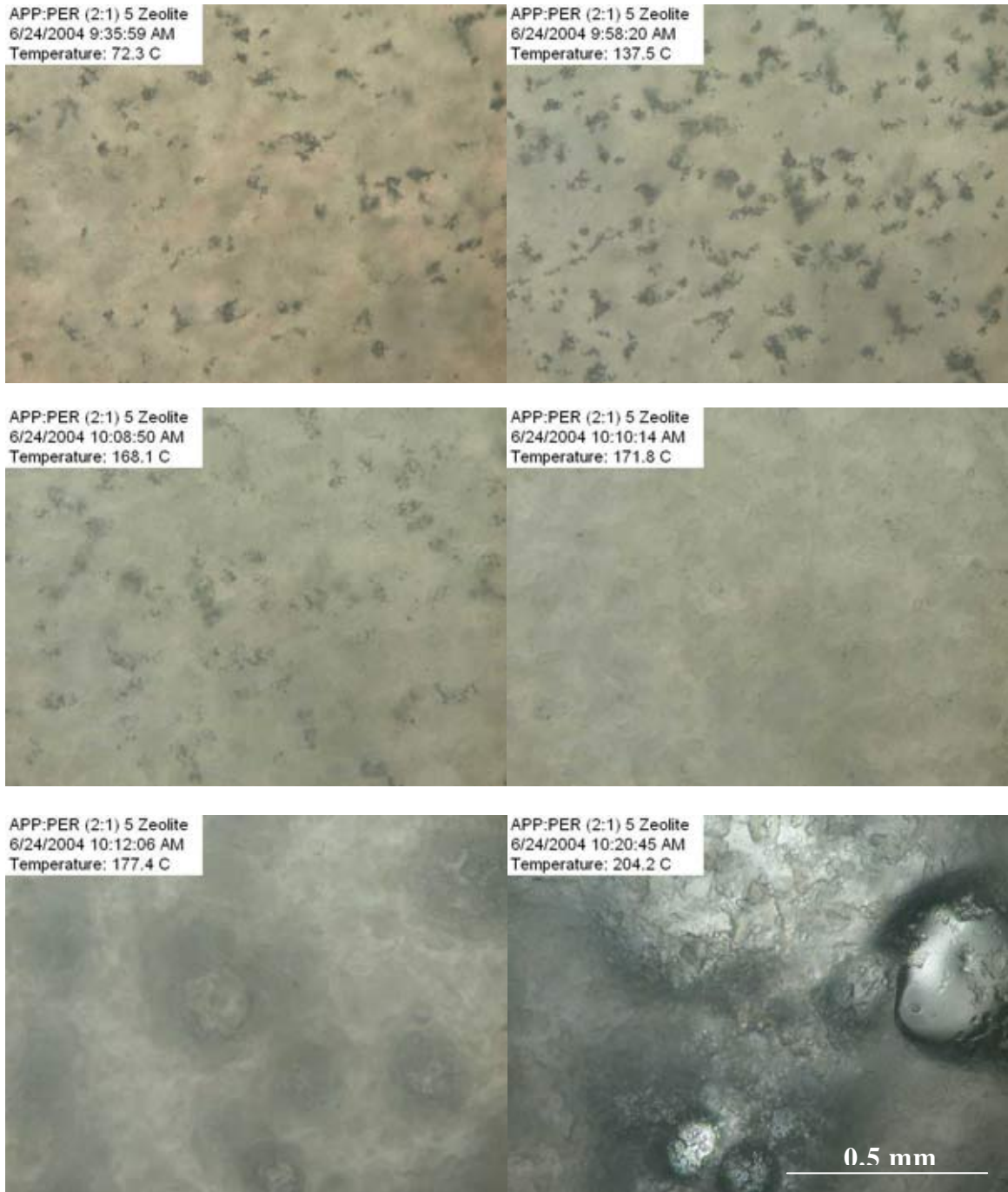
Figure 4.8 shows optical microphotographs of APP-PER (2:1)/PP composite at different temperatures. The films were illuminated from the bottom and microphotographs were recorded from top. A clear surface was observed for APP-PER (2:1)/PP composite at 48°C. During heating, opacity of polypropylene reduced. Solid particles in the film were appeared as black points at 103 and 129 °C. Polypropylene melts at 160°C become transparent above this temperature. Pentaerythritol melts at 170 °C. Molten pentaerythritol was observed as a second phase in molten polypropylene at 203 °C. In APP-PER (2:1)/PP composite, any bubble formation was not seen during heating up to 203°C.

Figure 4.9 illustrates optical microphotographs of APP-PER (2:1) + 5% Zeolite / PP composite at different temperatures. Solid particles were easily observed as dark points at 72 °C. At 137 °C, amount of the dark points, indicating filler particles, increased. Fillers began to melt at temperature around 168 °C and they completely disappear at 171.8 °C. These can be pentaerythritol particles as indicated by DSC curve of PER in Figure A2 in the Appendix. Molten pentaerythritol particles appeared as a second phase in molten polypropylene at

177 and 204 °C. The difference between with and without zeolite formulation was not observed significantly. Both of the composites behave similarly during heating. Bubble formation was not observed up to 203°C. Process temperature was around 190°C in preparation of composites by rheomixer and hot press. Flame retardants did not cause any foam formation at this temperature.



**Figure 4.8:** Optical microphotographs of APP-PER (2:1)/ PP composites



**Figure 4.9:** Optical microphotographs of APP-PER (2:1)/ PP 5% Zeolite composites

## 4.5 Rheological Properties

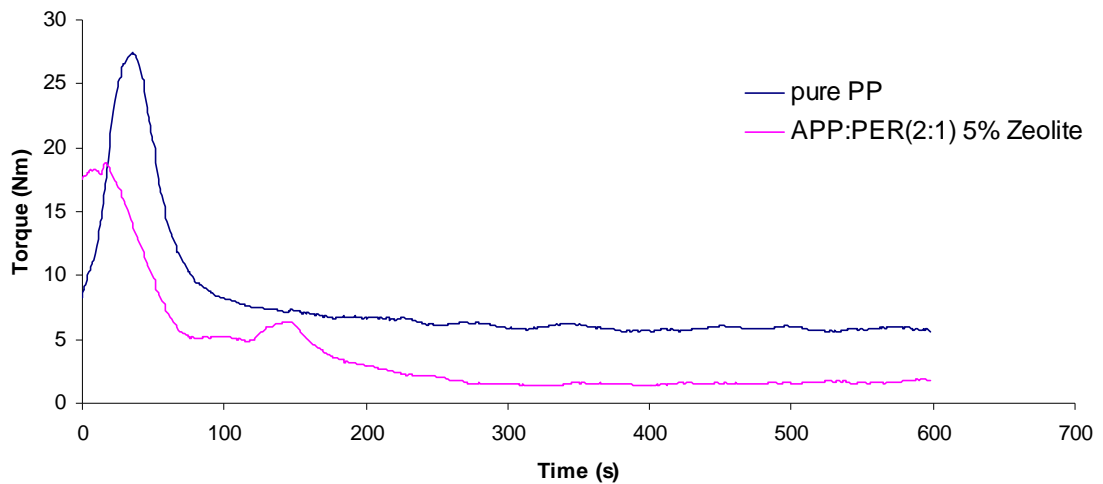
Mixing during polymer compounding is critical because the final properties of a polymer product depend on the quality of mixing achieved by the twin-screw mixer. Rheometer can not be used directly order to determine viscosity of polymer melts or filled polymers as a result of complexity of geometry of blades however torque value is an indicator of viscosity. At constant shear rate (rpm) and temperature, an increase torque (shear stress) is an indicator of increase of viscosity. This data is an important for understanding how fillers, filler loading, or surface treatments of fillers etc. influence the rheological properties of molten polymers.

Figure 4.10 illustrates typical torque vs. time curve for pure polypropylene and flame retardant PP composites. Filler additives were added to mixture around 120 s. Hence, torque increases instantaneously. Torque of mixture was recorded when it reached a constant value.

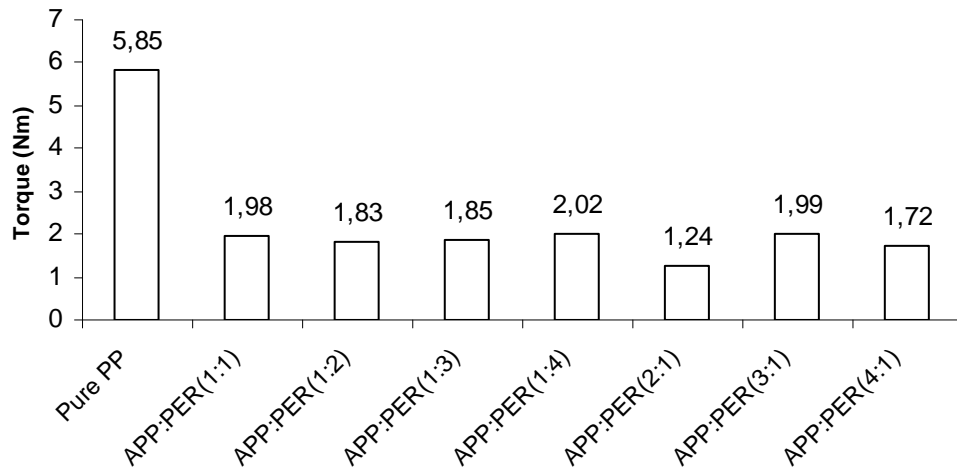
The rheological data of FR PP composites with different APP/PER ratio were revealed at Figure 4.11 to 4.14. Combination of APP and PER affects rheological properties of composites. Torque data of all composites consisting APP:PER decreased 70% compared the values of pure PP as shown in Figure 4.11. The results show that the rheological properties do not change significantly with respect to ratio between APP and PER. Torque values of 30w% of APP+PP and 30w% of PER+PP mixture were illustrated in Figure 4.12. Flame retardant additives could begin to melt at processing temperature 190°C. The torque decreased with melting PER due to molten PER behaves as a lubricant. The torque value of 30w% PER was 3.57. The torque value of 30w% APP was 5.47. These results prove that the PER decreases torque as well as viscosity. As a result, torque values of flame retardant PP composites were lower than that of the pure polypropylene. This is an advantage for processing of APP and PER. Because decrease in torque values decreases energy needed for compounding. The addition of zeolite in PP, torque increases around 13% with respect to concentration of zeolite as shown in Figure 4.12. The torque of zeolite PP composites was similar with each other. Rheological properties of different ratio APP:PER according to zeolite loading are illustrated in PP compounds with Figures 4.13. Generally, increase in zeolite concentration in formulation was

attempted to increase the torque values of composites. However, torque values of composites were still below torque of pure PP.

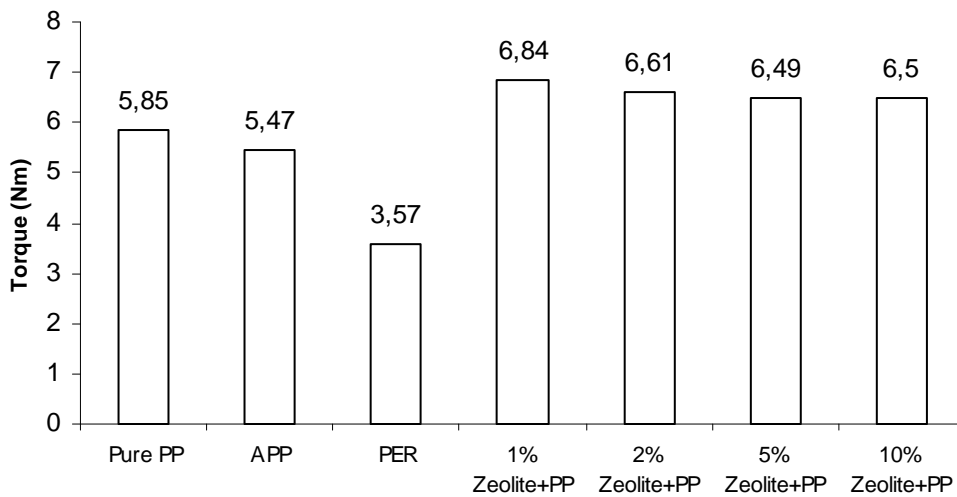
The widespread use of surface treatments for promotion of filler dispersion or enhancement of interfacial bonding between filler and polymer matrix may also strongly affects melt rheology and processability. Surface treatment of filler can result in increased melt viscosity due to enhanced interaction between filler and polymer (Jancar,1999). Figure 4.14 shows rheological data of pure PP and 1% Zeolite+APP:PER(2:1)+PP composites with untreated, amino silane and mercapto silane treated zeolite. Surface treatments of fillers increased the torque of composites 87%. However, torque values of treated composites exhibit lower values than pure PP. Amino silane and mercapto silane treatments did not show significant difference onto torque values of composites.



**Figure 4.10:** Typical torque vs time curve taken from rheomixer.

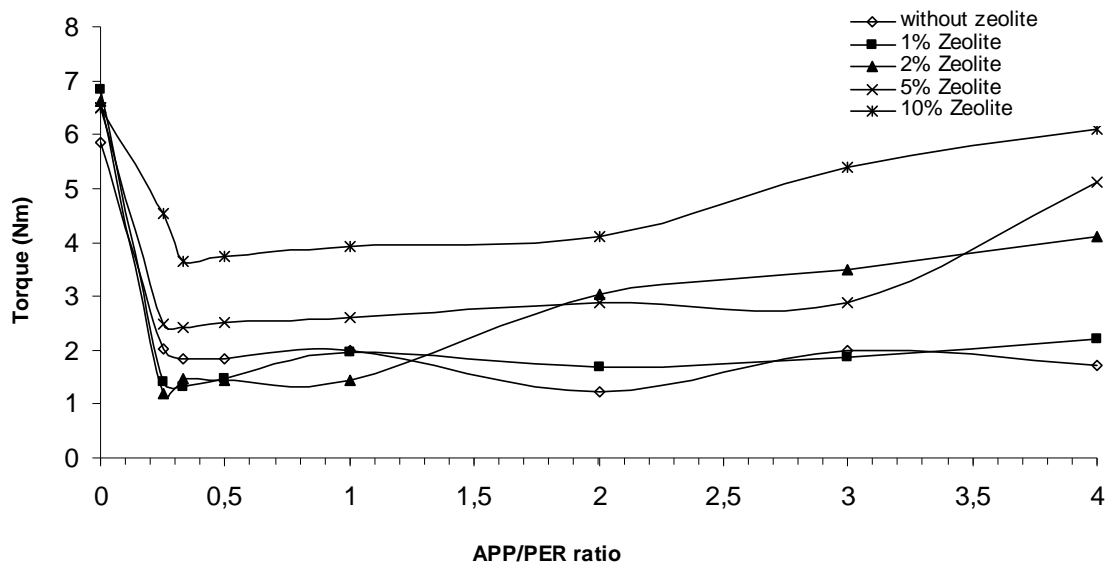


**Figure 4.11:** Rheological data of flame retardant PP composites with different ratio of APP:PER materials.

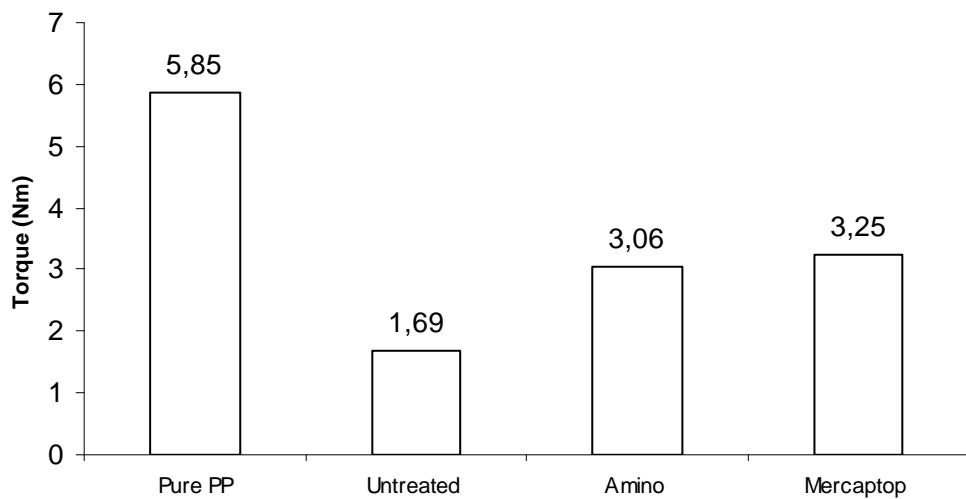


**Figure 4.12:** Rheological data of pure PP, 30% APP+ PP, 30% PER+PP, and different zeolite content PP composites.





**Figure 4.13:** Rheological data of FR PP composites with different zeolite concentration.

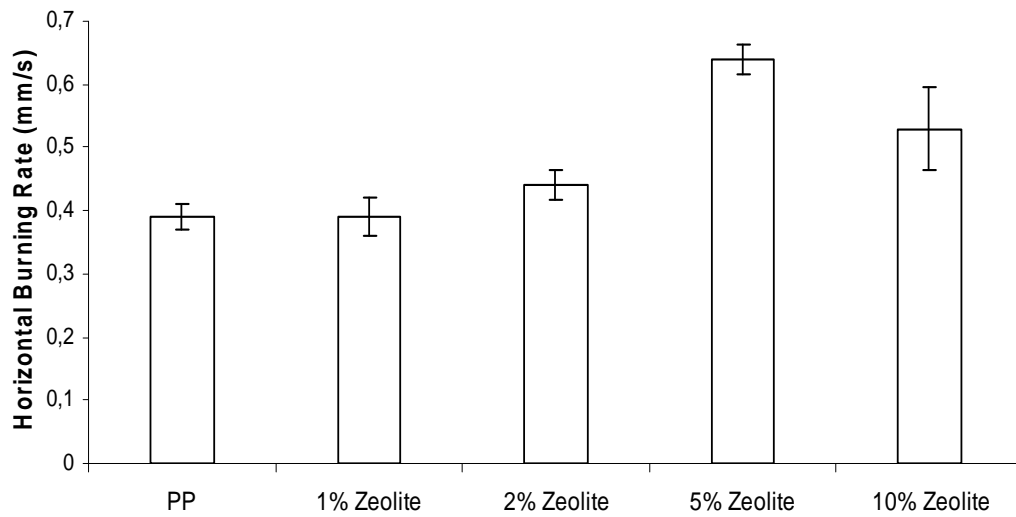


**Figure 4.14:** Rheological data of pure PP and APP:PER (2:1) + 1% Zeolite + PP, with Untreated, Amino silane and Mercapto treated.

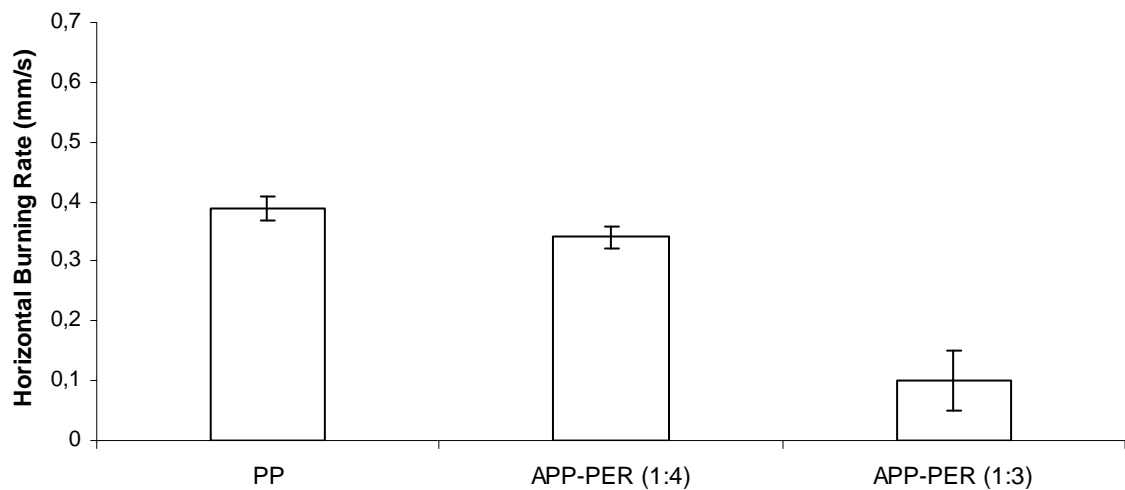
## 4.6 UL-94 Tests

Burning time, length and burning rate of composites were illustrated at Table 4.2. Most of composites did not burn in atmospheric conditions. Burning time and length must be taken account when burning rate of composites were compared. Since, some composites burned completely in air and some of them burned only a part. Another words, some composites extinguished itself in atmosphere. All composites having high APP/PER (1, 2, 3 and 4) ratio did not burn in air. Composites having low zeolite content (1, 2, 5w%) except having low APP/PER (1:3 and 1:4) ratio also did not burn in horizontal burning tests. Figure 4.15 shows UL-94 test results of pure PP and zeolite reinforced PP with different zeolite loading. Zeolite, addition in PP matrix, decreases flammability resistance of PP. Figure 4.21 illustrates horizontal burning rates of flame retardant PP composites. Addition of flame retardant materials in PP matrix increase flammability resistance of PP. APP-PER (1:4) and (1:3)+PP composites burnt in atmospheric conditions as shown in Figure 4.16. However, their horizontal burning rates were lower than pure PP. Figures 4.17-4.20 exhibits influence of flame retardant materials and zeolite combination on flammability of PP. Results indicate that flame retardant materials and zeolite addition to polymer enhanced flammability resistance of polymer. Burning rate of flame retardant PP composites changed disorderly and were not precise, because, this test method should be used to establish relative burning characteristics of plastic materials. This test method does not give comparable data for considering differences among formulations. When zeolite addition increased, the flammability resistance of PP composites decreased. All flame retardant PP composites formulations, containing 10w% zeolite, burned in atmospheric conditions as shown in Figure 4.20. The APP-PER (1:3)+PP composites, containing different zeolite concentration, indicated different burning rates as seen in Figure 4.21. Otherwise, burning rate of composites did not change only according to zeolite concentration. While the composition having 10% zeolite and 1:2, 1:3 and 1:4 APP/PER burned at slower rate than pure PP, the one with 1:1, 2:1, 3:1 and 4:1 APP/PER burned at faster rates. For considering the

difference among formulations, corresponding tests should be done as limiting oxygen index (LOI) and thermal gravimetric analysis (TGA).



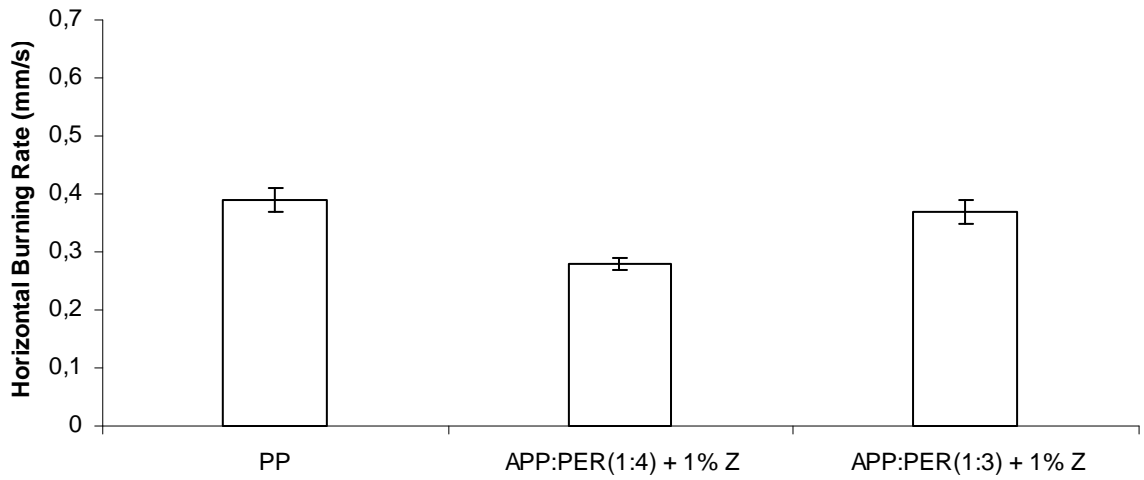
**Figure 4.15:** UL-94 test results of pure PP and reinforced PP with different zeolite loading.



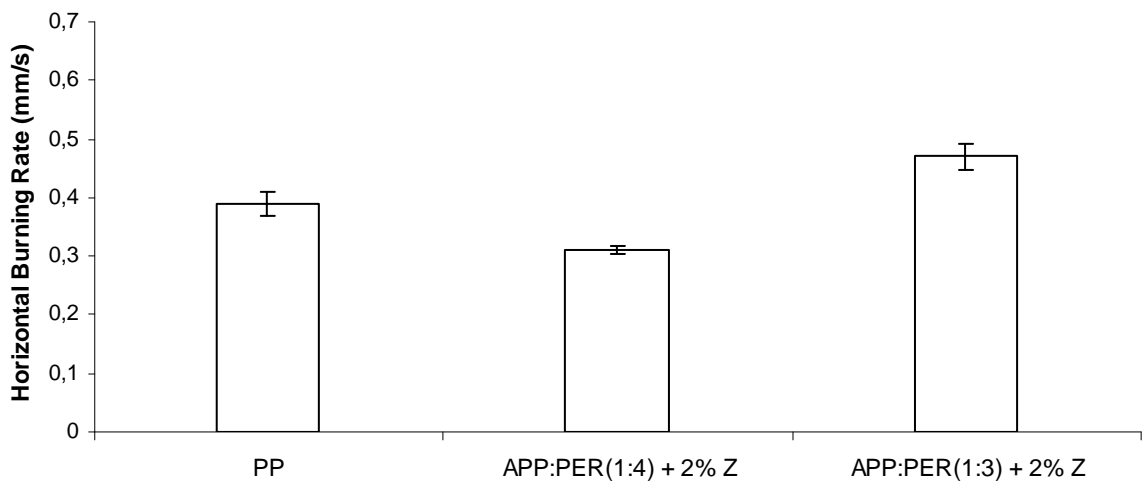
**Figure 4.16:** UL-94 test results of pure PP and flame retardant PP composites.

**Table 4.2:** UL-94 tests data for not-burnt flame retardant PP composites.

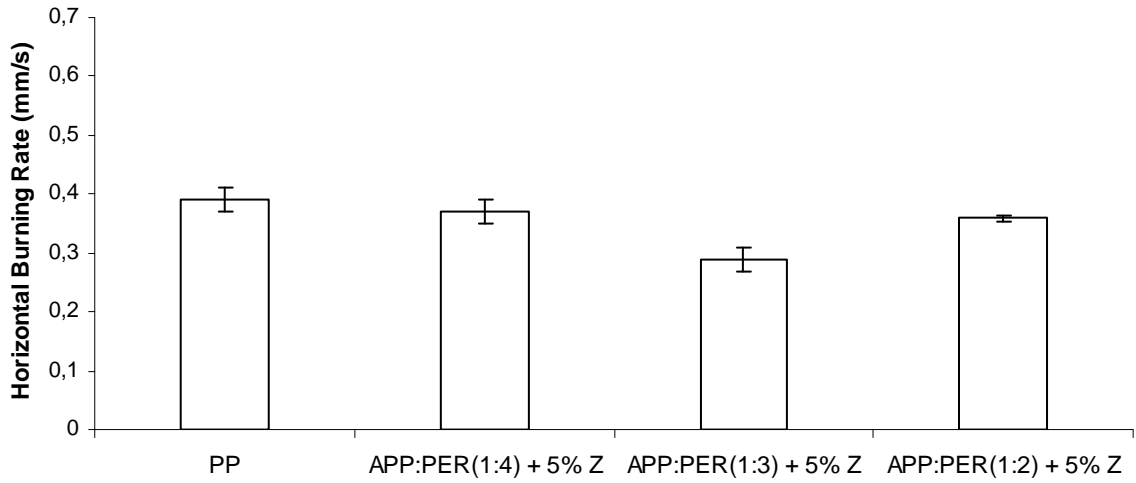
<b>Flame Retardant Composite</b>	<b>Burning Rate (mm/s)</b>	<b>Burning Length (mm)</b>	<b>Burning Time (s)</b>
Pure PP	0.39	100	259.34
APP:PER(1:4)+PP	0.34	51.4	150.9
APP:PER(1:3)+PP	0.1	18.2	179.83
APP:PER(1:2)+PP	Not Burn	-	-
APP:PER(1:1)+PP	Not Burn	-	-
APP:PER(2:1)+PP	Not Burn	-	-
APP:PER(3:1)+PP	Not Burn	-	-
APP:PER(4:1)+PP	Not Burn	-	-
APP:PER(1:4) + 1% Zeolite + PP	0.28	100	358.3
APP:PER(1:3) + 1% Zeolite + PP	0.37	41.6	112.56
APP:PER(1:2) + 1% Zeolite + PP	Not Burn	-	-
APP:PER(1:1) + 1% Zeolite + PP	Not Burn	-	-
APP:PER(2:1) + 1% Zeolite + PP	Not Burn	-	-
APP:PER(3:1) + 1% Zeolite + PP	Not Burn	-	-
APP:PER(4:1) + 1% Zeolite + PP	Not Burn	-	-
APP:PER(1:4) + 2% Zeolite + PP	0.31	100	323.37
APP:PER(1:3) + 2% Zeolite + PP	0.46	47	102.36
APP:PER(1:2) + 2% Zeolite + PP	Not Burn	-	-
APP:PER(1:1) + 2% Zeolite + PP	Not Burn	-	-
APP:PER(2:1) + 2% Zeolite + PP	Not Burn	-	-
APP:PER(3:1) + 2% Zeolite + PP	Not Burn	-	-
APP:PER(4:1) + 2% Zeolite + PP	Not Burn	-	-
APP:PER(1:4) + 5% Zeolite + PP	0.37	100	270.86
APP:PER(1:3) + 5% Zeolite + PP	0.29	100	341.77
APP:PER(1:2) + 5% Zeolite + PP	0.36	82	229.11
APP:PER(1:1) + 5% Zeolite + PP	Not Burn	-	-
APP:PER(2:1) + 5% Zeolite + PP	Not Burn	-	-
APP:PER(3:1) + 5% Zeolite + PP	Not Burn	-	-
APP:PER(4:1) + 5% Zeolite + PP	Not Burn	-	-
APP:PER(1:4) + 10% Zeolite + PP	0.35	100	287.82
APP:PER(1:3) + 10% Zeolite + PP	0.33	100	305.77
APP:PER(1:2) + 10% Zeolite + PP	0.30	81.4	271.28
APP:PER(1:1) + 10% Zeolite + PP	0.49	43.8	89.08
APP:PER(2:1) + 10% Zeolite + PP	0.51	15.6	30.88
APP:PER(3:1) + 10% Zeolite + PP	0.38	26.2	68.95
APP:PER(4:1) + 10% Zeolite + PP	0.51	35.8	70.51



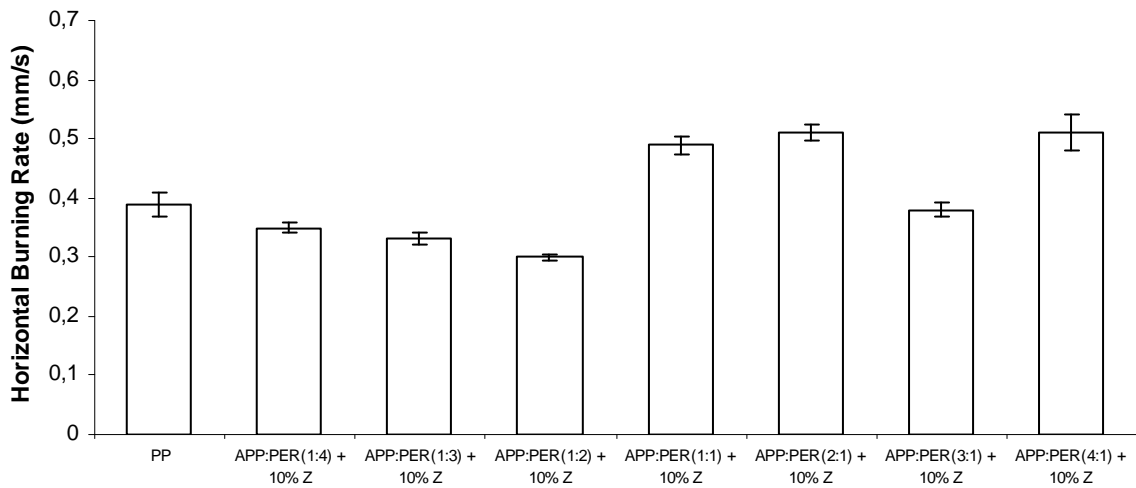
**Figure 4.17:** UL-94 test results of pure PP and flame retardant PP with 1w% zeolite loading.



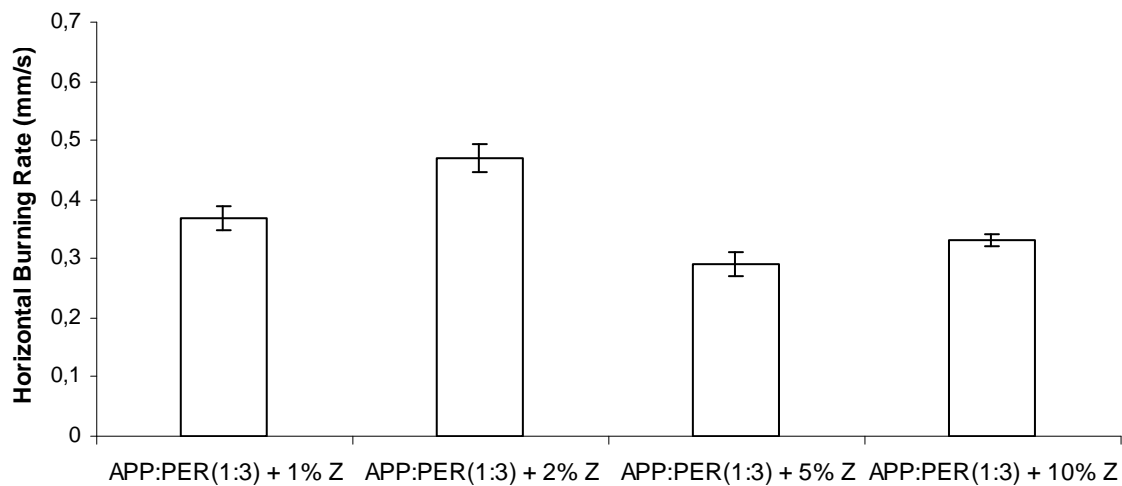
**Figure 4.18:** UL-94 test results of pure PP flame retardant PP with 2w% zeolite loading.



**Figure 4.19:** UL-94 test results of pure PP flame retardant PP with 5w% zeolite loading.



**Figure 4.20:** UL-94 test results of pure PP flame retardant PP with 10w% zeolite loading.



**Figure 4.21:** UL-94 test results of APP-PER(1:3)+PP with different zeolite loading.

## 4.7 Limiting Oxygen Index (LOI)

The limiting oxygen index test method provides to measure the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports combustion of pure PP, zeolite reinforced PP and flame retardant PP composites. Figure 4.22 shows influence of flame retardant materials and zeolite on flammability of PP separately. For researching synergism, each materials can affect flammability of PP must be known. Addition of 30w% APP into polypropylene, the LOI value (19%) remains constant. Pentaerythritol alone decreases 17% LOI value of PP. Composites with zeolite also decrease the LOI values. And increase zeolite concentration in composite formulations, the LOI was observed decreasing dramatically to 16%. The bars of LOI values versus zeolites content show that all APP:PER (1:1) formulations with and without zeolite (20.8-35.4%) indicate higher flame resistance than pure PP (19%) as shown in Figure 4.23. Combination of APP and PER (1:1) reduces flammability of polymer. Otherwise, flame retardant materials (APP and PER) reinforced polypropylene do not burn in atmospheric conditions and have high LOI value with 1:1 APP:PER ratio. A synergism may be defined as a case in which the effect of two components taken together is greater than the sum of their effects taken separately. Synergism between zeolite and flame retardant additives can be easily observed when figures 4.22 and 4.23 were compared. Combination of APP, PER and zeolite give better results than each one added to PP separately. Zeolite, 2w%, addition in APP:PER(1:1) PP formulation (35.4% LOI) increases oxygen concentration need for starting combustion of polymer. Synergistic effect was observed in formulation, having 2w% zeolite. When zeolite loading increase over 2w%, limiting oxygen index values begin to decrease as shown in Figure 4.23. At 10w% zeolite content, the LOI value decreases dramatically fewer than 21% of oxygen concentration. It means that 10w% zeolite content flame retardant PP composites burns easily in atmospheric conditions which is acceptable results according to our purpose.

Figures 4.23-4.26 illustrate LOI values of formulation, that APP/PER ratio was smaller than 1, versus zeolite loading. Results indicate that the APP has important role in combination of flame retardant materials and zeolite. Decreasing in amount of APP decreases LOI values of composites. Zeolite



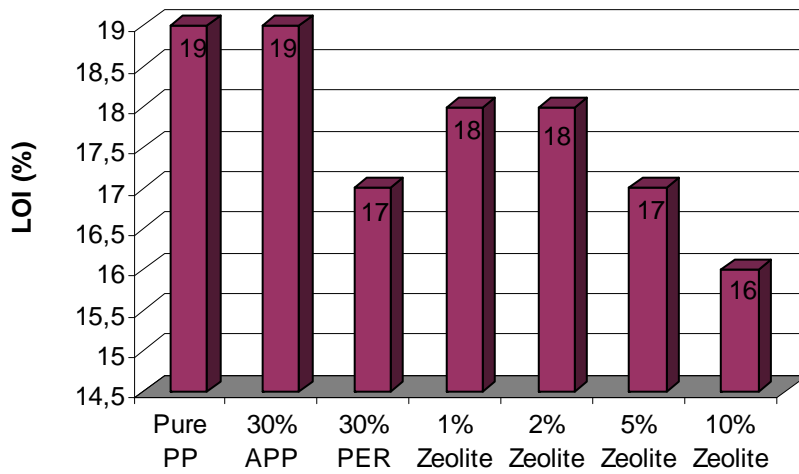
addition into FR-PP formulations caused to increase reduction of flame resistance of composite.

Figure 4.27 shows LOI values of pure PP, APP:PER (2:1)+PP composites with and without zeolite. This result shows when amounts of APP increased, the LOI values significantly increased. The addition of 5w% of zeolite into APP:PER(2:1)+PP formulation the limiting oxygen index values reach maximum value, 38% compared untreated flame retardant PP composites. Synergism can be easily observed between zeolite and flame retardant materials. The LOI of APP:PER(3:1)+PP composites with and without zeolite illustrates in Figure 4.28. The LOI reaches its maximum value 37.4% at 2w% zeolite + APP:PER(3:1) + PP composite. After that point, increase in zeolite addition reduces the flame resistance of composites. However, the limiting oxygen values of composites were higher than pure PP. There is critical concentration of APP. In the APP/PER (4:1) ratios, the results decrease significantly when comparison previous results as shown in Figure 4.29. Carbonisation agent (PER) does not provide sufficient for providing char formation which is important for intumescent system.

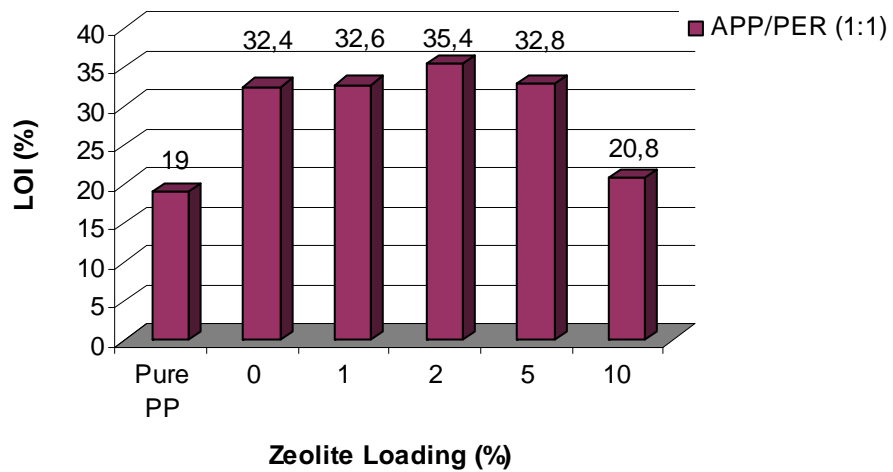
Researchers used many different minerals as synergistic agents such as china clay, calcium carbonate, talc and synthetic zeolite 3A, 4A, and 5A, Y, X, 10 X, 13 X, ZSM5. Bourbigot et al (1996) found out flame retardance performance of china clay are always lower than obtained with synthetic zeolite. They suggested that zeolite have to be used in order to obtain the best flame retardance performance. Zeolites act as a catalyst for the development of the intumescent carbonaceous material and stabilize the carbonaceous residue resulting to degradation of the intumescent shield. During thermal degradation of intumescent formulation, zeolite may adsorb some volatile components and it causes to enhance carbonaceous residue. Bourbigot et al., (1996) carried out flame retardant polymeric matrix composite formulation with consist APP/PER(3:1) + LRAM3,5 (polyethylenic copolymer) and synthetic zeolite in previous studies. They reached maximum LOI values (40% and 38.75%) with used 1.5% Y and 4A types of synthetic zeolites. When results were compared with literature, it can be seen that the LOI of formulation APP:PER(3:1)+PP+2% zeolite and APP:PER(2:1)+PP+5% zeolite exhibit 37.4 and 38% approximately similar flame retardance performance with literature. Almeras et al., (2003) investigated flammability of flame retardant PP matrix composite with consisting

talc, calcium carbonate as filler, and APP as flame retardant material by using LOI. The LOI of composites reached maximum 32%.

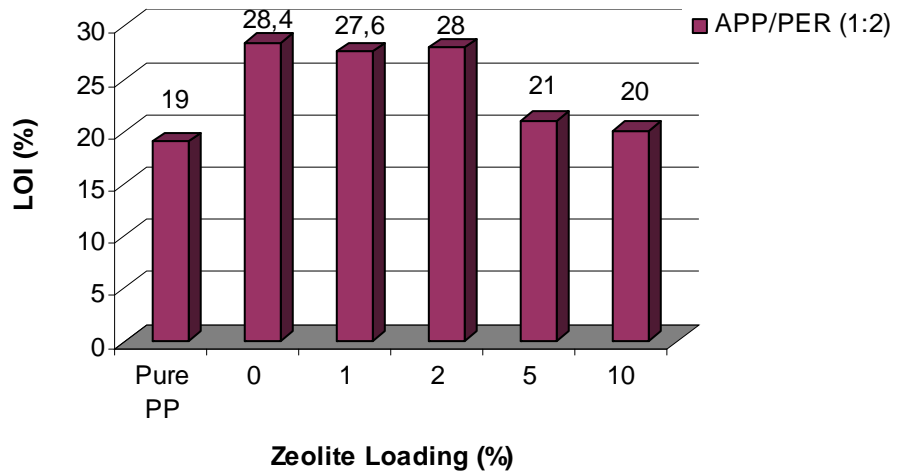
Figures 4.30-31 permit to compare all formulation of flame retardant PP composites. APP:PER ratio was selected as 1:1 , 2:1 and 3:1 and zeolite concentration was selected as 1, 2, 5w% for enhanced flame retardance performance of these formulations. The interface at the surface of particle inclusion plays a key role in the structure- property relationship. For this purpose, many additives use for modifying surface of fillers and interface between fillers and polymeric matrix, i.e. coupling agents. The chemical structure of these additives allows combining the function of dispersing and coupling agents, so they are capable of bonding the filler and PP matrix by chemical bonds. Hence, mechanical properties are improved. Meanwhile flame retardancy could be improved (Bertalan et al., 2001). In this respect, surfaces of APP and zeolite particles were modified with coupling agents, amino silane and mercapto silane. Figures 4.32-34 illustrate influence of coupling agent treatment on flame retardance performance of composites. Surface treatment of fillers does not significantly affect to LOI at lower zeolite concentration 1w% and 2w% as shown in Figure 4.32. At 5w% zeolite loading, LOI values of APP:PER(1:1)+PP+Z composites increase 11% with amino silane and 13% with mercapto silane. Because of the increase treated zeolite content, the enhancement of treatments can be observed. Figure 4.33 shows LOI values of untreated and treated APP:PER(2:1)+PP+Zeolite composites. At this time, treated fillers were increased with increasing APP:PER ratio to 2:1. For this reason, effects of coupling agents on LOI values can be seen also at lower zeolite concentration. LOI values were enhanced about 4-8% with silane treatments. And LOI values reached maximum values 41% with mercapto silane treated APP:PER(2:1) 5w% Zeolite PP composite. Mercapto silane treatment gives again better results than amino silane treatments. Figure 4.34 illustrates flame retardance performance of APP:PER(3:1)+PP+Zeolite composites. Influence of coupling agents on LOI values can be observed at 5w% zeolite concentration. The LOI values were developed to 6% and 10% with amino silane and mercapto silane treatments. The LOI value of mercapto silane treated formulation (APP:PER(3:1)+5%Z+PP) give better result than formulation of APP:PER(3:1) +2%Z+PP which synergism can be observed.



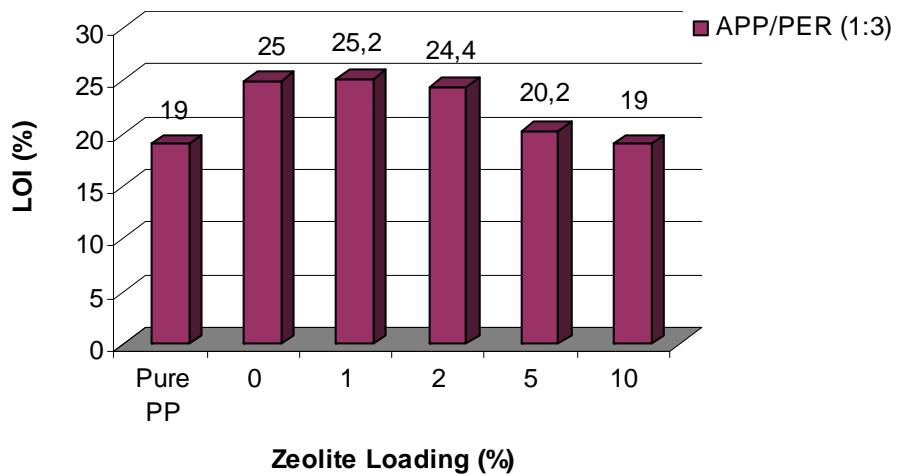
**Figure 4.22:** Limiting oxygen index of PP, 30w% APP+PP, 30w% PER+PP, and different zeolite loading to PP



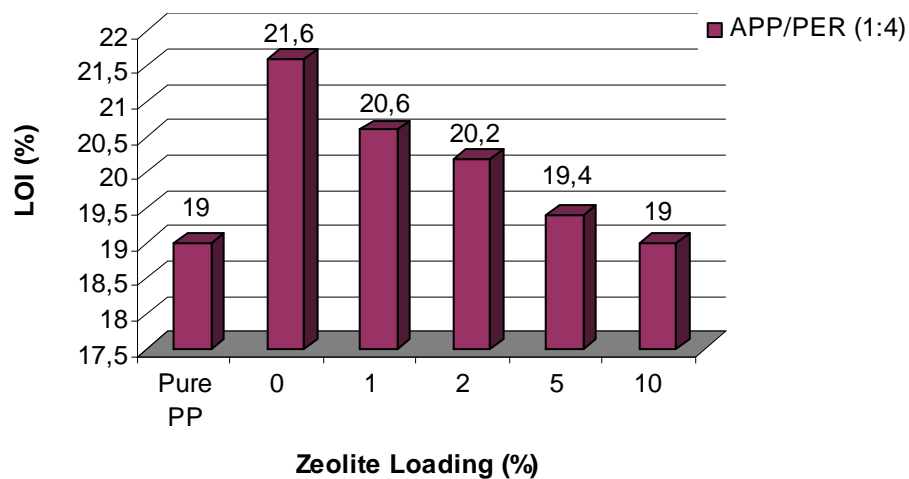
**Figure 4.23:** Limiting oxygen index of flame retardant polypropylene (APP/PER 1:1) versus zeolite content



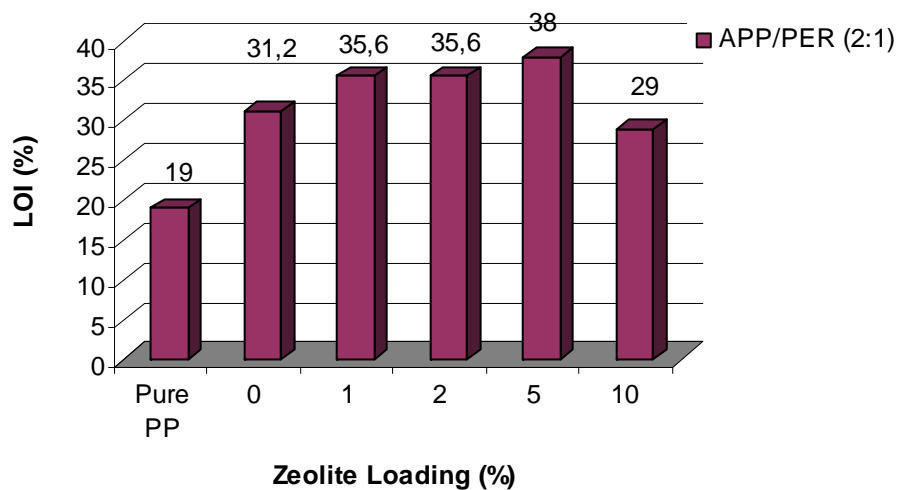
**Figure 4.24:** Limiting oxygen index of flame retardant polypropylene (APP/PER 1:2) versus zeolite content.



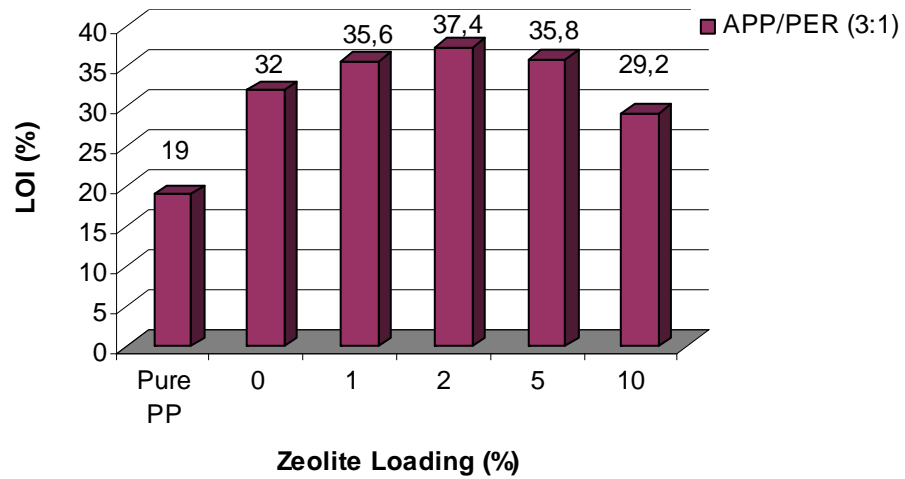
**Figure 4.25:** Limiting oxygen index of flame retardant polypropylene (APP/PER 1:3) versus zeolite content



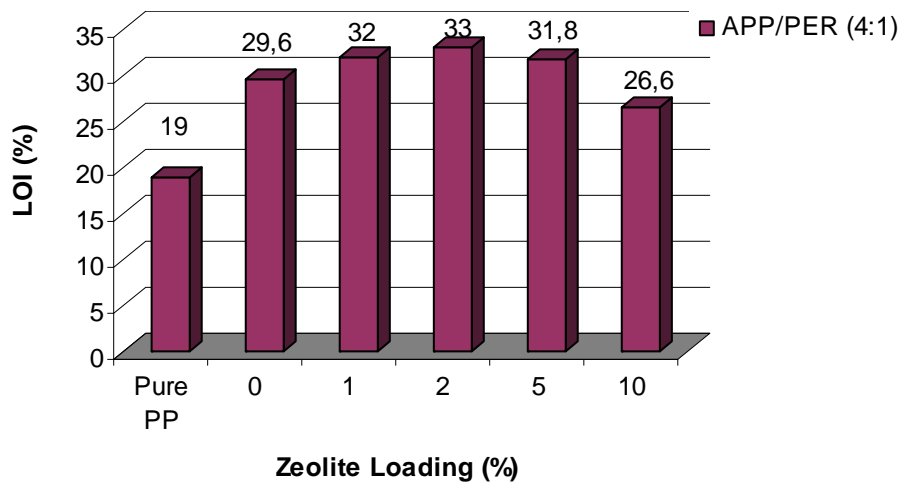
**Figure 4.26:** Limiting oxygen index of flame retardant polypropylene (APP/PER 1:4) versus zeolite content



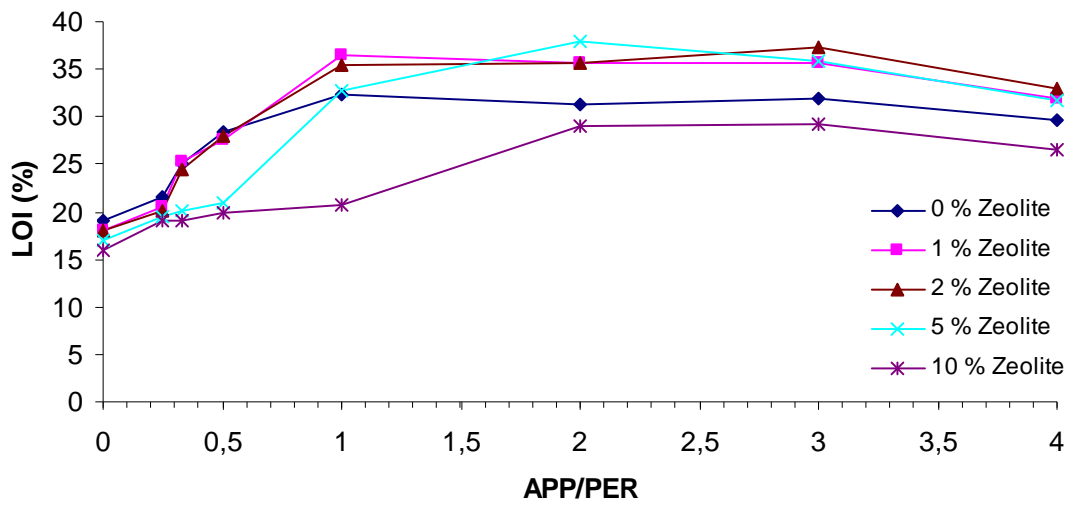
**Figure 4.27:** Limiting oxygen index of flame retardant polypropylene (APP/PER 2:1) versus zeolite content



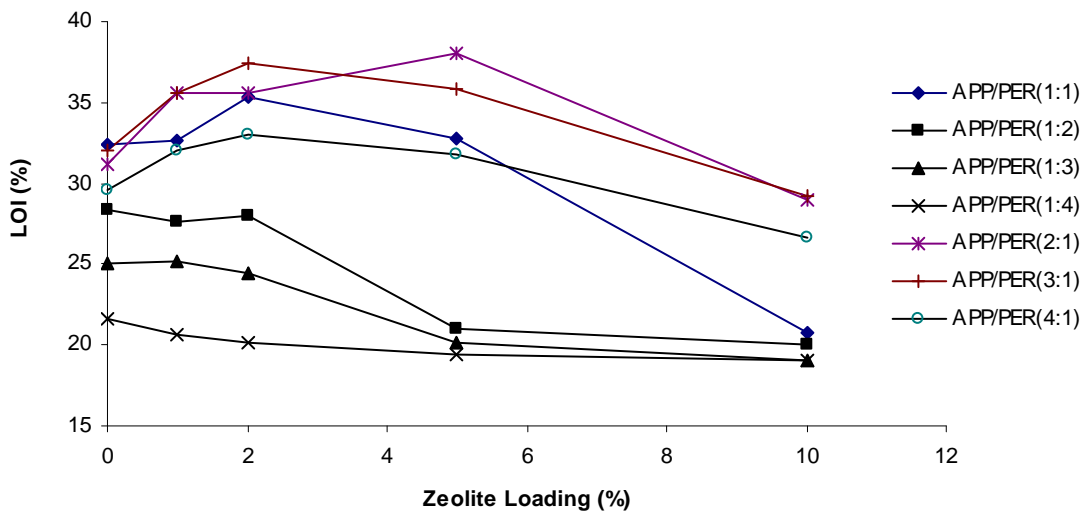
**Figure 4.28:** Limiting oxygen index of flame retardant polypropylene (APP/PER 3:1) versus zeolite content



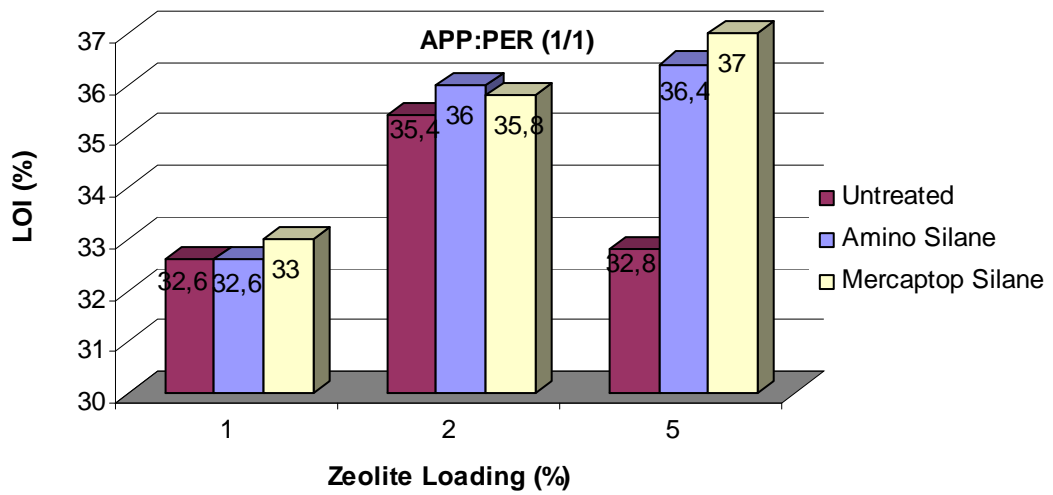
**Figure 4.29:** Limiting oxygen index of flame retardant polypropylene (APP/PER 4:1) versus zeolite content



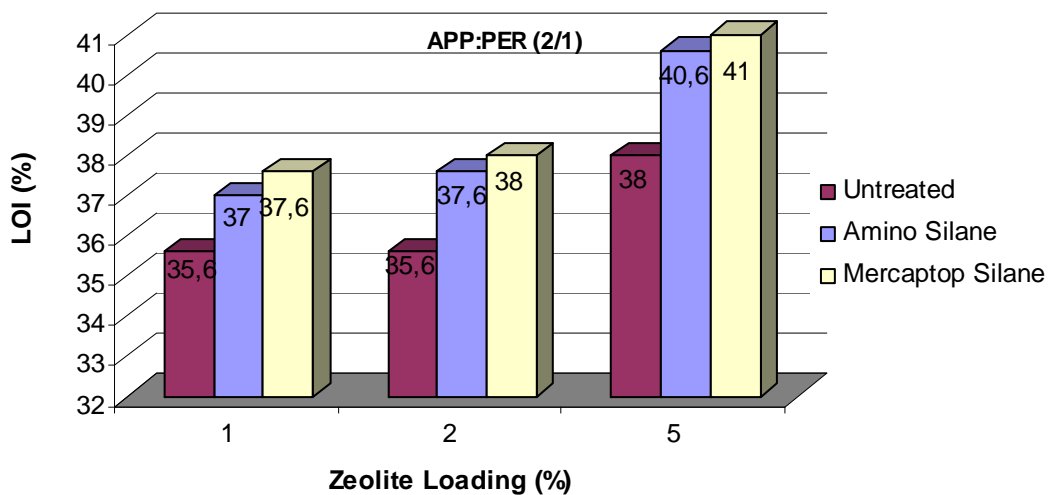
**Figure 4.30:** Limiting oxygen index of all flame retardant polypropylene composites versus APP/PER ratio according to zeolite concentration.



**Figure 4.31:** Limiting oxygen index of all flame retardant polypropylene composites versus zeolite content

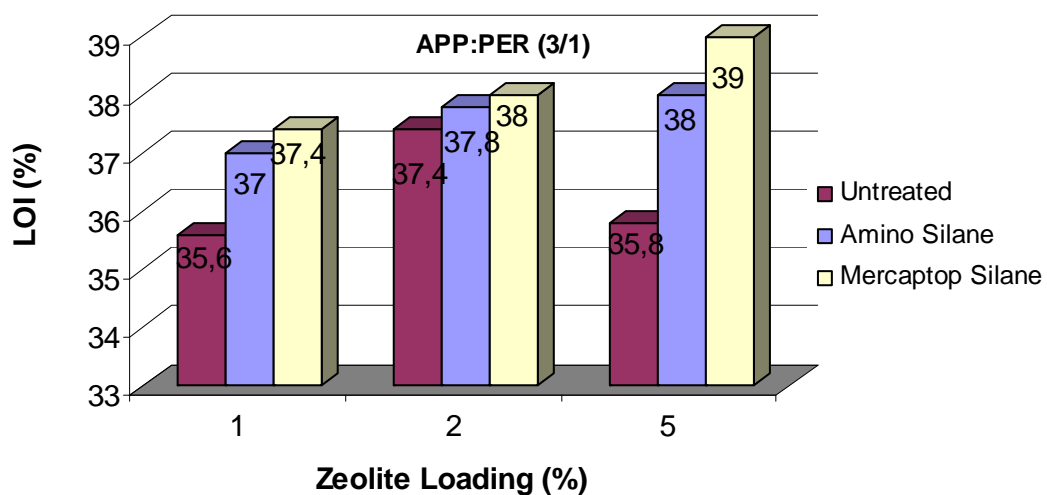


**Figure 4.32:** Limiting oxygen index of untreated and silane treated APP:PER(1:1)+PP composites versus zeolite content



**Figure 4.33:** Limiting oxygen index of untreated and silane treated APP:PER(2:1)+PP composites versus zeolite content.





**Figure 4.34:** Limiting oxygen index of untreated and silane treated APP:PER(3:1)+PP composites versus zeolite content.

## 4.8 Thermal Gravimetric Analysis

The raw materials (PER, APP, PP, Clinoptilolite Gördes II) were analysed individually as shown in Figure 4.35. Clinoptilolite lost 15% of its mass as water vapour at 600°C (Gottardi and Galli, 1985). It starts to lose its mass at 50°C. Polypropylene started degradation at 261°C and consumed completely at 600°C. Pentaerythritol began to degrade at 210°C and 4.75% residue remained at 600°C. APP showed two steps in its thermal degradation curve. First step started at 380°C and second step degradation began at 560°C. The weight loss of APP was 25% at 600°C and 8.3% at 800°C. Take an account that, the thermal behaviour of raw materials was investigated in N<sub>2</sub> medium. Hence, APP does not give an oxidation reaction. For that reason, APP gives only 25% of its mass at 600°C.

In Figure 4.36, the mass percent of FR PP composites is illustrated with different APP:PER ratio. Flame retardant materials shifted the decomposition curve over 400°C temperature. For polypropylene, decomposition started at 261°C. FR PP composites lost a big part of mass at 400°C. Formation of carbonaceous structure (char residue), indicating thermal stability, was also increased by adding flame retardant materials. Char of FR PP composites (24% mass) were higher than pure PP (0.87% mass). In every case, thermal stability of polypropylene was increased by adding flame retardant materials. According to APP/PER ratio, the mass loss of FR PP composites decreased with increasing amounts of APP in composites. The mass of residue was found 18.3, 20.2 and 23.37% for APP:PER(1:1), APP:PER(2:1), APP:PER(3:1) respectively.

In Figures 4.37 to 4.39, the thermal decomposition curve of FR PP composites was investigated with respect to zeolite content. Influence of zeolite was not significantly observed. Decomposition curves of without and with zeolite composites almost fitted into one another. However, residue increased with increasing zeolite loading in composites. Carbonaceous residue was found 22.66%, 23.43%, and 24.53% for APP:PER(1:1) 5% zeolite, APP:PER(2:1) 5% zeolite, and APP:PER(3:1) 5% zeolite respectively.

APP:PER(2:1) 5% zeolite PP composites were analysed as model system and compared to the theoretical TG values as shown in Figure 4.40. The theoretical values were calculated from TG data of individual components

without considering any interactions. The theoretical thermal degradation curves were calculated using Equation (4.1) at each temperature.

$$X_1m_1+X_2m_2+X_3m_3+X_4m_4=m_c \quad (4.1)$$

where,

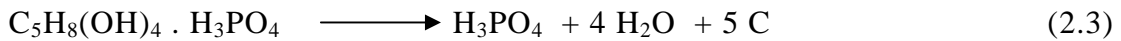
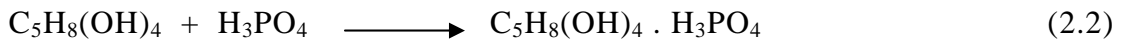
X: Mass fraction

m: Mass loss

1: Polypropylene, 2: Pentaerythritol, 3:Ammonium Polyphosphate 4:zeolite

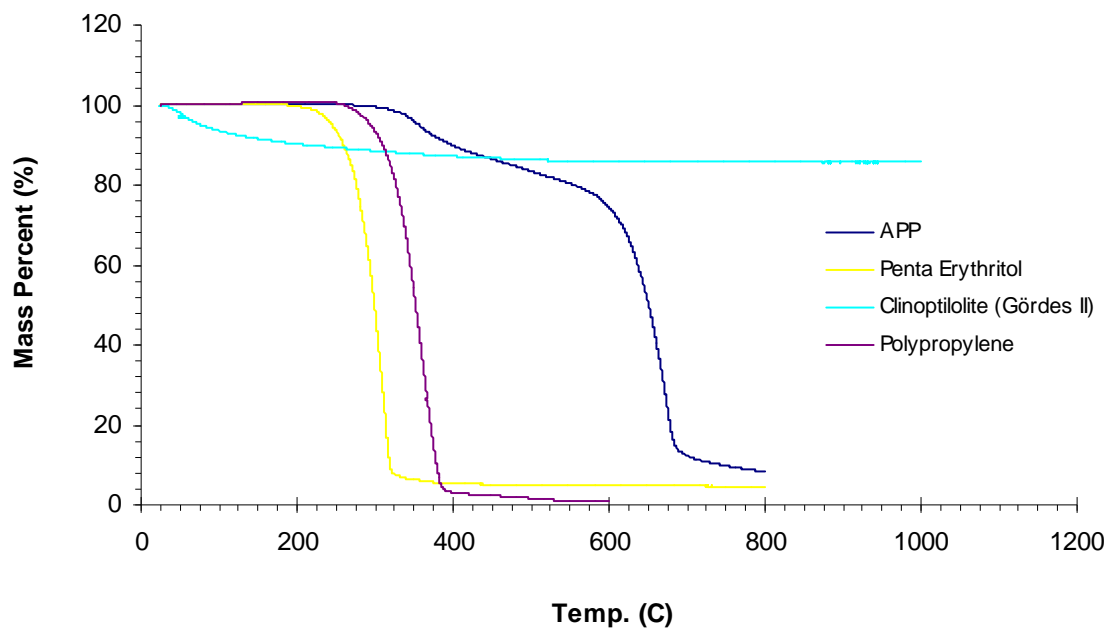
C: Composite

The experimental decomposition curve of FR PP started to degrade later than theoretical curve. The amount of carbonaceous residue, in experiment, was found higher than theoretical one. These results prove that there is an interaction between the flame retardant materials (APP and PER) and zeolite. The interaction between APP and PER

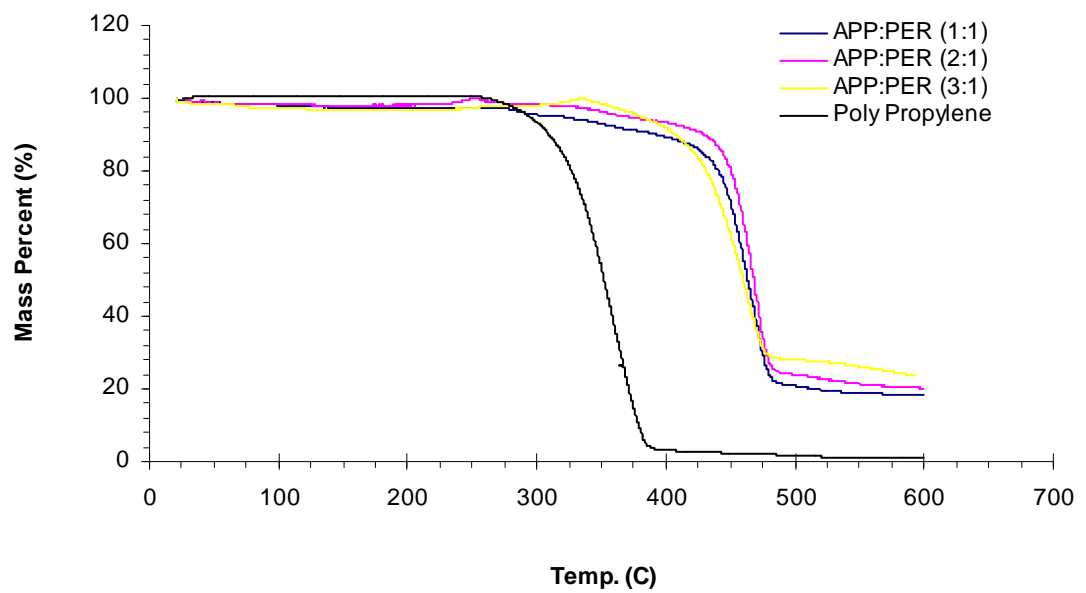


Bourbigot et al., (1996) revealed the flame retardant additives' (APP and PER) systems allows the formation of carbonaceous shield constituted by polyaromatic stack in the polymer degradation temperature range. Another case, they reported that zeolite reacted with APP to form Alumino and silicophosphates which may catalyse the synthesis of protective carbon species by forming an alumino-silico-phospho carbonaceous, thermally stable structure.

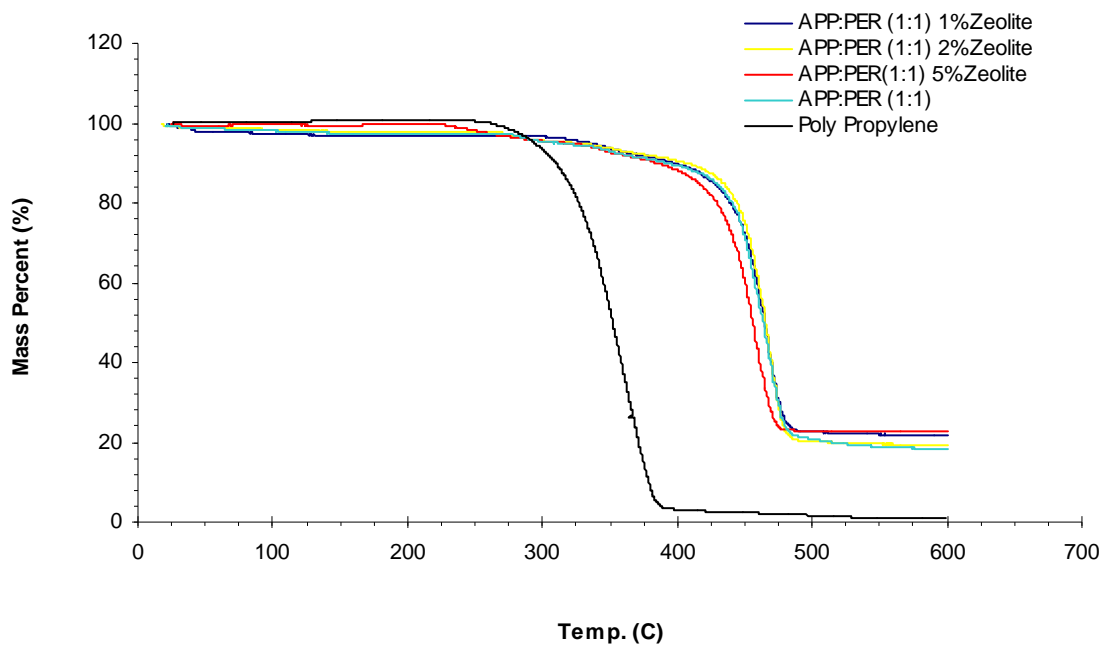
The residue of composites and poly propylene and maximum mass loss temperature were illustrated at Table 4.3. Influence of zeolite on mass of residue was not significantly observed. In general, zeolite addition into formulation increase carbonaceous residue. Maximum mass loss point due to temperature was shift higher value than pure polypropylene. When compared to flame retardant composite with each other, the temperature deviates between 457 and 471°C.



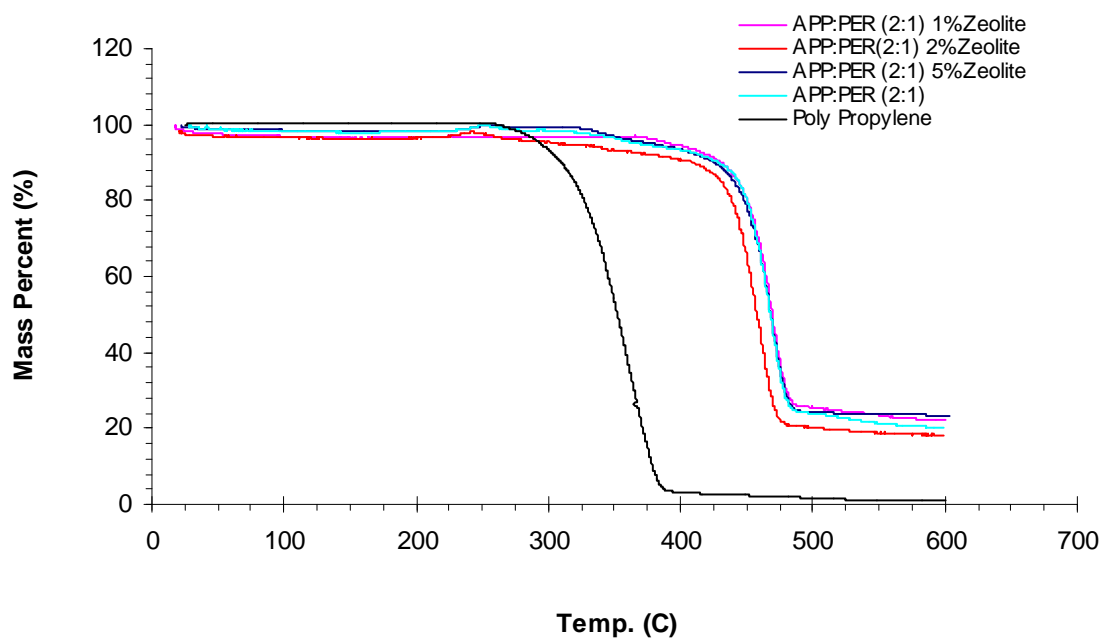
**Figure 4.35:** Thermal degradation curves of raw materials



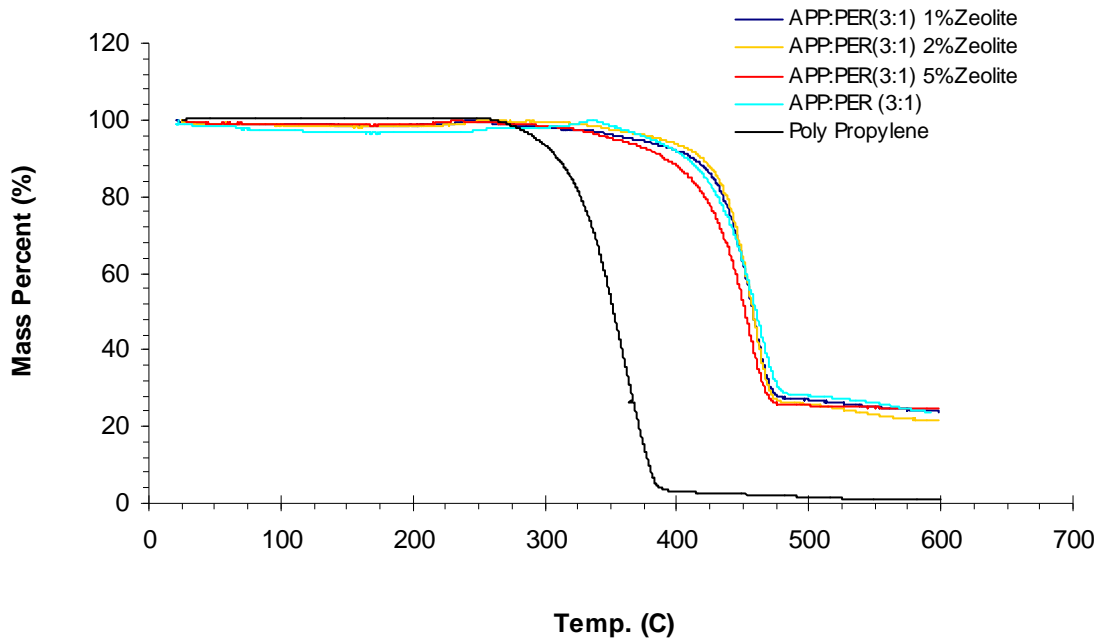
**Figure 4.36:** TGA thermograms of PP and FR PP composites with different APP/PER ratio



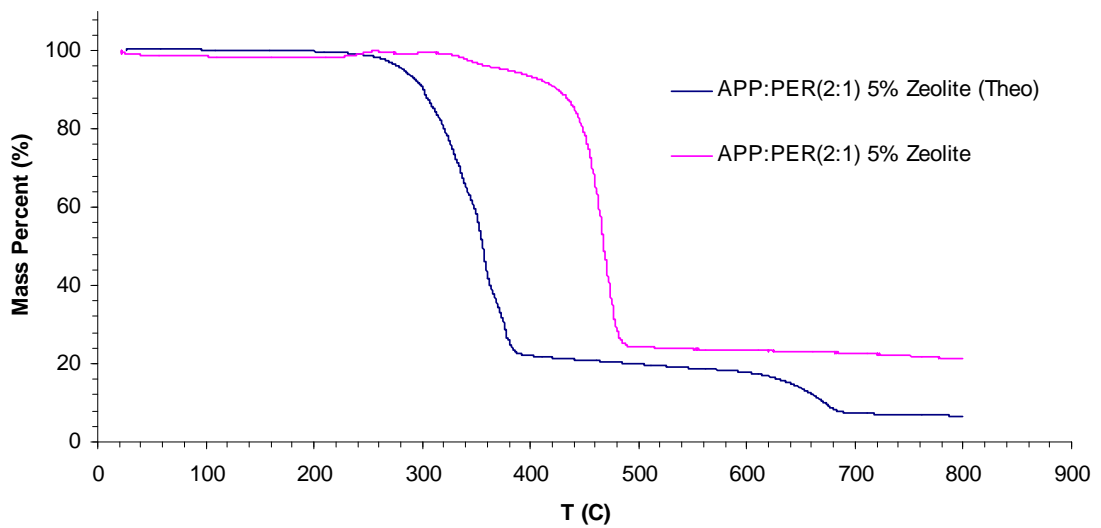
**Figure 4.37:** TGA thermograms of APP:PER(1:1)+PP composites with different zeolite loading.



**Figure 4.38:** TGA thermograms of APP:PER(2:1)+PP composites with different zeolite loading.



**Figure 4.39:** TGA thermograms of APP:PER(3:1)+PP composites with different zeolite loading.



**Figure 4.40:** Theoretical and experimental mass percent curve of APP: PER (2:1) PP+5%Zeolite composites

**Table 4.3:** Maximum rate mass loss Temperature and residue of composites at 600°C

<b>Samples</b>	<b>Max. rate of mass loss Temperature (°C)</b>	<b>Residue (%) at 600°C</b>
PP	369	0.867
APP:PER (1:1)	470	18.3
APP:PER (2:1)	471	20.2
APP:PER (3:1)	466	23.37
APP:PER (1:1) 1% Zeolite	469	21.51
APP:PER (1:1) 2% Zeolite	470	19.39
APP:PER (1:1) 5% Zeolite	461	22.66
APP:PER (2:1) 1% Zeolite	471	22.08
APP:PER (2:1) 2% Zeolite	463	18.07
APP:PER (2:1) 5% Zeolite	471	23.43
APP:PER (3:1) 1% Zeolite	462	23.93
APP:PER (3:1) 2% Zeolite	462	21.44
APP:PER (3:1) 5% Zeolite	457	24.53

## 4.9 Mechanical Properties of Composites

Tensile tests were carried out for understanding influence of coupling agents and reinforced fillers on the mechanical properties of flame retardant PP composites. The most important mechanical properties of polymeric composites are tensile strength, elongation and Young's modulus. Experimental mechanical test data of all sample are shown in Table A1 in the Appendix. Typical stress vs. strain diagram of pure PP and flame retardant PP composites was presented in Figure 4.41. Flame retardant PP composites The effect of zeolite loading, APP:PER ratio on the mechanical properties of composites were investigated. Influences of surface treatments of fillers with coupling agents were also researched. Tensile strength of composites did not change with composition of composites and was close to each other. Differences were not observed. Surface treatments did not modify the tensile strength properties of composites. However zeolite concentration almost increased and surface treatments with coupling agents decreased tensile strength of flame retardant PP composites as shown in Table 4.4. The tensile strength of pure PP is around 33MPa and this is much higher than 30w% filler reinforced flame retardant PP composites.

Metin (2002) calculated S parameter which describes weakness in the structure created through stress concentration at the filler-matrix interphase in the Nielsen's model in Equation (4-2). Unity in the value of S means a "no stress concentration effect", whereas the lower the value the greater the stress concentration effect or poorer the adhesion.

$$\sigma_c / \sigma_p = (1 - \Phi_f^{2/3})S \quad (4-2)$$

where,

$\sigma_c$  and  $\sigma_p$  are tensile strength of composites and matrix respectively

$\Phi_f$  is volume fraction of filler

Table 4.5 illustrates S parameter of treated and untreated flame retardant PP composites. Interfacial adhesion between the fillers and the matrix is an important factor affecting the tensile strength of the composites. In the case of no adhesion between the matrix and the filler, the interfacial layer can not transfer



stress. The Nielsen's model describes weakness in the structure created through stress concentration at the filler-matrix interphase. S parameters of FR-PP composites were lower than unity. It indicates that poor adhesion between filler and matrix. Surface treatments with coupling agents did not improve S parameter also adhesion between filler and matrix.

Elongation at break values of untreated and treated flame retardant PP composites was exhibited in Table 4.6. Strain values of FR-PP composites enhance with increasing amounts of APP in formulation. Coupling agents develop the strain properties of FR-PP composites. Bertalan et al., (2001) found out the same results. They indicated that consequence of homogeneous structure and improved adhesion between the matrix and filler via the modified interface. Although, increased elongation is not common influence of coupling agents. It may be assumed that coupling agents prevent formation of cracks between filler and polymeric matrix with modification interphase, hence deformation do not start so easily. Surface treatments with mercapto silane give better results than amino silane treatment. Elongation of pure PP was 418%. Filler addition almost decreases elongation properties of polymeric matrix to 6.37%-25.67%.

Young's modulus of treated and untreated flame retardant PP composites was illustrated in Table 4.7. Young's modulus of pure PP was 1339 MPa and 30w% filler reinforced FR-PP composites were 1383-2198 MPa varied due to their composition and surface treatments. Young's modulus decreases with increasing amounts of APP in composite on the contrary of elongation properties. Instead of APP, zeolite loading increases Young's modulus. Surface treatments cause to decrease Young's modulus. Young's modulus of mercapto silane treated FR-PP composites was lower than amino silane treated composites.

The Kerner equation is also used to calculate the modulus of a composite having nearly spherically particles in the case of some adhesion between the phases.

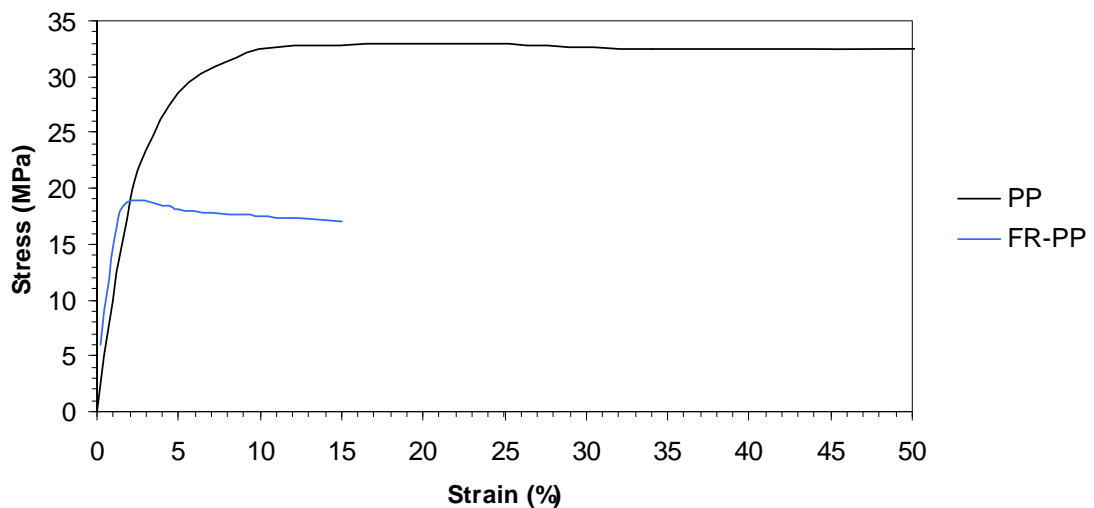
$$\frac{E_c}{E_m} = 1 + \left[ \frac{15(1 - \nu_p)}{8 - 10\nu_p} \right] \left[ \frac{\Phi_f}{1 - \Phi_f} \right] \quad (4-3)$$

where,

$\nu_p$  is the Poisson's ratio of the polymer taken as 0.35 for isotactic polypropylene

$\Phi_f$  is volume fraction of filler (Metin, 2002).

The comparison of theoretical and experimental Young's modulus of untreated FR-PP composites was showed in Figure 4.42. Kerner model predicted the experimental Young's modulus of untreated FR-PP composites when taken account the deviation of Young's modulus of untreated FR-PP composites. The Kerner model expresses the effect of filler concentration on Young's modulus of the polymer composite.



**Figure 4.41:** Stress vs Strain diagram of pure PP and FR-PP composites

**Table 4.4:** Tensile strength of treated and untreated flame retardant PP composites

Test Sample	Untreated (MPa)	Amino Silane (MPa)	Mercapto (MPa)
PP	33±1		
APP:PER (1:1) 1%Zeolite	18,1±1,17	17,4±1,9	17,0±0,59
APP:PER (1:1) 2%Zeolite	20,9±1,2	17,4±0,60	16,8±0,68
APP:PER (1:1) 5%Zeolite	21,3±1	19,7±0,74	19,2±0,88
APP:PER (2:1) 1%Zeolite	19,2±0,81	18,7±1,6	17,7±0,51
APP:PER (2:1) 2%Zeolite	19,1±0,5	18,5±0,35	18,5±0,58
APP:PER (2:1) 5%Zeolite	18,6±1,1	17,4±0,81	17,7±0,79
APP:PER (3:1) 1%Zeolite	19,1±0,92	17,6±0,43	17,1±0,69
APP:PER (3:1) 2%Zeolite	19,8±1,02	18,9±0,57	17,5±0,80
APP:PER (3:1) 5%Zeolite	19,2±1	17,3±0,66	16,0±0,57

**Table 4.5:** S parameter of treated and untreated flame retardant PP composites

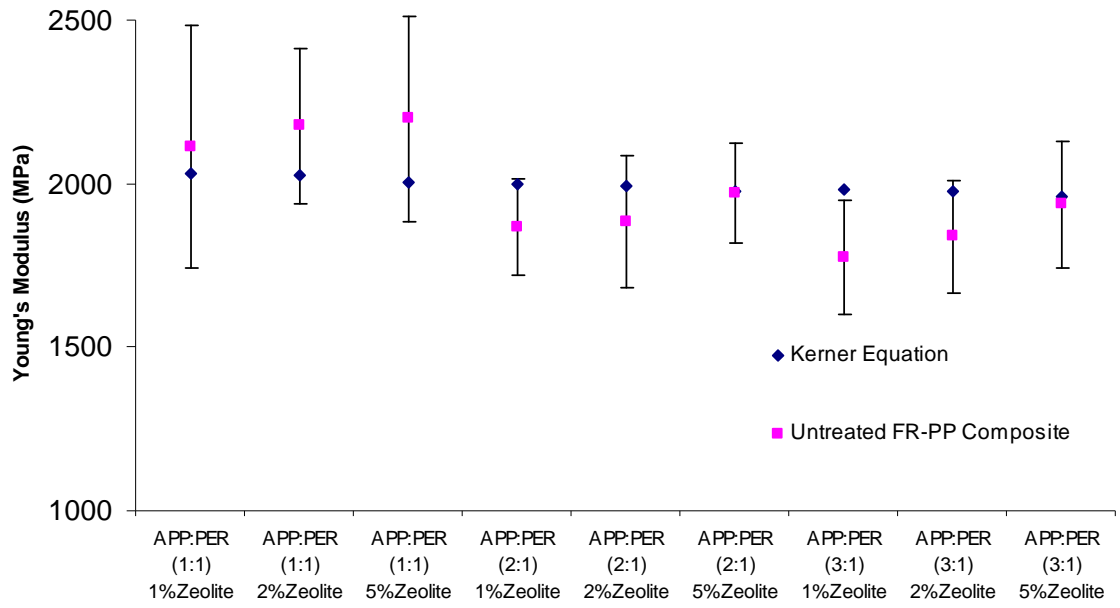
Test Sample	S Parameter		
	Untreated	Amino Silane	Mercapto
APP:PER (1:1) 1%Zeolite	0,82	0,79	0,77
APP:PER (1:1) 2%Zeolite	0,95	0,79	0,76
APP:PER (1:1) 5%Zeolite	0,96	0,88	0,86
APP:PER (2:1) 1%Zeolite	0,86	0,84	0,79
APP:PER (2:1) 2%Zeolite	0,85	0,83	0,83
APP:PER (2:1) 5%Zeolite	0,83	0,77	0,79
APP:PER (3:1) 1%Zeolite	0,85	0,78	0,76
APP:PER (3:1) 2%Zeolite	0,88	0,84	0,78
APP:PER (3:1) 5%Zeolite	0,85	0,77	0,71

**Table 4.6:** Elongation at break values of treated and untreated flame retardant PP composites

Test Sample	Untreated (%)	Amino Silane (%)	Mercapto (%)
PP	418±2		
APP:PER (1:1) 1%Zeolite	7,37±1,81	15,70±1,71	22,39±2,14
APP:PER (1:1) 2%Zeolite	7,17±0,6	14,71±3,47	18,51±2,85
APP:PER (1:1) 5%Zeolite	6,37±1,41	10,57±4,37	16,55±3,45
APP:PER (2:1) 1%Zeolite	18,77±4,14	20,47±3,18	25,67±5,87
APP:PER (2:1) 2%Zeolite	17,67±3,6	19,18±5,76	22,71±1,66
APP:PER (2:1) 5%Zeolite	16,92±1,56	17,45±3,97	20,79±2,92
APP:PER (3:1) 1%Zeolite	23,87±5,03	24,74±4,94	27,77±4,58
APP:PER (3:1) 2%Zeolite	21,82±1,93	22,61±0,93	25,20±2,19
APP:PER (3:1) 5%Zeolite	20,47±4,99	21,13±3,94	24,55±3,79

**Table 4.7:** Young's modulus of treated and untreated flame retardant PP composites

Test Sample	Untreated (MPa)	Amino Silane (MPa)	Mercapto (MPa)
PP	1339±123		
APP:PER (1:1) 1%Zeolite	2112±371	1829±224	1726±219
APP:PER (1:1) 2%Zeolite	2177±238	1862±102	1745±270
APP:PER (1:1) 5%Zeolite	2198±314	2099±129	1977±303
APP:PER (2:1) 1%Zeolite	1868±147	1714±229	1639±89
APP:PER (2:1) 2%Zeolite	1884±200	1801±218	1754±237
APP:PER (2:1) 5%Zeolite	1969±154	1899±143	1455±145
APP:PER (3:1) 1%Zeolite	1775±176	1458±158	1383±122
APP:PER (3:1) 2%Zeolite	1839±171	1596±124	1411±157
APP:PER (3:1) 5%Zeolite	1935±194	1676±130	1620±51



**Figure 4.42:** The comparison of experimental and theoretical Young's Modulus of untreated FR-PP composites

## CONCLUSION

Intumescent system requires three different functions of compounds, acid source, blowing and carbonific compounds. Ammonium polyphosphate (APP) was used as acid source and blowing agents. Pentaerythritol (PER) was used as carbonific compounds. Natural zeolite, clinoptilolite, was used as synergistic agents with intumescent flame retardant materials. The interface of the surface of particle inclusion plays a key role in the structure-property relationship. Surfaces of APP and natural zeolite were modified with Amino and Mercapto silane. Influences of silane treatments were investigated on mechanical properties and flame retardant performance of composites.

Flame retardant PP composites, with and without zeolite, did not show different behaviour during heating on hot plate by observing optical microscope. Flame retardants did not cause to any bubble formation during heating over 203°C. Pentaerythritol melted at 170°C and molten PER was observed as second phase in molten polypropylene at 203 °C. In SEM microphotographs of cross section of composites, flame retardant materials (APP and PER) were well distributed in polypropylene matrix and any bubble formation composites was not observed. Bubble formation on surface of burnt flame retardant polypropylene near the edge and non-burnt zone can be easily observed at the middle of the samples. Bubbles were distributed randomly and have different size and shapes. The zeolite addition did not indicate significant difference according to foam size and shape compared to composites without zeolite.

Combination of APP and PER affects rheological properties of composites. Torque of all composites having APP and PER decrease to 70% of the value of pure PP. The results show that the rheological properties do not change significantly with respect to ratio between APP and PER. The torque decreased with melting PER due to molten PER behaves as a lubricant. Amino silane and mercapto silane treatments increased the torque value of composites 87% of the value of the pure PP.

Addition of flame retardant materials in PP matrix increased flammability resistance of PP. Most of composites did not burn in atmospheric conditions. Burning rate of flame retardant PP composites changed disorderly and were not precise, because, this test method should be used to establish relative burning

characteristics of plastic materials. This test method does not give comparable data for considering differences among non-burnt FR-PP composites in atmospheric conditions.

Addition of 30w% APP into polypropylene, the LOI value (19%) remained constant. Pentaerythritol alone decreased to 17% LOI value of PP. Addition of zeolite in PP, the LOI was observed to be decreasing dramatically to 16%. Results indicated that the APP has important role in combination of flame retardant materials and zeolite. Decreasing in amount of APP decreases LOI values of composites. Synergism between zeolite and flame retardant additives could be easily observed for combination of APP, PER with zeolite in composites. The addition of 5w% of zeolite into APP:PER(2:1)+PP formulation the limiting oxygen index values reach its maximum value, 38%.

Surfaces of APP and zeolite particles were modified with coupling agents, amino silane and mercapto silane. At 5w% zeolite loading, LOI values of APP:PER(1:1)+PP+Z composites increased 11% with amino silane and 13% with mercapto silane. And LOI values reached maximum values 41% with mercapto silane treated APP:PER(2:1) 5w% Zeolite PP composite.

Flame retardant materials shifted the decomposition curve of composites over 400°C. For polypropylene, decomposition started at 261°C. FR PP composites lost a big part of their mass at 400°C. Formation of carbonaceous structure (char residue), indicating thermal stability, was also increased by adding flame retardant materials. Char of FR PP composites (24% mass) were higher than pure PP (0.87% mass). The weight of residue was found as 18.3, 20.2 and 23.37% for APP:PER(1:1), APP:PER(2:1), APP:PER(3:1) respectively. APP:PER(2:1) 5% zeolite PP composites were analysed as model system and compared to the theoretical TG values to find out interactions between flame retardants and zeolite. The theoretical values were calculated from TG data of individual components without considering any interactions. The experimental decomposition curve of FR PP started to degrade later than theoretical curve. And the amount of carbonaceous residue, in experiment, was found higher than theoretical one. These results proved that there was an interaction between the flame retardant materials (APP and PER) and zeolite.

The effect of zeolite loading, APP:PER ratio and surface treatments of fillers with coupling agents on the mechanical properties of composites were

investigated. Tensile strength of composites did not change with composition of composites and were close to each other. Surface treatments did not modify the tensile strength properties of composites. The tensile strength of pure PP was around 33MPa and this was much higher than 30w% filler added flame retardant PP (18 MPa) composites. The coupling agents develop the elongation at break values of FR-PP composites. Homogeneous structure yielded higher strain values compared to untreated composites. Young's modulus of pure PP was 1339 MPa and 30w% filler reinforced FR-PP composites reached 1383-2198 MPa varied due to their composition and surface treatments. Zeolite loading increased Young's modulus. Surface treatments caused to decrease Young's modulus on the contrary of elongation at break values. Young's modulus of mercapto silane treated FR-PP composites was lower than amino silane treated composites.



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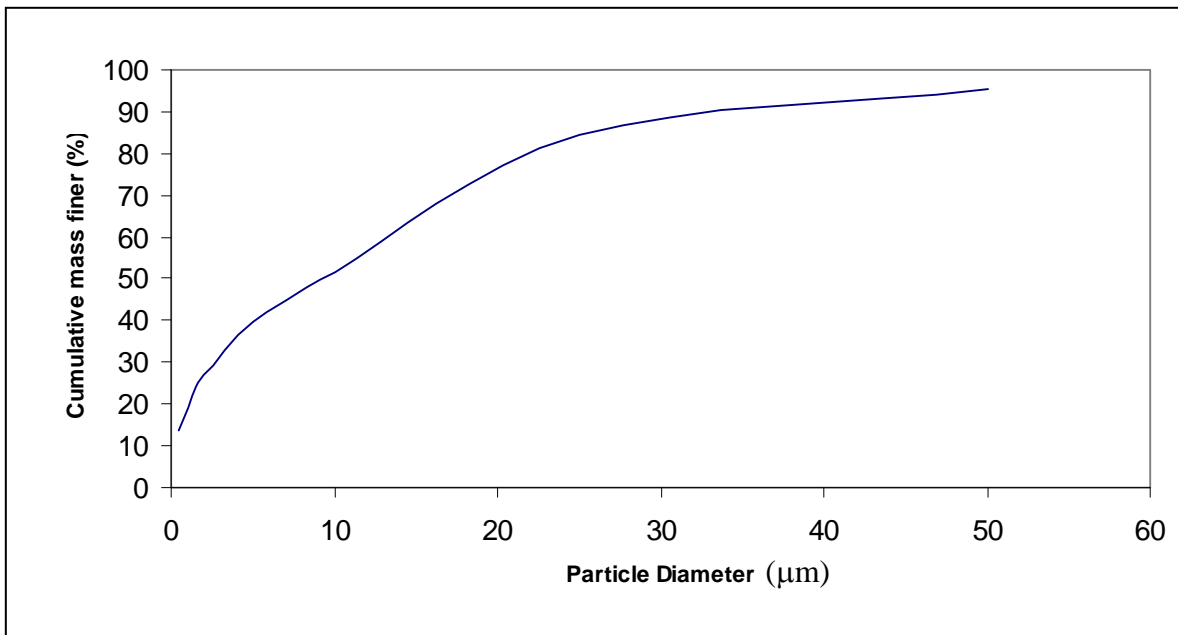
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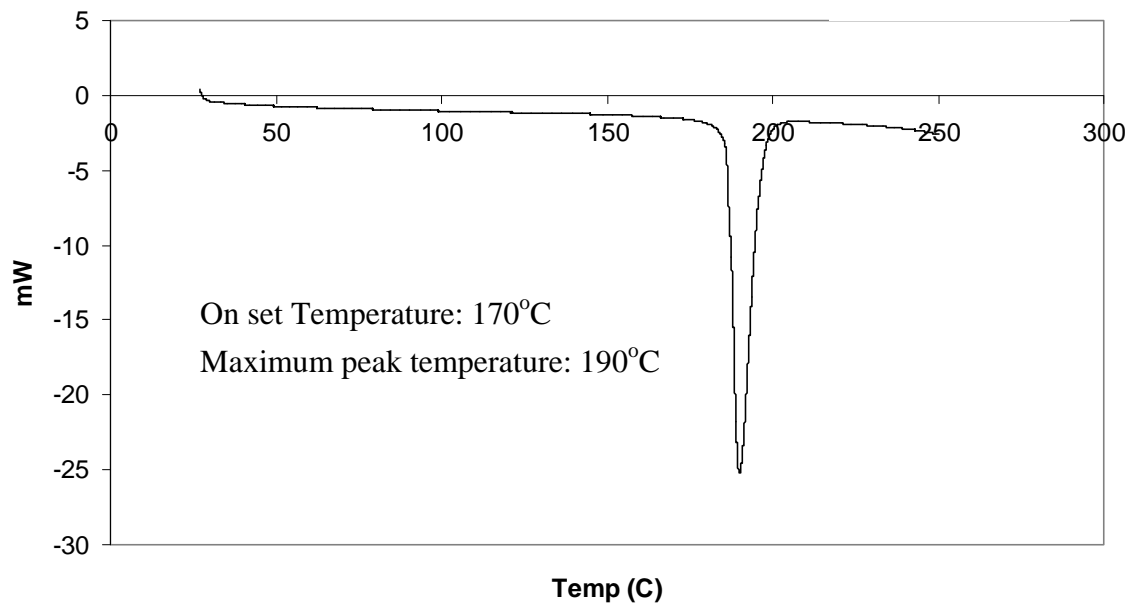
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## APPENDIX A



**Figure A1:** Particle size distribution of clinoptilolite



**Figure A2:** DSC curve of pentaerythritol