Synthese und Charakterisierung von Flammschutzschichten auf Polyolefinsubstraten

vorgelegt von

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Synthesis and Characterization of Fire-Retardant Layers onto Polyolefin Substrates

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Statement of Authenticity

The undersigned declare that this Ph. D. thesis is based on research performed by the candidate for fulfillment of the Ph. D. degree in material science and technology

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To whom it may concern

Beside the work carried out in this thesis the candidate **Zeinab Ramadan Farag Mohamed**

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1- Polymerspektroskopie

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وَأَنْزَلَ اللَّهُ عَلَيْكَ الْكِتَابَ وَالْحِكْمَةَ وَعَلَّمَكَ مَا لَمْ تَكُنْ تَعْلَمُ ۚ وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا

سورة النساء – ١١٣

(And Allah has revealed to you the Book and wisdom and has taught
you that which you did not know. And ever has the favor of Allah
upon you been great.)
The Noble Quran, 4:113

Dedication

I dedicate this thesis to the soul of my Father-in-law

Major-general Ali Abd-Eltawab

Who encouraged me to be the best I can be,

to have high expectations and to fight hard for what I believe. He always provided me with

best opportunities in life. I feel he is always with me supporting and guiding

May God Bless His Soul

Acknowledgment

Abstract

First goal of this work was to produce thick fire-resistant coatings, which are able to withdraw the direct contact to flames. Preliminary tests had shown that thicknesses more than 10 μm are needed to measure effects on flammability. Here, 40 μm thick layers are prepared. The adhesion of such thick layers mainly depends on the use of surface treatment of polyolefin substrates. Plasma exposure and deposition of plasma polymer layers are easiest and most efficient methods to promote the adhesion of thick layers used for the fire protection of materials. Indeed, plasma processing doesn't modify the intrinsic properties of materials such as the mechanical properties, easily processed, and can be applied over a wide range of materials even though for metals.

To achieve very high adhesion of such thick coatings to the polymer substrates it has to be considered that the chemical nature of coating and polymers is different, strong different thermal expansion coefficients exist and therefore adhesion was most often absent.

Different techniques were used to prepare such thick layers and to promote strong adhesion. Coatings have to withdraw high temperatures at exposure to flame without self-peeling; elsewise flames and oxygen have access to the subjacent easy flammable polymer substrates. Combinations of two deposition techniques allow fulfilling these preconditions. Generally, plasma pre-treatment was used to improve the adhesion property of polyolefin substrates and deposition of plasma polymers onto the plasma-pretreated polyolefin served as adhesion-promoting basecoat responsible for maximal adhesion between polyolefin and thick coating. This basecoat was 0.1 to 1.0 μm thick. To deposit layers with thickness of 20 or 40 μm this plasma technique was too much time-consuming. Therefore, the thick layers were deposited onto such basecoat by simple dipping into coating solution or by spraying.

Such combination of adhesion-promoting basecoats and thick coatings were tested using peel strength measurements and flammability tests. The most important problem was to find a suitable basecoat, which adheres very well onto the nonpolar polymer substrates (or plasma-pretreated substrates) but show also good adhesion to the dip or spray coating material as well as balancing of thermally induced stress at the interface of substrate and coating.

As flame retarding coating materials inorganic structures were chosen, which are inflammable, char former and, therefore, act as a barrier to oxygen. Here, precursors or materials forming siloxane-like structures were preferred. Intumescent layers releasing ammonia and nitrogen were also used. For this purpose urea and melamine products were preferred. Moreover, several melamine precursors were also in the focus. A third variant consists of the deposition of polyphosphates well-known as fire-retarding substances. It was expected that combination of these inorganic and organic layers are best suited for flame retarding under the condition of permanent high adhesion of coatings.

The layers were characterized by analytical methods such as X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) in the Attenuated Total Reflectance mode (ATR), Thermal Gravimetric Analysis (TGA) as well as by 90° peel strength measurement, fire tests (according to DIN 4102-1) etc.

Apolar polyolefin surfaces were made hydrophilic on a few seconds exposure to oxygen low-pressure plasma. Thus, several types of oxygen-containing groups were formed at the polymer surface capable to interact with the plasma polymer layer deposited for adhesion-promoting purpose.

To further promote the adhesion of thick silicate layers additional thin siloxane-like layers were deposited by low-pressure plasma polymerization of hexamethyldisiloxane

(HMDSO) in presence of oxygen. The prepared 0.5 to 1.0 μm thick layers have SiO_2 stoichiometry. Alternatively, SiO_2 layers could by deposited under atmospheric pressure conditions very rapidly by a pyrolytic method (Silicoater process). Another possibility was the tested Electro Spray Ionization deposition (ESI) of Na-silicates. These atmospheric pressure processes for preparation of basecoats were also developed with regard to technical realization. Thick layers were deposited by dipping into Na-silicate solution (water glass) or by spraying it. Thus, 40 μm thick SiO_2-like fire-retardant coatings were prepared.

To prepare well adherent thick coatings of melamine pre-polymers at the surface of polymer substrates allylamine as well as allyl alcohol plasma polymer layers were deposited. Moreover, the combination of plasma processing and layer-by-layer technique was also used for the deposition of fire-retardant layers made from poly(allylamine hydrochloride) and sodium polyphosphate.

Affirming the expectations it was possible to prepare very highly adherent thick coated laminate systems. In case of flammability tests the thick coatings had fulfilled the precondition of high adhesive bond strength to the polymer substrates and have withdrawn strongly any self-peeling at high temperatures. The successive change of material properties (gradient) from polymer substrate to inorganic or N-rich organic coatings by preparation of multi-layer system was the key for best adhesion.

The flammability tests have confirmed the efficiency of such coatings generally. Addition of polyphosphates has optimized the fire-retardant action of coatings. It should be mentioned that all fire-retardant coatings cannot produce complete non-combustibility because of limited thickness of coatings but they can at least retard the flammability significantly.

Advantage of such coatings is the safe and cheap use of technical polymers as construction material and the safe protection of surface at pronounced points. The fire-retardant material is localized at the place of flame attack. A homogeneous addition of considerable amounts of fire retardant material is not necessary. The substrate materials retain its original properties.

It could be also demonstrated that these coatings can be also prepared easily, rapidly and with good properties by more simple methods working at atmospheric pressure.

In future, these techniques should be further developed and tested.

Zusammenfassung

Erstes Ziel dieser Arbeit war es, dichte Brandschutz-Beschichtungen auf Polyolefin-Bauteile aufzubringen. Diese Schichten sollten dem direkten Kontakt mit einer Flamme für eine Weile standhalten können. Erste Tests hatten gezeigt, dass Schichtdicken von deutlich mehr als 10 µm notwendig sind, um die Entflammbarkeit des Materials meßbar zu verringern. Aus diesem Grund wurden hier 40 µm dicke Schichten hergestellt. Voraussetzung für die flammschützende Wirkung dieser dicken Schichten ist eine gute Haftung auf den Polyolefinsubstraten. Diese besitzen jedoch keine polaren Gruppen an ihrer Oberfläche und haben deshalb sehr schlechte Hafteigenschaften. Deshalb war eine Oberflächenvorbehandlung unumgänglich. Zwei Varianten wurden angewendet, die Sauerstoffplasmabehandlung, die verschiedenartige polare Gruppen an der Polyolefinoberfläche erzeugt, die als Wechselwirkungspunkte bei Beschichtungen dienen können, sowie eine nachfolgende dünne Beschichtung mit Plasmapolymeren, die funktionelle Gruppen besitzen, die sowohl zum plasma-oxidierten Polyolefinsubstrat als auch zur aufgebrachten dicken Flammschutzschicht starke Wechselwirkungen eingehen können oder gar chemische Bindungen ausbilden können. Durch die haftvermittelnde Plasmapolymerenschicht konnten auch die bei der Beflammung auftretenden inneren Spannungen in den Schichtsystemen wegen unterschiedlicher thermischer Ausdehnungskoeffizienten ausgeglichen werden. Die Beschichtung ist eine der einfachsten und effizientesten Methoden, um Brandschutz von Materialien zu erreichen. Durch die Beschichtung werden die Eigenschaften der Materialien, wie vor allem die mechanischen Eigenschaften nicht verändert. Es wird nur dort Flammschutz installiert, wo er gebraucht wird, was im Vergleich zur homogenen Zumischung von Flammschutzmitteln bei der Herstellung der Polyolefin-Bauteile auch sehr viel

Flammschutzadditive einspart. Dieses Beschichtungsverfahren eignet sich für eine Vielzahl von Materialien, auch für Metalle.

Wie bereits erwähnt, war es ein wichtiges Ziel, eine sehr hohe Haftfestigkeit solcher dicken Beschichtungen auf den Polymersubstraten zu erreichen. Chemische Bindungen zwischen den Beschichtungen und den Substraten sowie flexible Zwischenschichten mit haftvermittelnden und spannungsausgleichenden Eigenschaften sollten bei der Beflammung ausreichenden Schutz gegen Abplatzen der Schichten erbringen. Verschiedene Techniken wurden verwendet, um solche dicken Schichten herzustellen und haftfest mit den Polyolefinsubstraten zu verbinden. Die Beschichtungen sollten diffusionsdicht sein, bei der Oxidation die Flamme eine dichte Oxidschicht ergeben, ggf. radikalquenchende Eigenschaften haben oder die Flamme ersticken, sie sollten wärmeisolierend sein und möglicherweise intumeszierende Eigenschaften haben.

Kombinationen von zwei Abscheidetechniken wurden gewählt, physikalisch-chemische und mechanische. Die Ausrüstung der Polyolefinoberfläche mit funktionellen Gruppen und die Plasmapolymerenschicht dienten im Wesentlichen der Verbesserung der Hafteigenschaften einer sehr dicken flammschützenden Schicht von etwa 40 µm Dicke. Die Abscheidung von 40 µm dicken Schichten wäre zu zeitaufwendig gewesen. Aus diesem Grunde wurde die Flammschutzschicht durch simples Eintauchen in die Beschichtungslösung erzeugt oder durch Besprühen.

Die Haftung dieser Kombinationsschichten wurde mit Hilfe von Schälfestigkeitsmessungen gemessen und die Entflammbarkeit mit entsprechenden Testverfahren.

Als flammhemmende Beschichtungsmaterialien wurden beispielsweise anorganische Siloxan-Strukturen (SiO_2) ausgewählt wurden, die bekanntermaßen nicht entflammbar sind und die eine Barriere für den Zutritt von Sauerstoff darstellen. Ein anderes Beispiel

betraf Ammoniak- und Stickstoff-freisetzende Beschichtungsmaterialien aus Melamin- oder Harnstoffharzen. Eine dritte Variante bestand in der Beschichtung mit Ammoniumpolyphosphaten. Es war zu erwarten, dass die Kombination von diesen anorganischen und organischen Schichten sich am besten für flammhemmende Beschichtungen eignet, sofern entsprechende Haftfestigkeiten erreicht werden können.

Die Schichten wurden durch folgende analytische Methoden charakterisiert, wie z. B. Röntgen-Photoelektronen-Spektroskopie (XPS), Fourier Transform Infrarot Spektroskopie (FTIR) im Abgeschwächten Total-Reflektionsmodus (ATR), Thermogravimetrische Analyse (TGA) sowie mit dem 90° Schälfestigskeitstest und einem an die DIN 4102-1 angelehnten Brandversuch.

Die unpolaren Polyolefinoberflächen wurden im Niederdruckplasma behandelt und hydrophil gemacht. Sauerstoff- und Ammoniakplasma wurden getestet, wobei das Sauerstoffplasma die Standard-Vorbehandlungsmethode darstellte. Wenige Sekunden Behandlung im Sauerstoff Niederdruck–Plasma reichten für die Erzielung maximaler Haftfestigkeiten aus. Verschiedene Arten von O-enthaltenden funktionellen Gruppen wurden dabei an der Polyolefin-Oberfläche erzeugt. Diese Gruppen konnten dann Wechselwirkungen oder kovalente Bindungen mit den danach aufgebrachten Plasmapolymerschichten eingehen. Diese Plasmapolymerschichten besaßen ihrerseits wiederum funktionelle Gruppen (SiOH, OH, NH_2), die mit funktionellen Gruppen der Flammschutzschicht wechselwirken oder chemisch reagieren konnten.

So wurde zur besseren Haftung von dicken Silikat Schichten Hexamethyldisiloxan (HMDSO) in Gegenwart von Sauerstoff als SiO_2-artige Schicht abgeschieden. Alternativ konnten auch derartige Schichten durch Flammpyrolyse von Silanen abgeschieden werden (Silicoater-Verfahren) oder durch Elektro Spray Ionisation (ESI) von wasserlöslichen Na-Silikaten (Wasserglas). Diese atmosphärischen Prozesse sollten als

Beispiele für eine technische Umsetzung erprobt werden. Auf die HMDSO-erzeugte SiO_2-Schicht wurde durch Eintauchen in Na-Silikat (Wasserglas) oder durch Besprühen die Flammschutzschicht erzeugt.

Zur Auftragung gut haftender dicker Beschichtungen mit NH_3- und N_2-Freisetzung im Brandfall gelangten vorzugsweise Melamin-Präpolymere. Die zwischen Polyolefinsubstrat und Melaminharz liegende Haftvermittlerschicht wurde durch Plasmapolymerisation von Allylamin oder Allylalkohol hergestellt. Diese Zwischenschichten waren auch für die nachfolgende Beschichtung mit Polyphosphat geeignet.

Für jedes Schichtsystem gelang es, eine ausreichende Haftung und wirksame Flammhemmung zur erreichen. Es wurde anstelle einer Grenzfläche Substrat-Beschichtung ein sukzessiver Materialübergang (Gradient) erzeugt, der Voraussetzung für maximale Haftung war.

Die flammhemmenden Eigenschaften aller Beschichtungen konnten nachgewiesen werden. Allerdings sollten zur Maximierung des flammhemmenden Effekts Schichtdicken größer als 50 µm angestrebt werden. Vorteil dieser Beschichtungstechnik ist, daß eine sichere und günstige Flammschützung von bereits hergestellten technischen Polymeren-Bauteilen nachträglich erreicht werden kann. Die Nutzung von atmosphärischen Plasmaprozessen, wie Coronaentladung oder Plasmaspritzen sollten das Verfahren vereinfachen und verbilligen.

Contents

Chapter 1: Introduction

Chapter 2: Experimental:

List of abbreviations

μm = micrometer

AFM = atomic force microscopy

APCI = Atmospheric-pressure chemical ionization

ASTM = American Society for Testing and Materials

BL = bilayer

C = Cured

CAE = constant analyzer energy

CAM = contact angle measurements

CAP = competitive ablation polymerization

cmPMF = cured methylated poly(melamine-co-formaldehyde)

cps = counts per second

CS = Cold Spray

cw = constant wave

DBD = Dielectric barrier discharge

DC = duty cycle

D-gun = detonation guns

ECR = electron cyclotron resonance

EDX = energy dispersive X-ray analysis

EG = ethylene glycol

ESCA = electron spectroscopy for chemical analysis

ESI = Electrospray ionization deposition

eV = electron volt (1 eV = 1.6022×10^{-19}J)

FR = fire retardants

FTIR- ATR= Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance

HMDSO = hexamethyldisiloxane

HREELS= High-resolution Electron Energy Loss

HRR = heat release rate

HVAF = high velocity air-fuel flames

HVOF = high velocity oxy-fuel flames

ICP-OES = Inductively Coupled Plasma Optical Emission Spectroscopy

LbL = Layer-by-layer

LOI = limiting oxygen index

MAS = magic-angle spinning

MEMS = micro electro-mechanical systems

mPMF = poly(melamine-co-formaldehyde)methylated

NEXAFS = Near-Edge X-ray Absorption Fine Structure

NFPA = National Fire Protection Association standards

NMR = Nuclear Magnetic Resonance

O_2 = oxygen

Pa = Pascal (1 Pa = 1 N/m^2)

PAH = poly(allylamine hydrochloride)

PE = poly (ethylene)

PECVD = plasma enhanced chemical vapor deposition

PEM = polyelectrolyte multilayer films

PER = pentaerythritol

PFBA = Pentafluorobenzaldehyde

pp = plasma-polymerized

ppAAl = plasma polymerized (allyl alcohol)

ppAAm = plasma polymerized (allylamine)

PS = poly(styrene)

PSP = sodium poly(phosphate)

PTA = plasma transferred arcs

RBS = Rutherford Backscattering

rf = radio frequency

SAM = Self-Assembling Monolayers

SEM = scanning electron microscope

SSIMS = Static Secondary Ion Mass Spectrometry

T = temperature

TEM = transmission electron microscopy

TFAA = trifluoroacetic anhydride

TGA = thermal gravimetric analyses

ToF-SIMS = time of flight secondary ion mass spectrometry

TOF = time of combustion or extinction

TSR = total smoke released

TTI = time to ignition

UL = Underwriters Laboratories

UV/VIS = Ultra violet/Visible

VP-SEM = variable pressure scanning electron microscopy

W = Watt (W = 1 J/s)

Wg = Water-glass

XPS = X-ray photoelectron spectroscopy

XRF = X-ray Fluorescence

List of figures

List of tables

1. Background and basics

1.1 Aim of work

The intention of this work was the fire protection of poly(styrene) and poly(ethylene) building materials by deposition and covering with thick fire retardant multi-layer systems using different coating techniques such as plasma processing, electro spraying, pyrolytic spraying (Silicoater process), dip coating (casting), and layer-by-layer deposition.

It is well known that coatings with thickness of several tenths of micrometers show only weak adhesion to polyolefins because of absence of functional groups on polyolefin surface and the different thermal expansion coefficients of inorganic or crosslinked resins and polyolefin substrates. Therefore, sufficient high adhesion of such thick coatings to the polymer substrates has to be produced. The different chemical nature of coating and polyolefin substrate hinders wetting and formation of physical and chemical interactions and therefore adhesion was most often absent. However, the coatings have to with draw high temperatures at exposure to flame without self-peeling or crack formation elsewise flames and oxygen have access to the subjacent easy flammable polymer substrates.

Different techniques were used to prepare such thick layers with strong adhesion to the polymer substrates. To solve the lack of adhesion of the fire-retardant layers the non-polar polyolefin surfaces were equipped with polar functional groups able to undergo both physical as well as chemical interactions to the coating. Polyolefin surfaces can be made wettable and polar by surface oxidation. Then, different O-containing groups were formed on their surface, such as hydroxyl or carboxylic groups. To solve the problem of internal stress during flame exposure caused by the different thermal expansion

coefficients a flexible interlayer was deposited as adhesion promoter and mechanical relaxant between the polyolefin substrate and the deposited fire-retardant layer. The interlayer should be a flexible polymer able to produce strong interactions to both the polyolefin substrate and the fire-retardant coating with some flexibility. In case of inorganic fire-retardant coatings, such as siloxane-like coatings, an interlayer with organic and inorganic elements is preferred because these elements can be interacts to both sides of the composite interface. It was expected that such covering with thick coatings can improve the fire-retardancy of polyolefins.

To solve the problems of introduction of polar groups onto the polyolefin surface and to implement adhesion-improving flexible interlayer plasma processing is well suited, comfortable, easy and fast. Plasma treatment can modify the polymer surface by oxidation and subsequently by plasma polymer deposition. To achieve fire-retardant coatings with a thickness of 50 μm or more the plasma polymerization process is too slow and therefore time-consuming. To produce thick layers it is more easy to use simple coating techniques such as dip-coating or spray-coating. It should be noticed that atmospheric-pressure plasma processing may replace the low-pressure plasma polymerization and also the dip or spray coating. To demonstrate the principle possibility the known low pressure plasma processing was used to oxidize the polyolefin surface at exposure to oxygen plasma or the deposit organic/inorganic layers by plasma polymerization. A layer thickness up to about 1 μm can be deposited by plasma polymer deposition within several minutes processing.

Fire-retardancy of films, foils, and sheets may be achieved by coating with thick flame-retardant inorganic or polymer layers of sufficient thickness. First principle of action of such an inorganic coating is to shield the flammable polymer from heat and direct action

of fire by a thermally insulating, inflammable and oxygen barrier layer. Moreover, intumescent organic or inorganic layers blow up additionally and develop sticking gases such as nitrogen, ammonia, or water as possible by decomposition of melamine resins or ammonium polyphosphates. Besides sticking of flames by such gases they have also radical scavenging property and inhibit the radical chain reactions in the flame as well as their formation or evaporation is an endothermal process that takes some energy from the process and thus the temperature in the flame zone decreases. Next principle is char formation using substances like pentaerythritol, which is also sticking flames by decomposition and formation of solid barrier. Ammonium polyphosphates release ammonia or phosphoric acid acting as radical scavengers in the gas phase and other inorganic layers can also form insulating layers thus also supporting the flame retardancy. In future, combination of polyphosphate inorganic layers, melamine prepolymer layers or inorganic SiO_2 layers are planned to improve the fire retardancy further.

In this work plasma-induce surface oxidation by exposure to the low-pressure oxygen plasma and subsequent low-pressure plasma polymerization of allyl alcohol (AAl), allylamine (AAm) and hexamethyldisiloxane (HMDSO) monomers were used to deposit adhesion-promoting plasma polymer interlayers. As precursors for the thick fire retardant layers ($\geq$ 50 µm) such as water glass Na-silicate), melamine-formaldehyde pre-polymers, cured melamine polymers, as well as polyphosphates. All the modified layers were studied and investigated by measuring FTIR-ATR, XPS, NMR, AFM, thermal analysis, peel strength and fire tests. Peeled laminate surfaces were also investigated to find the locus of peeling.

1.2 Plasma

The term ''**Plasma**'' is derived from an ancient Greek word '' $\pi\lambda\alpha\sigma\mu\alpha$'' which means ''Jelly'' by the Czech scientist, Johannes Purkinje (1787-1869) to denote the clear fluid which remains after removal of all the corpuscular material in blood.

The first use of the term ''Plasma'' was made by Irving Langmuir et al. in 1929 [1] to describe a collection of charged particles.

Faraday pointed out that matter can be classified in four states: solid, liquid, gas, and radiant (in his own words). The new form of matter was initiated by Heinrich Geiβler (1814-1879), who invented the sealed glass tube (now called Geiβler tube). Julius Plücker (1801-1868), published his results about the action of the magnet on the electric discharge in rarefied gases [2,3]. With his pupil Johann Wilhelm Hittorf (1824-1914) made many important discoveries in the spectroscopy of gases. Later on Sir William Crookes took again the term ''radiant matter'' coined by Faraday, to designate this new ''form'' of matter [4].

Later, the definition was extended to define a state of matter ('the fourth state of matter') in which a significant number of atom and/or molecules are electrically charged or ionized and has unique physical properties distinct from solids, liquids and gases [5]. So the term ''**Plasma**'' means a mixture of charged, excited and energy-rich neutral species, including some or all of the following: electrons, positive and negative ions, excited atoms and molecules, radicals, and photons. Plasma is electrically neutral, because any isolated charge would result in electric fields, thus hindering charge separation. It should be added that most of energy contained in the plasma is emitted as short-wavelength vacuum ultra-violet radiation (λ<200 nm). The general significance of

plasma is illustrated by the fact that the majority of matter in the visible universe, i.e. gaseous nebulae, interstellar gas, stars, including our sun [6, 7] is in the plasma state.

Plasmas are generated artificially by continuous supply of energy to gases or liquids (underwater plasma) and can be produced in laboratories. The energy transfer within the low-pressure plasma glow is more or less exclusively performed by inelastic collisions between the electrons and atoms, particles, and molecules. The elastic collisions among ions and atoms are insignificant because of their low acceleration in the electrical field in comparison to the acceleration of light electrons. On the other hand, heavy species can release their energy easily at the walls of the plasma reactor. Thus, ion and gas temperature is near room temperature, advantageous for polymer treating. Electrons cannot transfer their energies to heavy ions or atoms by elastic collisions. However, when their kinetic energy exceeds the ionization potential inelastic collisions occur and the ionization avalanche is started. An electron energy distribution is established, ranging to about 30 eV in maximum.

Low-pressure plasma are produced by direct current (dc), radio-frequency (rf), micro wave (mw) or electron cyclotron resonance (ECR) discharges, or may be by the combination of them [5].

Plasma processing has a wide range of applications. The best known field is situated in technical applications such as in the fabrication of semiconductor devices, solar cells, as well as in automotive, textile, food packaging, biomedical, polymers industries. In low-pressure plasmas the material consumption is very low; therefore, it is a more or less environmentally friendly process, producing an extremely low level of industrial by-products, especially when compared to more traditional wet chemical treatments.

1.3 Types of plasma

Plasmas are classified according to their temperature, degree of ionization, and (charge) density. At low pressure the collision rate between electrons and gas molecules is very low and therefore electrons can easily accumulate kinetic energy from the electrical field.

1.3.1 Cold plasma

As explained before when the energy of the gas molecules is approximately room temperature, then the plasma is called "cold or non-thermal plasma". The degree of ionization is below 10^{-4}. [8]. Cold plasmas exist in the Earth's ionosphere, the flow discharge in a fluorescent tube [9].

1.3.2 Hot plasma

In a high pressure gas discharge the collision between electrons and gas molecules occurs frequently. This causes thermal equilibrium between the electrons and ions (gas) molecules, and in this case it is defined as "hot or thermal plasma''. The temperature-ionization degree relation is described by the Eggert-Saha equation[10]. Outside sun such plasmas can be produced by atmospheric aurora borealis, lightning, arc welding, sparks and flames [11].

1.3.3 Ultra-cold plasma

Ultra-cold plasma could be formed by photo ionizing laser-cooled atoms, and normally carried out in vacuum [12] and at low temperatures (1K) [13].

1.4 Polymer surface treatment by plasma exposure

1.4.1 Surface functionalization

Introduction of functional groups into polymer surfaces based on the attachment of plasma species onto the surface; thus, exposure to oxygen plasma produces a broad variety of O-functional groups at polymer surfaces. The same is true if the polymer is exposed to the nitrogen plasma. Different N-containing groups were found. Exposure to the ammonia plasma did not produce the desired amino groups in significant concentration [14] as also fond for carbon dioxide plasma and the formation of carboxyl groups [15]. Only the plasma exposure of polyolefins to bromine or bromoform plasma exclusively formed the desired C-Br groups in high concentration without side reactions [16].

1.4.2 Plasma polymerization

Low-pressure plasma polymerization for coating and therefore for modifying polyolefin surfaces are of much significance. Two types of monomers or precursors are used in literature [17], chemically easily polymerizable vinyl and acrylic monomers, such as styrene or acrylic acid and non-polymerizable precursors of any composition, which are gases or are evaporable, such as HMDSO. These monomers may be chemically hardly polymerizable monomers, such HMDSO or allyl monomers as allyl alcohol and allylamine. By clever choice of the non-polymerizable precursors, by managing of deposition rate and plasma parameters, the film quality and therefore the surface properties can be controlled, thus the adhesion-promoting property for enhancing of both the adhesion strength of plasma polymerized layers on polymer substrates and their adhesion to coatings.

Thus, surface functionalization, polymer etching, or plasma polymer deposition can be carried out by low pressure plasma processes. In order to characterize the modified polymer surface or the deposited layers and coatings X-ray photoelectron spectroscopy (XPS), Rutherford Backscattering (RBS), High-resolution Electron Energy Loss (HREELS), Near-Edge X-ray Absorption Fine Structure (NEXAFS) or Static Secondary Ion Mass Spectrometry (SSIMS) as well as contact angle measurements (CAM)/surface energy measurements were used [18].

Polymer surface functionalization and plasma polymer deposition were used in various medical and biological applications, in microelectronics, anti-fouling, anti-corrosive, televisions, solar cells etc. Deposition of thin films includes sputter deposition [19], and plasma enhanced chemical vapor deposition PECVD [20].

1.4.3 Polymerization mechanism

Conventional polymerization of vinyl or acrylic monomers by chain-growth polymerization [21] did not occur under harsh plasma conditions, at low pressure with low monomer density in the gas phase and under high energy input conditions [22]. The reason why is the high energy level in the plasma to sustain the steady-state of plasma and the low pressure, which causes a too seldom attachment of monomer molecules onto the active radical sites. Thus, recombination or disproportionation occur frequently and thus produce very low kinetic chain lengths and therefore low molecular weight products. Classic chain growth polymerization produces more or less linear polymers of high molecular weight and high chemical regularity. The lower the percentage of chain growth products the plasma polymer the more irregularly structured is its structure.

The energy excess can be partially lowered by use of low wattage and use of pulsed plasmas. The very low monomer density under vacuum conditions can be minimized by use of pressure-pulsed plasmas or use of underwater plasmas[23].

The dominating process in low-pressure plasma polymerization is the precursor dissociation to atoms and fragments followed by their random (poly) recombination to a chemically irregular structured crosslinked "polymer" with included monomers, oligomers, trapped C and peroxy radicals. The fragmentation of precursors is caused by inelastic collisions with electrons in the gas phase. Poly-recombination of fragments and atoms or ions occurs in both the gas phase or in the adsorption layer.

The most influential parameters for the composition of such plasma polymer layer are the power (rf power) of the plasma per amount of monomer injected into the system. The Yasuda parameter (W/FM) describes the power density, where W is the wattage, F the flow rate, and M the molecular weight of the monomer. It was calculated that more than 1000 eV were used to transform one molecule of n-hexane to a plasma polymer [24]. Yasuda [25-27] proposed polymer forming process which can be related to the elimination of hydrogen and scission of C–C bonds forming mono-radicals M_i, and bi-radicals M_k, and thereafter, the addition of the radicals to monomer and the recombination between two radicals proceeds to make large molecules with or without radical, see Figure 1.1 [28].
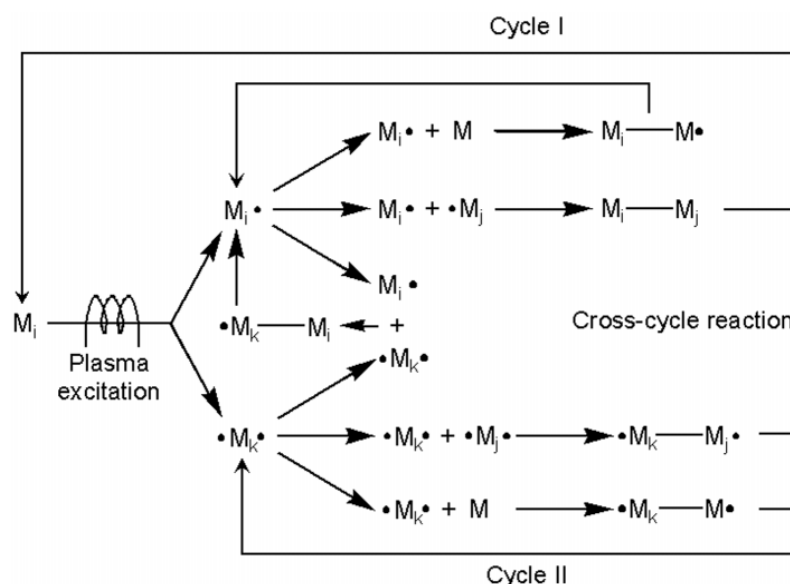
Figure 1.1 Schematic diagram of the bicyclic step-growth mechanism of plasma polymerization

Mono-radicals $M_i \cdot$ add monomer molecules and form a new radical $M_j - M \cdot$. A further mono-radical $M_i \cdot$ may recombine with $M_j \cdot$ to build a neutral or stable molecule $M_i - M_j \cdot$. A bi-radical can also attack the monomer to form a new bi-radical $\cdot M_k - M \cdot$, or recombine with another bi-radical to form a new bi-radical $\cdot M_k - M_j - M_k - M_j \cdot$. This cycle I is the repeated activation of the reaction products from mono-functional activated species, cycle II describes the recombination of the mono and bi-radical to form larger radicals. However, this reaction process suggests that a more or less intact and regular linear or branched polymer is formed. Yasuda has also assumed the "Atomic Polymerization" of completely fragmented precursor molecules corresponding to the here preferred "Fragmentation-Polyrecombination Polymerization".

Besides surface functionalization and plasma polymer coating some etching can happen simultaneously as a result of the bombardment of both the substrate and the growing coating by ions. The short wavelength plasma as radiation (vacuum ultra violet

radiation-VUV) can modify the polymer near surface layers by $\sigma \rightarrow \sigma^*$ processes resulting

in polyene formation and crosslinking. These different processes have been described by

Yasuda as competitive ablation polymerization (CAP) [26, 29], as seen Figure 1.2 [26].
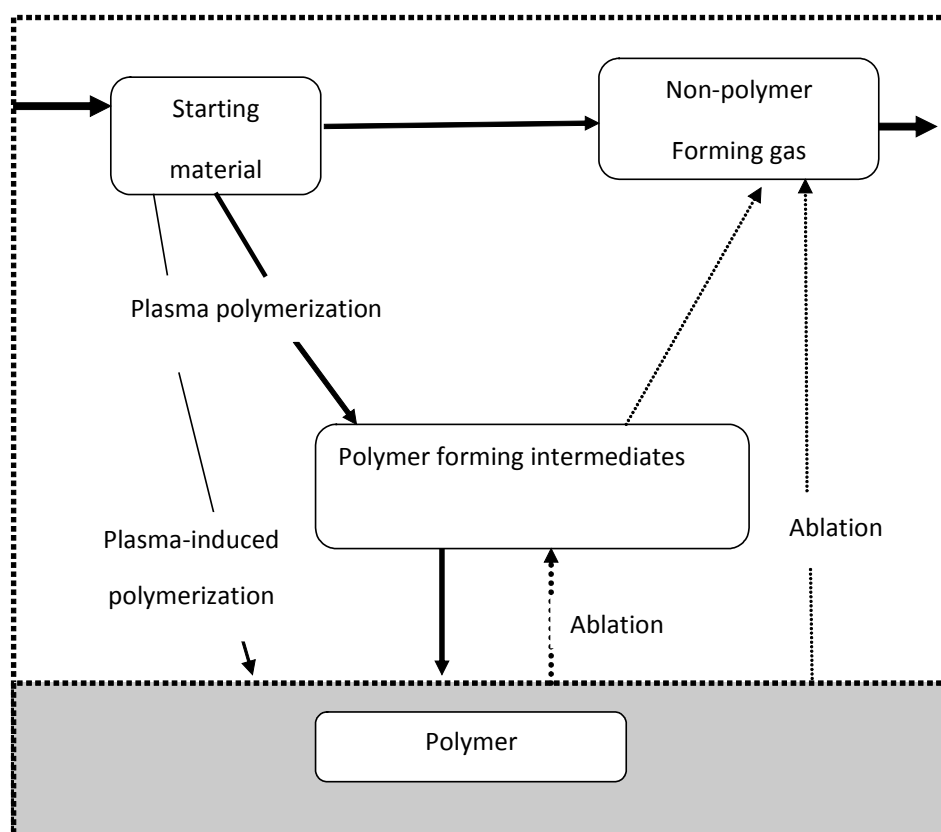
Figure 1.2 Schematic diagram of the mechanism of the plasma polymerization process

In classic polymerization monomers are linked together by chain-growths reactions

without alteration of the monomer structure in the repeating units. Other variants are

polyaddition as known from polyurethanes formation, ring-opening polymerization

known from polyamides and caprolactame, polycondensation two monomers with

release of small molecules as known from phenol-formaldehyde condensates [30],

Therefore, the chemical structure of the polymer is more or less fully determined by that

of the monomer. In contrast to that plasma polymerization of the same monomer forms a polymer, which has no or marginal accordance to the classic polymer and, therefore, to the monomer. This is attributed to the total monomer fragmentation, the random recombination of fragments, and the post-plasma reaction of trapped radicals in the plasma polymer layer with oxygen from air and start of auto-oxidation reactions.

1.4.4 Plasma polymerization of self-assembled mono-layers

Monomolecular Langmuir-Blodgett (LB) layers offer a unique opportunity to prepare model surfaces with known thickness and molecular architecture [31-35]. It is a useful method to modify systematically the chemical properties of solid surfaces in order to control their functions in such processes as wetting, adhesion, and friction [36]. This technique is used to deposit highly oriented, ultrathin films [37, 38]. A well-defined monolayer is transferred onto the substrate, and highly ordered multilayers can be deposited. Self-Assembling Monolayers (SAM) were used as adhesion promoter and as corrosion-inhibiting layer [39].

1.4.5 Plasma-induced grafting of monomers

A method used to modify the surface chemical characteristics of natural and synthetic polymers through the activation of the polymer by exposure to the plasma, producing radical-sites, which are able to react with the introduced vinyl or acrylic monomer, thus forming regularly structured graft chains on polymer surfaces [40]. The second variant is plasma treatment of polymer and its exposure to air, thus transforming C-radical sites into peroxide radical sites, which can decomposed thermally or irradiative and then

react with vinyl or acrylic monomers [41]. The third here used graft variant is the plasma-induced introduction of functional groups onto the polymer surface followed by their consumption with molecules, oligomers or polymer chains [42]. Depending on the choice of precursors, it is possible to insert specific functional group [43, 44]. The surface treatments occur at temperature close to room temperature. Therefore, the physical properties of the polymer cannot change.

1.5 Surface modification

Polymers have special and definite bulk mechanical properties which meet specific applications such as coating, optical and biomedical applications. Nevertheless surface properties are of the same technical importance. However, polymers do not possess the required surface properties. They belong to the "low-surface energy materials" in contrast to "high-surface energy materials", such as metals and inorganics. Thus, intensive researches have been made to develop surface treatment methods to improve the surface properties, in particular to increase the surface energy [45]. The reason of increasing of surface energy by introduction of polar groups is to adjust the surface energies of polymer to that of the inorganic coating. In case of similar surface energies, it was found that the adhesion was maximal [46, 47].

The principal applications of plasma treatments concern the processes that induce a limited and selected transformation of the outermost surface layer (nanometer scale). Many fundamental processes take place during surface treatment of a material: the surface undergoes bombardment by fast electrons, ions, and free radicals, combined with the continued electromagnetic radiation emission in the UV-Vis spectrum

enhancing chemical-physical reactions in order to obtain the desired functional and aspect properties.

Many properties and functionalities can be obtained by plasma treatment depending on the application. The plasma can be used to change the surface wettability which can be changed from hydrophilic to hydrophobic and vice versa, to enhance the barrier characteristics, adhesion, dye-ability, printability, or the oleophobicity [48-50].

Surface modification is mainly used to [5]:

- produce special functional groups at the surface - increase surface energy, increase hydrophobicity or hydrophilicity [51, 52]

- improve chemical inertness

- introduce surface cross-linking [53]

- remove weak boundary layers or contaminants [54, 55]

- modify surface morphology - increase or decrease surface crystallinity and roughness [56]

- increase surface electrical conductivity [57]

- increase surface lubricity and Improve dyeability [58].

- application of antibacterial [59] and fire retardant [60]

1.6 Surface treatments of polymers

All solids communicate or interact with another solid or medium via surface. Therefore, the composition and design of surface is of great importance. Different techniques were used for surface modification such as simple chemical, thermal, or complex physical and radiation processes.

14

1.6.1 Chemical modification

Chemical modification includes reactions such as crosslinking, grafting, degradation, oxidation, isomerization, and cyclization. Its chief use is to produce polymers with desirable physical and chemical properties that are not accessible by standard polymerization techniques [61]. Also, use of oxidizing and etching acids such as chromo-sulfuric acid, $KMnO_4$, nitric acid, sodium hydroxide etc. was made to introduce O-functional groups into the surface of polymers [11].

1.6.2 Flame treatment

High flame temperature is applied up to 2000°C and this leads to increasing in the oxygen content at the surface by formation of a broad variety of different oxygen containing groups. The flame treatment basically used to improve adhesion by this formation of polar O-containing groups, and it enhances wettability, printability and adhesion improvement of coatings, metal deposits, ceramics, in polymer industry etc.. The disadvantage of this method is the heterogeneity of the surface modification, the susceptibility to damage, the delicate controlling. Moreover, this method is limited and cannot be applied to a range of materials and complicated 3D shapes [62].

1.6.3 Dielectric barrier discharge/corona discharge

Dielectric barrier discharge (DBD) is a type of plasma operating at atmospheric pressure. DBD is initiated if one or two dielectric(s) (ceramic) are positioned in the gap between the electrodes. DBD is widely used in surface modification of polymers for adhesion and printing [63]. A corona discharge is produced when air is ionized by high

electric field strength. It is seldom used because of its strong inhomogeneity. Nowadays, the corona discharge is combined with electrospray ionization deposition (ESI) of polymers [64]. The advantage of this combined process (Atmospheric-pressure chemical ionization – APCI) is the spraying of a polymer solution, the formation of ionized polymer molecules with only low or moderate degradation. Thus, the deposited polymer layer is predominantly of regular structure but is activated by the plasma for proper adhesion to the substrate.

Both DBD/corona and flame treatments can be used in the continuous operation mode but it is difficult to control the uniformity and the chemical nature of the surface. This is because that both treatments are carried out in air and variations in ambient conditions such as temperature and humidity or contaminations occurred.

UV irradiation in presence of initiators is also used (photoactivation, photografting, photopolymerization) under atmospheric-pressure conditions [65] or use of excimer lamps under vacuum conditions [66].

1.6.4 Low pressure plasma treatment

The most common applications of low pressure plasma treatments are surface etching [67], increase the wettability and bondability [68] as well as bio-compatibility [69].

In this thesis low-pressure plasma treatment is applied for surface modification of polyolefins with a non-polymerizable gas such as oxygen [70] or by plasma polymer deposition of thin films using liquid precursors [71-74].

Advantages of low-plasma processes could be summarized in the following points:

- plasma modification is limited to the top surface layer and does not affect the bulk properties

- exhibits good and uniform surface coverage

- due to the variation of the used gas or precursor, a wide range of functional groups can be introduced at the surface also; the produced functional groups or the deposited layers at the surface are independent on the structure or chemical nature of the substrate.

- low operation temperature

- lower chances of cracking of the deposited layers

- good dielectric properties of the deposited layer

- one-step process, no solvent required (dry process)

- high layer quality, wide variety of applications

Disadvantages of using plasma polymer formation (Plasma-Enhanced Chemical Vapour Deposition-PECVD)

- chemically irregular layer composition and structure

- high post-plasma reactivity (ageing)

- toxic byproducts, however, in low amounts

- relatively high equipment costs caused by the needed vacuum system

- low material throughput, often low selectivity, low yield in desired product

- plasma treatment is a complex process and a good control over the chemical composition of the modified surface could not be achieved. Different parameters

such as reactor geometry, input power, and gas flow may also affect the chemical

composition of the modified surfaces.

1.7 Fire retardants

Despite of the numerous advantages of synthetic polymers, which are used in a variety of materials, including textiles, electronics, building materials, plastics and foams, there is an obvious disadvantage in question of their distinct flammability.

Fire hazard includes ignitability, ease of extinction [75], flammability of the volatile products, heat release during burning, flame spreading, smoke obscuration, and smoke toxicity [76].

Polymer materials and polymer composites for light-weight transportation, aerospace and automotives etc. have often a high fire risk because most polymer construction and insulation materials are flammable. A distinction according to DIN 4102-1 is made between non-flammable materials of class **A** and flammable materials of class **B**. PS foam are usually classified as **B1** as a flame-resistant building material and during building fires the high temperatures lead the insulating materials melt and drip. Because of this fact the fire spread easily. Due to the enormous fire load of foamed PS it comes to devastating fires with catastrophic consequences. An additional protection layer on the surface or general processing the polymer bulk with additional fire retardants can prevent the spread of the fire or at least retard it. Coating can be applied after manufacturing the material, addition of fire retardants has to be made before production of the construction element.

1.7.1 Classification of fire retardants

Flame retardants are classified according to their chemical nature into different classes: Brominated additives [77, 78], phosphorus [79, 80] and nitrogen containing additives [81, 82], chlorinated [83], and inorganic [79, 84] fire retardants.

Depending on its chemical nature the interaction of the fire retardants with the fire cycle takes place at different stages.

The main role of flame retardants is to stop the fire or significantly slow a fire down through the interaction with the fire cycle in the gas phase to stop the chemical chain reaction that leads to flame formation. Figure 1.3 represents the interaction of fire retardants with the fire cycle [85].
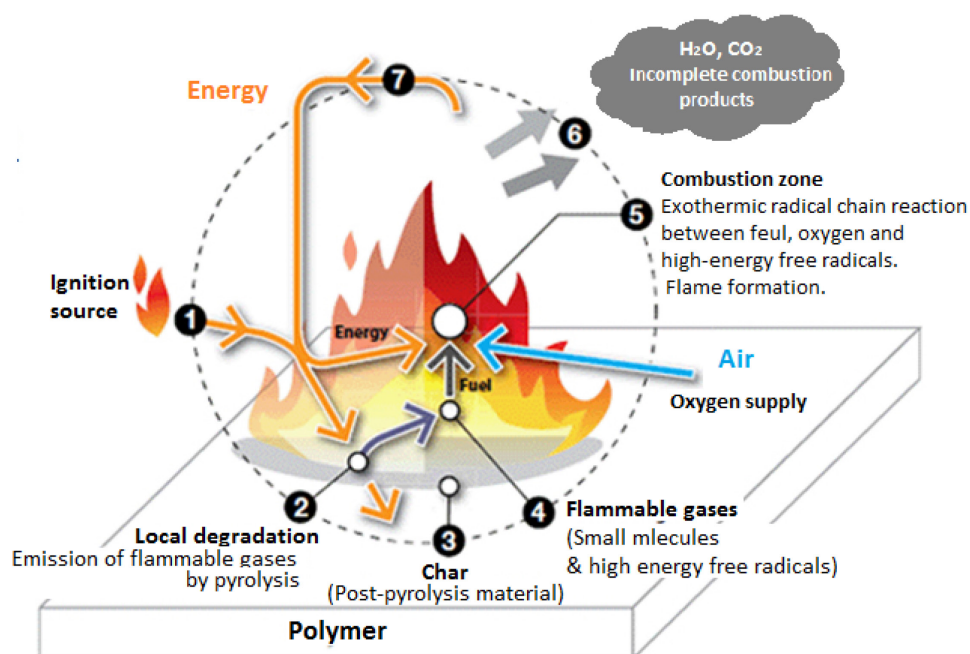
Figure 1.3 Interaction of fire retardants with the fire cycle in order to stop or delay it

The use of flame retardants to reduce combustibility, smoke, or toxic fume production of polymers is a pivotal part of the development and application of new flame-retardants. Amongst the major markets where flame retardants are indispensable required, construction, electrical and electronics components and transportation are of greatest importance.

1.7.2 Mechanism of polymer flame retardancy

The definition of polymer flame retardants has been developed since the Second World War [86] these developments includes chlorinated paraffin, chlorine containing unsaturated filler-like retardants; oxygen index method of evaluating relative polymer flammability and intumescent flame retardant systems.

All flame retardants act either in the vapor phase or in the condensed phase through a chemical and/or physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition, or flame spreading [87-89].

1.7.2.1 Fillers

Fillers are mainly used to dilute the polymer, to adsorb and to reduce the concentration of decomposition gases, to release non-flammable gases, or decompose endothermically to cool the pyrolysis zone at the combustion surface. Examples are antimony –III oxide, aluminum hydroxide etc.

1.7.2.2 Halogen, phosphorus

They act in the vapor phase and interrupt the exothermic processes and to suppress combustion. Halides, such as bromine, and also phosphoric acid are known as radical scavengers in the flame area. Red phosphorous forms an intumescent layer.

1.7.2.3 Ammonium polyphosphates

Ammonium polyphosphates act also in the condensed phase promoting char formation on the surface, which acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air. Release of ammonia interrupts the chain process of rapid oxidation.

1.7.2.4 Intumescent fire retardants

As mentioned before another major category of flame retarding produce intumescent layers during flaming, in which materials swell when exposed to fire or heat to form a porous foamed mass, usually carbonaceous, which in turn acts as a barrier to heat, air and pyrolysis product [90, 91]. In an intumescent materials formulation, there is usually a char forming agent and possibly a catalyst for char formation as well as foaming agent. Sometimes, it is desirable to use the synergistic approach through combination of these mechanisms involving more than one compound. An excellent example of this is the use of melamine phosphates, which, to some extent, perform three roles simultaneously as foaming agent, catalyst, and char former.

Although halogen atoms (e.g. bromine or chlorine) form some of the most widely applied flame retardant materials, in particular for polymers used in organic matrices of composites or in electronic equipment, they have clear disadvantages such as the potential to corrode metal components and, more pressingly, the toxicity of the hydrogen halide and dioxins formed during combustion.

Furthermore, it has been reported that epoxy resins containing high (ca. 30%, w/w) chlorine content may have lower thermal stability particularly when cured with amine curing agents [92].

Recently a new category of fire retardant 'non-halogen' fire retardants was developed to avoid the generation of toxic and corrosive gases during thermal degradation [93, 94]. Phosphates, Phosphine oxide [95] and flame retardant epoxy resins also used because of their wide applications in adhesives, coatings, and advanced composites in aerospace and electronics industries [96].

1.7.3 Action of fire retardants

Flame retardants (FR) are intended to stop or inhibit the combustion process. Depending on their nature FR interferes during the combustion process via different actions as described in details in the following [97, 98]:

1.7.3.1 Physical action

An endothermic decomposition of fire retardants could be achieved by several ways in order to retard the combustion process among these methods:

- **Cooling:** some flame retardants such as magnesium hydroxide $Mg(OH)_2$ and hydrated alumina $Al_2O_3.3H_2O$; upon combustion decomposed endothermically with the evolution of inert diluent gases (H_2O, CO_2) which cools down the combustion process.

- **Formation of protective layer:** some fire retardant additives can form a shield in the form of a solid protective layer with low thermal conductivity which can reduce the combustion rate and decreases the fuel flow.

- **Dilution:** Addition of inert additives and fillers evolve inert gases during combustion and therefore retard the ignition process. Emitted gases and vapors can also cool down the process. Water and ammonia quench radicals.

1.7.3.2 Chemical action

Chemical interaction occurs either in the gaseous or the condensed phase. Following processes have to be considered.

1.7.3.2.1 Gas phase reaction

During the combustion process the free radicals from the FR additives (Cl· and Br·) act as scavengers for the free radicals form the combustion process through the reaction with active species (H· and OH·) forming inert or less reactive molecules Figure 1.4. By such recombination processes the chain reaction of auto-oxidation is limited and a remarkable retardation in the exothermic behavior of the combustion process could be achieved.

$$H\cdot + O_2 \longrightarrow OH\cdot + O$$
$$O + H_2 \longrightarrow OH\cdot + H\cdot$$
$$RX \longrightarrow R\cdot + X\cdot$$
$$X\cdot + RH \longrightarrow R\cdot + HX$$
$$HX + H\cdot \longrightarrow H_2 + X\cdot$$
$$HX + OH\cdot \longrightarrow H_2O + X\cdot$$
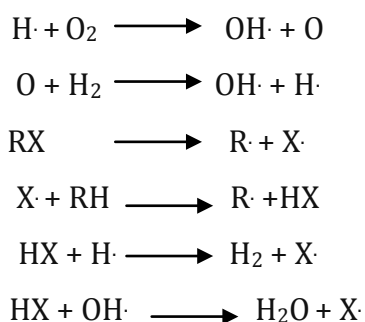
Figure 1.4 Gas phase reaction of free radicals during combustion process

1.7.3.2.2 Condensed phase reactions

Two types of reaction are possible, first FR can accelerate the mechanical rupture and chemical degradation of the polymer. In this case the polymer drips and moves away from the flame zone. Alternatively, the FR forms a carbonized (charring), ceramic, glass-like layer on the polymer surface by chemical transformation of the degraded polymer chains. The formed char layer acts as a physical insulating layer between the gas phase and the condensed phase.

1.7.4 Approaches of fire retardants

Two approaches to achieve flame retardancy in polymers were known, the 'additive' and the ''reactive'' type. The additive type of fire retardants are widely used and generally incorporated in the polymers by physical means during the transformation process and react with the polymer only at higher temperature, at the start of a fire; they includes mineral fillers, hybrids or organic compounds and macro molecules.

On the other side, reactive flame retardants:, are usually introduced into the polymer during synthesis (as monomers or precursor polymers) or in a post-reaction process (e.g. via chemical grafting). Such flame retardants are integrated in the polymer chains[97]. The application of "reactive" flame retardants involves either the design of new, intrinsically flame retarding polymers or modification of existing polymers through copolymerization with a flame retarding unit either in the chain or as a pendent group. The modification approach is most favored because covalently incorporating of the flame-retarding unit in the polymer backbone imparts the flame retardancy permanently and the original physical and mechanical properties are maintained. The

majority of the research efforts are focused on this approach and results show that the incorporation of even a few weight percent of the unit into the polymer chains can lead to remarkable improvements in the overall flame retardancy of the polymer.

1.7.5 Flammability tests

Flammability test methods includes ignitability tests (or UL94), flame spread tests, limiting oxygen index (LOI), heat release tests (Cone calorimeter), Ignitability Apparatus according EN ISO 11925-2 and DIN 4102-1) (burning-box) and smoke tests [95, 99].

LOI measures the minimum oxygen concentration (in a flowing mixture of oxygen and nitrogen gas) required to support candle-like downward flame combustion.

The LOI is expressed as: LOI = 100 $[O_2]/[O_2] + [N_2]$

As air contains 21% oxygen, materials with an LOI below 21 are classified as ''combustible'' whereas those with an LOI above 21 are classified as ''self-extinguishing'', because their combustion cannot be sustained at ambient temperature without an external energy contribution; the higher the LOI the better the flame retardant property [97]. LOI serves as a measure of the ease of extinction of the materials. This method is suitable as a semi-qualitative indicator of the effectiveness of flame retardants during research and development stage, because the equipment is inexpensive and requirement for sample size is small. Real scale fire performance of a material cannot be accessed solely based on LOI value because of the low heat input and the simulated high oxygen concentration [95, 100].

The other useful indicator is the char yield estimated from thermal gravimetric analysis (TGA) under either air or nitrogen atmosphere. A Thick char layer is better thermal

insulator. It undergoes slow oxidative degradation and prevents heat to reach the remaining polymer. Lewin pointed out that the chars obtained in the intumescent systems are different from the chars from TGA [101, 102]. The former are prepared at lower temperatures and are not fully pyrolysed or oxidized. Their rates of formation are high and involve thermo-oxidation though they serve the same purpose, namely acting as barriers to the passage of molten polymer and decomposition gases.

Some laboratories adopt UL (Underwriters Laboratories) tests, e.g. UL94 [97]. These methods are adapted from American Society for Testing and Materials (ASTM) or National Fire Protection Association (NFPA) standards.

During the test, five sample bars of 130 mm in length, 13 mm in width, and 1.6 mm in thickness suspended vertically over surgical cotton were ignited by a Bunsen burner. A flame was applied twice to the lower end of the bar for 10 s. The ratings of V-0, V-1 were achieved if burning stops within 10 s, 30 s after two applications of 10 s each of a flame to a test bar, and no flaming drips allowed. The class of V-2 was achieved if burning stops within 30 s after ignited, but the surgical cotton below the specimen was ignited with the flaming drippings[100].

Cone calorimetry is one of the most effective medium-sized polymer fire behavior tests. The principle of cone calorimeter experiments is based on the measurement of the decreasing oxygen concentration in the combustion gases of a sample subjected to a given heat flux (in general from 10 to 100 kW/m^2).

A sample (100 x 100 x 4mm^3) is placed on a load cell in order to evaluate the evolution of mass loss during the experiment. A conical radiant electrical heater uniformly irradiates the sample from above. The combustion is generated by an electric spark.

The combustion gases produced pass through the heating cone and are captured by means of an exhaust duct system with a centrifugal fan and a hood. The gas flow, oxygen, CO and CO_2 concentrations, and smoke density are measured in the exhaust duct. The measurements of the gas flow and oxygen concentration are used to calculate the quantity of heat released per unit of time and surface area: HRR (heat release rate) expressed in kW/m^2. In addition, the cone calorimeter test also enables characterization of the time to ignition (TTI), time of combustion or extinction (TOF), mass loss during combustion, quantities of CO and CO2, and total smoke released (TSR) [97]. Ignitability Apparatus according EN ISO 11925-2 and DIN 4102-1 were also known [103].

1.8. Adhesion of coating

Adhesion of coating or thin film is most important for example in microelectronics and magnetic recording industries, but also for emerging technologies such as data transmission through optical switches that are dependent on micro electro-mechanical systems (MEMS) [104, 105]. In general, coatings find use in a wide variety of industries, normally to serve one or more of the following purposes [106] :

> i. protect the surface from corrosion
>
> ii. control friction and wear
>
> iii. alter physical properties, such as reflectivity, color, conductivity, etc

Adhesion refers to the chemical or physical bonding between two adjacent materials, and is related to the force required to affect their complete separation. Cohesive forces are involved when the separation occurs within one of them rather than between the two at the interface [107].

The ASTM defines adhesion as the "condition in which two surfaces are held together by either valence forces or by mechanical anchoring or by both together". Adhesion depends on three factors [108-110]:

1) bonding across the interfacial region

2) type of interfacial region (including amount and distribution of intrinsic stresses)

 3) the fracture mechanism which results in failure

Failing of adhesion may be related more to the fracture mechanisms than to the type of bonding. In thin films, the intrinsic stress may result in adhesive (interface) failure even though chemical bonding may be high. Also, the interfacial morphology may lead to easy fracture though bonding is strong.

1.8.1 Methods of coating technology

Coating is a very important process involved in manufacture of coated products. Various technologies can be used to deposit or coat an appropriate surface for desired applications [111,112].

They are usually distinguished by coating thickness:

- Deposition of ultra-thin films (<100 nm)

- deposition of thin films (below 10 to 20 μm)

- deposition of thick films (mostly produced at atmospheric pressure; and have a thickness more than 30 μm, up to several millimeters and are used when the functional performance and life-time of component depend on the protective layer thickness).

The coating technology can be divided into two categories "wet" and" dry " coating methods, the crucial difference being the medium in which the deposited material is processed. The former group mainly involves electroplating, electroless plating, dip coating, and hot-dip galvanizing while the second includes vapor deposition, thermal spray techniques, brazing, or weld overlays.

Gravure coating, comma coating reverse roll coating, hot melt coating, metering rod / Myer bar coating, knife over roll coating ,Slot Orifice coating, immersion / dip coating and curtain coating were also known [113].

Dip coating consists of the withdrawal of a substrate from a fluid sol followed by gravitational draining and solvent evaporation, resulting in the deposition of a solid film. While thermal spraying comprises a group of coating processes in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten condition to

form a coating. The processes comprise: direct current (d.c.) arcs or radio frequency (r.f.) discharges-generated plasmas, plasma transferred arcs (PTA) [111], wire arcs, flames, high velocity oxy-fuel flames (HVOF), high velocity air-fuel flames (HVAF), detonation guns (D-gun). Another spray technology has emerged recently; it is called cold gas-dynamic spray technology, or Cold Spray (CS).

Thermal spray technique was also used mainly for metals and ceramics; because polymers are more sensitive to temperature than metals (e.g. their low softening temperature, their small thermal conductivity). This thermal sensitivity of polymers is a handicap.

Most processes are used at atmospheric pressure in air, except r.f. plasma spraying, necessarily operated in soft vacuum. Also, d.c. plasma spraying can be carried out in inert atmosphere or vacuum and Cold Spray is generally performed at atmospheric pressure but in a controlled atmosphere chamber to collect and recycle the spray gas (nitrogen or helium) because of the huge gas flow rates used (up to 5 $m^3.min^{-1}$).

1.8.2 Choice of adhesive

There are different factors affect the choice of adhesive [114]:

- materials to be joined (the substrates, also called adherends)
- quality of the substrate surfaces (e.g. roughness, any surface treatment, contaminants)
- forces the joint will be expected to withstand (magnitude, direction, duration etc)
- environment in which the joint will be operating (e.g. temperature, humidity)
- required durability of the joint (its required lifetime)
- application/process factors (e.g. cure time, volume used, dispensing systems)

1.8.3 Physics of adhesion

The interaction between polyolefin adherend and coating are determined by:

- primary forces: Covalent, metallic bonding

- secondary forces: Hydrogen bonding, dispersion, dipole and induced dipoles

1.8.4 The importance of adhesion of thin films

Adhesion of thin films is of a great importance in all fields; this can be summarized in the following [115]:

1) Adhesion is very important in thin film technology because the thin films, have usually <1μm thickness and in some applications in the order of <100 nm (ultra-thin), are so fragile that they must be supported by more substantial substrates and the degree to which the film can share the strength of the substrate depends upon the adhesion between the two components.

2) Adhesion is very important in determining the durability of thin film devices, for example, in microelectronic circuits.

3) Adhesion plays an important role in governing the kinetics of the growth and structure of the films (formed by vacuum deposition; for example), with the result that performance of thin films is dictated by adhesion forces. Film structure will be aggregated whenever the cohesional energy exceeds the energy of adhesion. This dependence of film integrity upon adhesion forces is not only important from the viewpoint of performance of such films but it also has a basic scientific import.

4) The durability and longevity of thin films are largely dependent upon their adhesion to the substrate since this determines the ease of removal.

5) It is highly desirable that films should be capable of being cleaned and polished, particularly where these are used for front surface reflectors and it means they should have good adhesion in addition to other factors like resistance to corrosion.

6) Wear is intimately related to the extent of adhesion of thin film to the substrates; if the adhesion is poor, the film will wear off quite rapidly.

7) Adhesion is a fundamental parameter in surface chemistry and physics because it depends directly on interatomic and intermolecular forces. Thin films should provide an ideal situation because it is in such systems that conditions of true interfacial contact can most nearly be attained. For example, a film deposited on a clean substrate under high vacuum conditions faithfully contours all surface irregularities and imperfections and almost perfect contact between the film and the substrate should be readily obtained.

8) Good adhesion of thin films, used as protective overcoats, is very vital for the environmental protection (e.g. protection from corrosion) of the substrates. If the adhesion is poor, the extent of deterioration of the substrates by environmental factors (humidity, corrosive gases, etc.) is greatly accelerated.

9) The metallization of polymeric materials reduces considerably the gas permeability of the polymeric, and this reduction is strongly influenced by the adhesion between the metal and the polymer.

10) Internal stress by different thermal expansion coefficients is of importance because these coefficients can be different by two orders of magnitude. Therefore, strong mechanical stress is introduced to the interface and the bonds along the interface at any thermal loading.

Coatings can fail in several modes including delamination, fracture, erosive wear, and general yield. The weakest part in coating systems is commonly the interface; thus, for

many material systems, interfacial delamination becomes the dominant failure mechanism [116], especially at long term exposure to challenging environments.

Delamination of a coating refers to the loss of adhesion of the coating from the substrate, and, if the coating stresses are compressive, it may result in buckling driven delamination.

Adhesion basically depends on the nature and strength of the binding forces between the two materials in contact to each other. These forces could be either primary valence type (Ionic, covalent, co-ordinate metallic), pseudo primary valance type (hydrogen bonding), or secondary valance type (van der Waals forces) [115].

Residual stresses, thermal mismatch stresses, environmental attack, and impact or contact stresses are some of the causes of delamination. Another important delamination – induced failure mechanism seen in metallic or ceramic coating systems, for example, thermal barrier coating systems, is due to the thermal gradient and thermal mechanical fatigue [117, 118].

Adhesion of a coating to its substrate is critical to its function. Mechanical, chemical, and metallurgical factors may contribute to such adhesion. Good adhesion performance of a coating depends on a variety of the attributes of the interface region, including its atomic bonding structure, its elastic moduli and state of stress, its thickness, purity and fracture toughness [119].

1) strong bonding across the interfacial region.

2) low stress gradients, either from intrinsic or applied stress.

Low stress gradients by flexible and stress-balancing polymer interlayers as preferably produced in this work using plasma polymer layers.

   3) absence of easy fracture modes.

4) no long term degradation modes.

5) Adhesion to plastics could be enhanced by:

- interdiffusion of resin molecules of the coating into the surface layer of substrate. It is observed if substrate and coating have similar composition an structure [120].

- in case of powder coatings, smaller average particle size of resins provides better adhesion than larger particles, combination of very small and large particle provides stronger adhesion.

- adhesion of thermoset coatings to plastics can be enhanced by incorporation of low concentrations of chlorinated polyolefin resin.

- resins with sub-micron or nano particles improve adhesion.

1.8.5 Types of adhesion

Adhesion can be broken down into the following categories [121]:

1. Interfacial adhesion: the adhesive forces are centered around a narrow well defined interface, with minimal atomic mixing, such as gold on silica [119].

2. Interdiffusion adhesion: the film and substrate diffuse into one another, over a wider interfacial region. For example, gold, evaporated onto freshly etched silicon (removing the surface oxide layer) at 50°C produces a diffuse interface extending many atomic layers. Polymers are often incompatible and interdiffusion does not occur [120].

3. Intermediate layer adhesion: in many cases the film and substrate are separated by one or more layers of material of different chemical composition, as in the case of films deposited on unetched silicon whose surface is covered with several nanometers of oxide.

4. Mechanical interlocking: this will occur to some degree wherever the substrate surface is not atomically flat and will account for some degree of random fluctuation of adhesive forces, chemical bonds, flexibilizing spacers, etc.

1.8.6 Adhesion testing

Adhesion tests divided to:

- quantitative tests: are quite adequate and are certainly easier and cheaper to perform, and it includes tensile, shear, peel, ultrasonics, centrifuge, and flyer plat.
- qualitative tests: are required for engineering applications they are often inadequate and must be replaced with tests that provide quantitative date. Examples are scotch tape, bending, abrasion, heating, scribing, grinding, impacting and crosshatch test.

The different basic techniques for adhesion assessment are pressure sensitive tape test, acceleration (body force) testing, electromagnetic stressing, shock wave testing, tensile and shear testing, laser techniques, acoustic imaging, indentation tests, scratch testing [105] and ultra-centrifuge test [122].

Qualitative tests such as the tape test or the pull-off test [123] are often used to monitor coating adhesion, since they are quick and easy to perform.

Quantitative adhesion values are often desired for understanding factors contributing to coating adhesion, for numerical simulations and life-time predictions. Most adhesion tests empirically infer the adhesive strength by subjecting the specimen to some external load and measuring the critical value at which the test specimen fails.

In this work peel strength measurement was used. Peel test is one of the simplest quantitative tests for determining adhesion. The first use of this test has been used since 1965 [124]. In this test tape can be peeled from a standard metal surface at 90°, or at 180° (i.e. pulled back on itself). For 90°, a friction-free wheel fixture may be used, for 180° tests, the tape can be applied to a vertical metal plate which is pulled up, away from the secured end of the tape.

1.9 Characterization methods

The main applications of plasma treatments in material science are surface functionalization and coating. So, Quantitative analysis and mapping of surfaces at atomic, molecular, and nanometric resolutions is available from a comprehensive set of techniques. Surface science offers a valuable approach of the nature, composition, and reactivity of the surface components of plasmas, and is an indispensable for material surfaces analysis prior to design and surface treatment development.

1.9.1 Surface analyses

Surface-sensitive analytical methods provide an exhaustive characterization of the surfaces, including thermodynamics, structure, morphology, and chemical composition. And it is applicable for all types of materials: polymers, textiles, glasses, biomaterials, films, fibers, and powders [5].

The important analytical methods used to characterize plasma-treated surfaces includes

- XPS (X-ray photo electron spectroscopy) which used to obtain qualitative and quantitative elemental surface composition, chemical bonding analysis, depth profiling, and mapping.

• AFM (atomic force microscopy) for high resolution morphology, roughness, adhesion, surface, and friction forces, and visco elastic module measurements.

• SEM (scanning electron microscopy) with X-ray analytical facilities (X-SEM) (X-ray scanning electron microscopy) and variable pressure scanning electron microscopy (VP-SEM).

• Contact angle to measure surface energy, wettability, and adhesion.

• ToF-SIMS (time of flight secondary ion mass spectrometry) high resolution molecular analysis, chemical depth profiles, and molecular imaging

• Gas and water vapor permeation to measure the efficiency of barrier coatings.

• TEM (transmission electron microscopy) to determine the structure of deposited layers, thickness, and homogeneity of the coatings.

1.9.2 Bulk analyses

Bulk composition is determined with techniques that give deep information such as Fourier Transform Infrared Spectroscopy (FTIR), Thermo-Gravimetric Analysis (TGA), Nuclear Magnetic Resonance (NMR), X-ray Fluorescence (XRF) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) are the most relevant techniques that can quantify both major and minor elemental components.

In this work XPS, FTIR, NMR, TGA, AFM, and contact angle were used to characterize the coated polymers.

1.10 Chemical derivatization of amino and hydroxyl groups

Derivatization (labeling) of the functional groups is a method used for the quantitative estimation of the functional group at the surface and it takes place in liquid or gas phase. In liquid phase the solvent were restricted to liquids of low boiling points or to gases. Mostly reactions are applied under vacuum in order to work at room temperature.

The most frequently used solvents are pentane and anhydrous ethanol. Reaction times are 2-4 hours, after derivatization, the sample is washed carefully in order to remove the unreacted and adsorbed reagents.

Figure 1.5 represents the chemical structure of different labeling agents.

pentaflurobenzaldehyde **PFBA**   p-trifluoromethyl benzaldehyde **TFBA**   trifluoroaceticanhydride **TFAA**
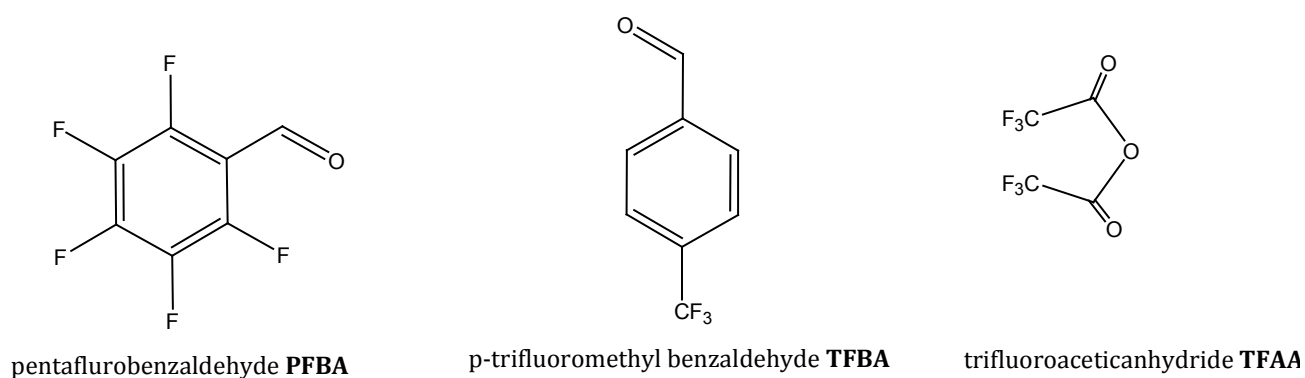
Figure 1.5 The chemical structure of pentafluorobenzaldehyde (PFBA), p-trifluoromethyl benzaldehyde (TFBA) and trifluoroaceticanhydride (TFAA)

The activity of amino group was studied by means of labeling reactions with pentafluorobenzaldehyde (PFBA), with p-trifluoromethylbenzaldehyde (TFBA) in the vapor phase followed by XPS analysis. Trifluoroaceticanhydride (TFAA) in liquid and in vapour phases was used for the derivatization of hydroxyl group; TFAA reacts also with primary and secondary amines [125-127]. Consequently, the reagent is not specific towards

OH groups if amines were present at the same time. The expected reactions during derivatization are shown in Figure 1.6.
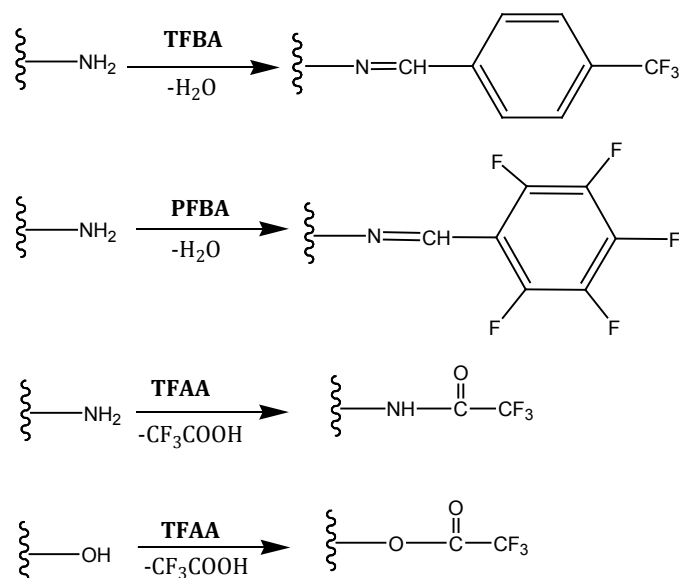
Figure 1.6 A scheme of surface derivatization reactions of amino and hydroxyl groups

Due to the sensitivity of TFAA to air, more care must be taken. Therefore, TFAA was only used for the derivatization of hydroxyl groups.

In addition to TFAA derivatization also acetylchloride CH_3COCl (AcCl) and heptafluorobutyryl chloride $CF_3(CF_2)_2COCl$ (HFBuCl) were used for the derivatization of hydroxyl groups. The results showed that none of the three reagents were hydroxyl selective in the presence of other oxygen carrying functional groups [128], see Figure 1.7.
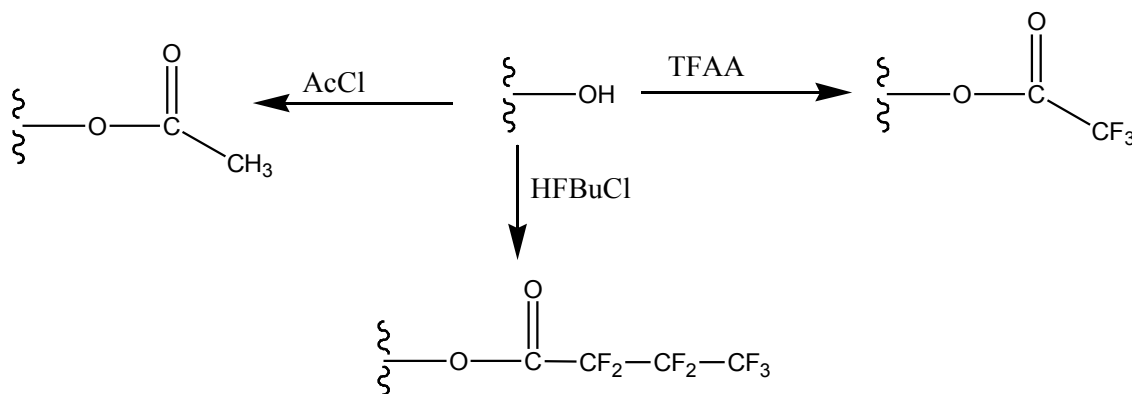
Figure 1.7 Hydroxyl derivatization reactions with trifluoroaceticanhydride (TFAA), acetylchloride (AcCl) and heptafluorobutyryl-chloride (HFBuCl)

2. Experimental

2.1 Materials

Polyethylene foils of a thickness of 0.1 mm (Goodfellow) and polystyrene [0.4 mm PS obtained from Petri dishes used for the deposition of inorganic layers and 0.05 mm PS (Goodfellow) used in the deposition of the N-rich and polyphosphate layers] were used as substrates. Before coating polymer foils were washed in an ultrasonic bath with diethyl ether (PE) and ethanol (PS) for each 15 min to remove residual slip agents, light stabilizers, anti-oxidants etc. as much as possible.

Hexamethyldisiloxane (HMDSO, 99.9% grade) as precursor for SiO_2-like layers was obtained from Merck-Schuchardt and were used as received.

Allylamine and allyl alcohol (each 99.9% grade) used for plasma polymerization were obtained from Merck-Schuchardt. Methylated poly (melamine-co-formaldehyde) (mPMF) solution used for dip-coating was obtained from Sigma-Aldrich and has a number average of molar mass $M_n \sim 432$, 84 wt.% dissolved in 1-butanol. Ethylene glycol, urea and pentaerythritol were purchased from Merck-Schuchardt.

Poly(allylamine hydrochloride) (Sigma Aldrich, average Mw $\simeq$ 15 000 g/mol) and sodium polyphosphate (Across Chemicals, ref 256-779-4), were dissolved at 1 mg.mL-1 in 0.15 M NaCl (g.mol-1) buffer (pH =6.6 ± 0.1). All solutions were prepared from doubly distilled water (Millipore Simplicity system, ρ=20.2 MΩ.cm).

Single-side-polished silicon wafers were used as model substrate for morphological characterization of deposited films by AFM. The silicon wafers were ultrasonicated for

15 min in acetone and ethanol respectively, and were kept in ethanol solution, and dried with a dry N_2 gas flow directly before using.

2.2 Plasma polymerization

The plasma polymerization was carried out in a cylindrical stainless steel reactor (Ilmvac, Germany, volume of 50 dm³). The grounded reactor was equipped with a powered electrode (5 x 35 cm) which was supplied by continuous-wave radio-frequency (rf) generator (13.56 MHz, Dressler Caesar 13) and an automatic matching unit. The rf power was pulsed with a duty cycle of 0.1 and a repetition frequency of 10^3 Hz Figure 2.1[129].
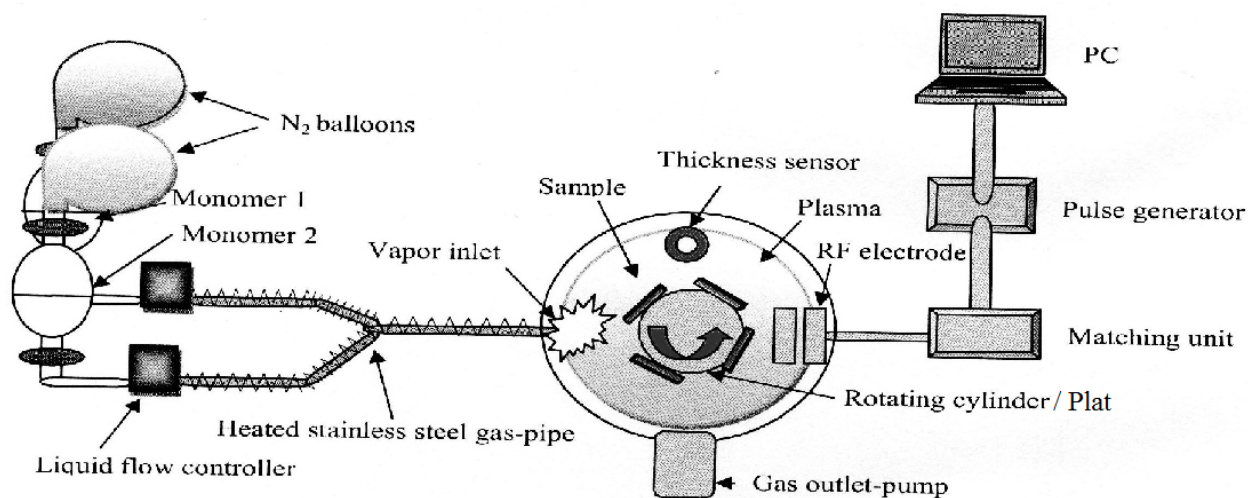
Figure 2.1 Plasma reactor

A stainless steel plate with dimensions 25 x 10 cm served as a ground electrode. It was mounted at a distance of 2.5 cm with respect to the powered ("hot") electrode. The effective area of the ground electrode was 1.5 times larger than that of the rf one. The sample (substrate polymer) was placed onto the ground electrode. The liquid monomer

was dosed by mass flow controller for liquids (liquid-flow®, Bronkhorst). The liquid flows were adjusted to 5 g/h in case of HMDSO and the base pressure of allyl alcohol and allylamine vapor was adjusted to 5 Pa. The media were introduced by heatable gas/liquid distributors consisting of perforated metallic tubes. The pressure was adjusted by varying the speed of the turbo molecular pump and adjusting an automatic butterfly valve (V.A.T., Switzerland). A quartz microbalance was used for monitoring the deposition rate (EDWARDS, FTM7, England). As the densities of ultra-thin layers are difficult to measure, a density of 1 g·cm^{-3} was assumed to calculate the film thickness. This means that the absolute values of the thickness can have some error, but this potential error is the same for all the cases discussed. Moreover, one can argue that the density of the deposited layers can depend on the plasma conditions like the pressure and wattage. This might be the case but the expected differences in the density values are small and negligible as compared to other effects.

In case of plasma polymerization of poly(allyl alcohol) and poly(allylamine) a density of 1.0 g/cm^3 was taken to calculate the film thickness of poly(allyl alcohol) and the density of 2.0 g/cm^3 was used for SiO_2-like layers (HMDSO + O_2) adapted from the known density polydimethylsiloxane (PDMS).

All the HMDSO deposited layers are additionally exposed to oxygen plasma for 1 min in order to remove any residual carbon from its surface.

Moreover, sometimes preceding exposure of polymer substrates to oxygen plasma for 5 s was also applied to introduce oxygen-containing functional groups onto the surface of polyolefins.

2.3 Preparation of thick layers

2.3.1 Preparation of thick inorganic layers

The deposition of SiO_2 or SiO_x layers on the polymer surface produces intumescent flame retardants (IFR) and generates an oxygen barrier as it is well known in the packaging industry with ultra-thin layers as well as in fire-protective coating (water-glass. Chalk) of the roofs known and widely used in the Second World War.

Here, 0.5 or maximal 1 μm SiO_2 plasma polymer layers were used. They served as adhesion-promoting primer for additional coating of thick layers by dipping. Thus, thicker layers of water-glass with thicknesses of 5, 20 and 40 μm were deposited onto $HMDSO/O_2$ layers. All polymer substrates were prior coated with thin SiO_2 layers (ppHMDSO/ O_2) polymer layers using the low-pressure plasma deposition. Alternatively, 10 nm thick SiO_2 layers using silane pyrolysis in air (Silicoater process, STS08, Sura Instruments GmbH, Jena) as primer for realization of sufficient adhesion of water glass layers. Precursor for flame pyrolysis was also hexamethyldisiloxane dissolved in 2-propanol (30 vol. %). The fed gas composition of HMDSO–air was 1:20. The slit nozzle of the burner had a width of 10 cm and the gas flow amounted to 1 mL/min.

Sodium silicate solution (10% NaOH, 27% SiO_2, "water glass") was used for additional (subsequent) deposition of thick silicate layers (5–40 μm) by dipping and drying onto the adhesion-promoting HMDSO-SiO_2 coated samples at room temperature.

The silicate solution was purchased from Riedel-de Haën.

2.3.2 Preparation of N-rich thick layers based on melamine resin

All polymer substrates were oxygen plasma treated (5 s) coated with 100 nm plasma polymerized allylamine (ppAAm) or allyl alcohol (ppAAl) layers acting as adhesion promoter. It follows repeated dipping into mPMF/1-butanol solution (1:1 and 4:1 wt/v (g/ml) respectively), thus producing layer thicknesses of 10 and 50 μm respectively. The dipped foils were subsequently dried in an oven under vacuum for 24 h at 80°C.

The thickness of the layers was measured using a Mitutoyo 3305(2) DIGIMATIC Messuhr, ID-C, Germany, 3 times in different regions and the average was calculated.

2.3.3 Curing of melamine resins

The methylated poly(melamine-co-formaldehyde) resin mPMF was cured using different polyol compounds (ethylene glycol, pentaerythritol) [130] or amines such as urea [131], with a percentage of 10% with respect to the mPMF, p-toluene sulphonic acid (pTSA) was used as catalyst. Figure 2.2 presents the presumable curing mechanism of melamine resin.
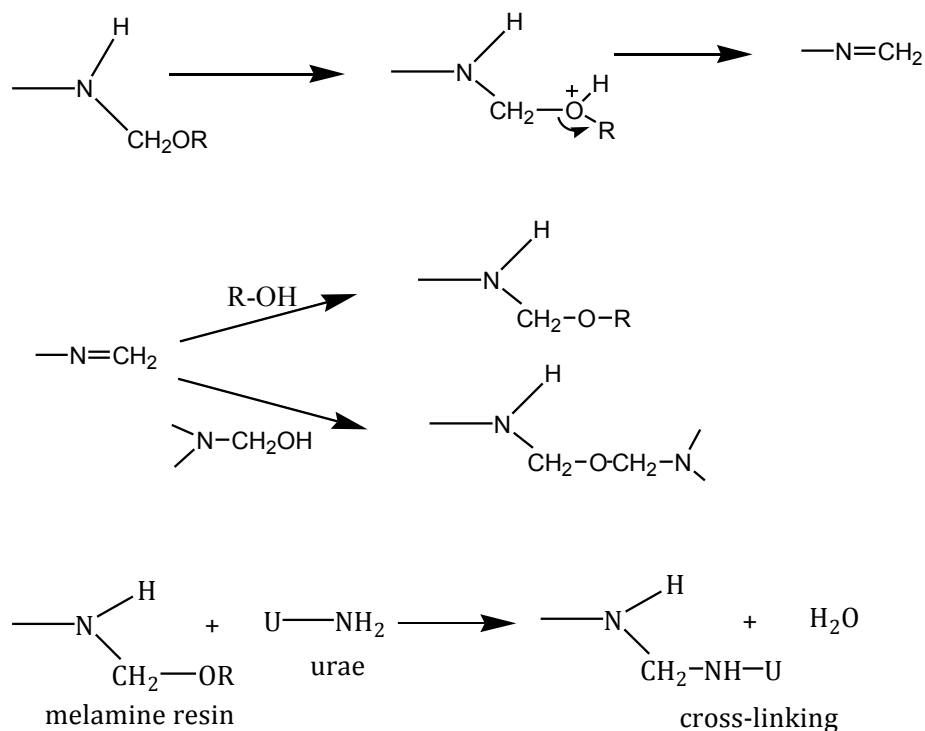
Figure 2.2 Mechanism of the curing reaction of melamine resin

All the cured systems were prepared by heating the mixtures at 80°C for 2 h, then used directly for dip-solution of polymer foils.

2.3.4 Deposition of intumescent polyphosphate fire retardant layer using Layer-by-Layer technique

All polymer substrates were pre-coated with 50 nm plasma polymerized allylamine (ppAAm) layers acting as adhesion promoter.

PS and PE samples were immersed alternatively into solutions containing negative species of sodium polyphosphate (PSP) and positive species of poly allylamine. Hydrochloride (PAH), the alternating deposition of polyanions and polycations on the polymer foil leads to the formation of nanometer to micrometer films called polyelectrolyte multilayers [Layer-by-layer (LbL)] deposition process as illustrated in Figure 2.3 [132,133].
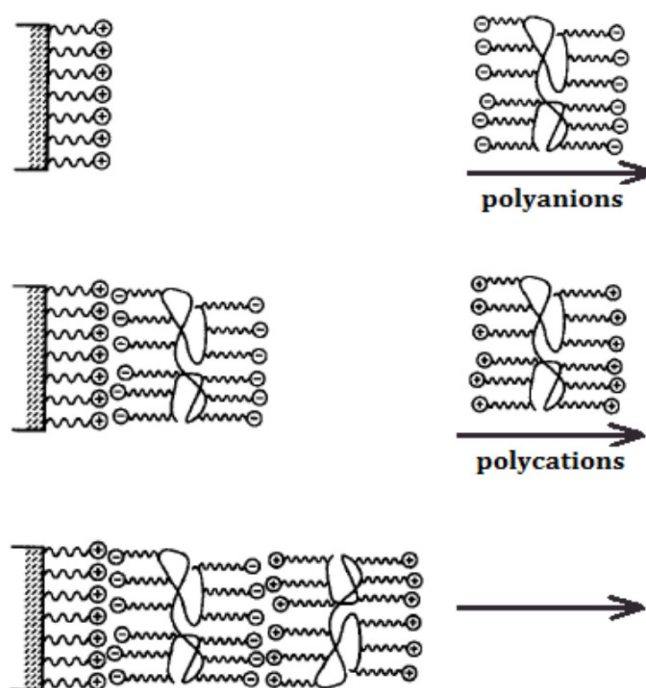
Figure 2.3 Schematics representation of Layer-by-Layer deposition process

Between each immersion step, the substrates were rinsed with the buffer solution and water. The buffer and water rinse steps were aimed to desorb weakly adsorbed PAH and PSP, respectively. The adsorption and rinsing step times were set at 1 min. After reaching the number of the desired bilayers (BL) desired, the samples were dried at ambient temperature. Before starting the elaboration step, the substrates (silicon wafers or polymer foils) were presoaked in each polyelectrolyte solution for 5 minutes to increase the surface charge and therefore the adhesion

2.4 Characterization methods

2.4.1 Surface analysis using XPS

The elemental composition of the deposited films and structural units at the polymer surface were analyzed by X-ray photoelectron spectroscopy (XPS) and monitoring the C1s, O1s, N1s, F1s, P2p and Si2p peaks. For recording of spectra a SAGE 150 spectrometer (Specs, Berlin, Germany) was used equipped with the hemispherical analyzer Phoibos 100 MCD-5. Non-monochromatic Mg K_α radiation with 11 kV and a power of 220 W was employed at a pressure of ca. 10^{-7} Pa in the analysis chamber. The angle between the axis of X-ray source and the analyzer lenses was 54.9°. The analyzer was mounted at 18° to the surface normal. XPS spectra were acquired in the constant analyser energy (CAE) mode. The analysed surface area was about 3 × 4 mm. The information (sampling) depth of XPS measurements is between 5 and 7 nm. Peak analysis was performed using the peak fit routine from Specs using a Gaussian–Lorentzian ratio of 33 to 67 for peak fitting or CASA XPS. Then, the results were transferred to Origin software (Origin Lab Corp., USA) for a better representation of data.

2.4.2 Derivatization of functional groups for improved XPS analysis

To estimate the number of introduced NH_2-groups by XPS the layers were exposed to vapors of pentafluorobenzaldehyde (PFBA) and the thus introduced fluorine percentage was measured by XPS [134]. Schiff's base or azomethine bonds were formed. 1 PFBA molecule was bonded to 1 NH_2 group, thus introducing 5 F atoms for 1 NH_2 group [135].

The samples were exposed to PFBA vapors in a closed container under low pressure conditions (p=500 Pa) for 2 h at 45°C. In this case 2 h were adequate for such

derivatization as tested before. It should be also noted that NH_2-containing plasma

polymers need exposure times to PFBA at least 6 h [38,134].

To estimate the OH groups of plasma polymerized allyl alcohol (ppAAl), the polymer

substrates coated with ppAAl were exposed for 15 min to trifluoroacetic anhydride

(TFAA) in the vapor phase [136,137] Figure 2.4.

a) $R-NH_2 + OHC-C_6F_5 \rightarrow R-N=CH-C_6F_5 + H_2O$
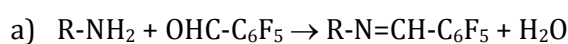
b)
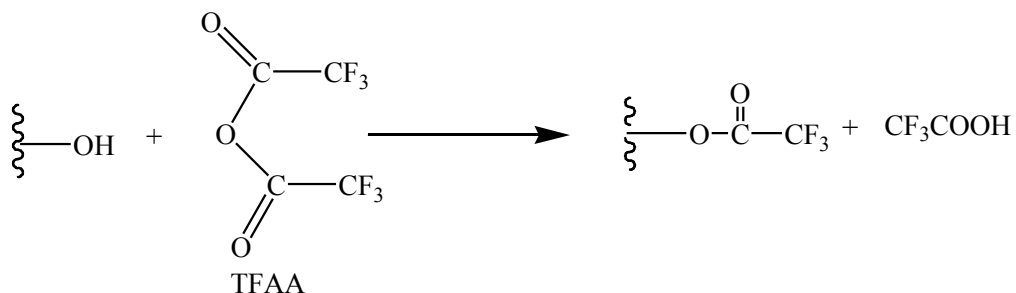
Figure 2.4 Derivatization reaction of a) -NH$_2$ and b) –OH groups

TFAA was used to estimate the concentration of the hydroxyl groups at the polymer

surfaces. In this reaction the OH groups converted into trifluoroacetates and, therefore,

the F 1s peaks in XPS spectra were used for quantifying the presence of OH groups (1 OH

= 3F).

2.4.3 Fourier Transform Infrared Spectroscopy (FTIR) - Attenuated Total Reflectance (ATR)

FTIR spectra were recorded in the region from 550 to 4000 cm^{-1} accumulating 64 scans at a resolution of 4 cm^{-1} using a Nicolet Nexus 8700 FTIR spectrometer (Nicolet, USA) in the ATR mode of the diamond cell (Diamond Golden Gate, Nicolet, USA, 1 reflection). All spectra were subjected to the ATR-correction for diamond, smoothed and baseline corrected. In contrast to XPS, a sampling depth up to 2.5 μm is analyzed by ATR.

2.4.4 Solid state NMR

^{29}Si NMR experiments were run at 78.9 MHz (9.4 T) using a Bruker DSX 400 (9.4 T) spectrometer with a 7 mm MAS probe and MAS rotation frequencies of 6 kHz. Single pulse (direct excitation) measurements were carried with 15° two pulse phase modulation (TPPM) ^{1}H decoupling [138]. The ^{29}Si 90° pulse length was 5 μs, the repetition time was 600 s and between 80 and 160 scans were accumulated. The ^{29}Si chemical shifts (δ) have been calibrated using solid Q8M8.

2.4.5 Contact angle measurements (CAM)

To estimate the surface energy of samples, (static) contact angle measurements were carried out. Diiodomethane, ethylene glycol and water have been used as test liquids. The automated contact angle system G2 (Krüss, Germany) and the sessile drop method were used. For the calculation of surface energy and the polar and dispersive components, the method after Owens [139]–Wendt [139] –Rabel [140] and Kaelble [141] was selected as given by the Krüss software. All test liquids were purchased from Aldrich

and used as received, unless stated otherwise. Solvents were at least analytical-grade quality.

2.4.6 Atomic Force Microscopy (AFM)

Topographical images of plasma polymerized HMDSO, HMDSO: O_2=1:12 layers, and also a dried 40 bilayers (PAH-PSP) films were investigated using (Nanopics 2100). The investigated films were deposited onto was a silicon wafer as substrate just to have a nicely flat surface. The images were acquired over squares of 20 x 20μm2.

The thicknesses of 20 and 40 bilayers of (PAH-PSP) films were measured using Profilometer XP2, AMBIOS Technology.

2.4.7 Scanning Electron Microscope SEM

SEM micrographs were taken using a Zeiss Gemini Supra 40 microscope equipped additionally with energy dispersive X-ray analysis (EDX), Thermo NSS 2.1-Bruker Quantax 400 (Mag. 10.00 KX 2 μm and 100. 00 KX 200 nm).

2.4.8 Thermal properties of layers

Thermo gravimetric analysis was performed using the TGA equipment NETZSCH/STA 409 PC/PG, GmbH in synthetic air. The samples were measured in the temperature range from room temperature to 1000°C with a heating rate of 10 K/min.

2.4.9 Peel strength measurements

A 90° peel test was carried out in accordance with DIN EN 60249 at a speed of 25 mm/min using the tensile testing machine TH2730 (Thümler, Germany). A double-sided tape (TESA Type 4965, Beiersdorf AG, Germany) was applied. The calculated standard deviation varied between 10-15%. Here, the deposited thick layers are schematically represented in Figure 2.5. Optical microscopic pictures of the peeled polymer surfaces were also investigated using ZEISS Axioskop, epipton-Neo Fluar (5/0.15 HD), Germany

a)

Plasma Polymer i)0.5 µm ppHMDSO ii)0.5 µm ppHMDSO:O_2=1:12	0.5 µm ppHMDSO:O_2=1:12 i)Plasma O_2 ii)0.1 µmppAAl iii) Plasma O_2 +0.1 µmppAAl	Water-glass 1 µm ppHMDSO:O_2=1:12
Substrate (PS or PE)	Substrate (PS or PE)	Substrate (PS or PE)

b)   **c)**

mPMF
Adhesion promoter ppAAm or ppAAl or O_2 plasma
Substrate (PS or PE)

Cured mPMF
Adhesion promoter ppAAl
Substrate (PS or PE)

d)

PAH-PSP BL
Adhesion promoter ppAAm
Substrate (PS or PE)

Figure 2.5 Schematic of thick-coated layers in PS/PE systems

For the deposition of inorganic layers deposition onto PS and PE, these polymers were first modified with O_2 plasma, subsequently coated with ppAAl or the combination of both O_2 plasma and ppAAl pre-layer deposition followed by deposition of (HMDSO: O_2=1:12) (Figure 2.5a). HMDSO: O_2=1:12 molecular ratio corresponds to the formation of pure SiO_2:

$$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + 12\ O_2 \rightarrow 2\ SiO_2 + 6\ CO_2 + 9\ H_2O.$$
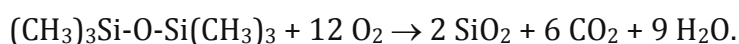
For the deposition of N-rich layers, adhesion-promoting layers of each about 100 nm of plasma-polymerized AAm and AAl films were used, followed by dip-coating into mPMF solutions (mPMF or mPMF with curing agent) for deposition of 10-50 μm thick mPMF layers as schematically shown in Figure 2.5b,c**.**

In case of coating with polyphosphate layers, a pre-layer of 50 nm ppAAm was firstly deposited by plasma polymerization followed by deposition of 20 or 40 BL of poly(allylamine hydrochloride) and sodium(poly phosphate) (PAH-PSP), see (Figure 2.5d). To localize the mechanical failure in the coated PE or PS systems at peeling, the peeled surfaces were inspected using XPS, cf. Figure 2.6 [142]. The peel front propagation determines the type of mechanical failure, e.g., whether the peel front propagated along the interface (interface failure) or within the material (cohesive failure).
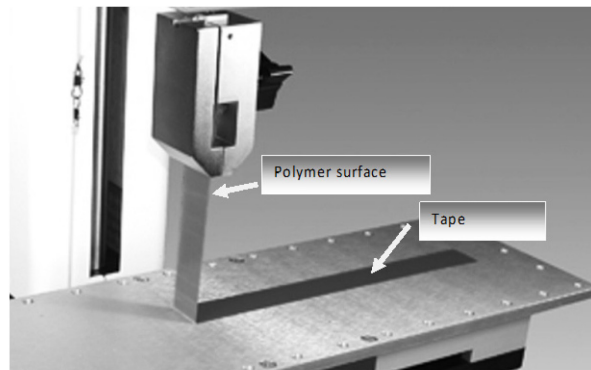
F*igure 2.6 Inspection of peeled surfaces (polymer and tape) to XPS*

2.4.10 Measuring the fire retardant effect

The fire retardant tests were carried out on the basis of DIN 4102-1 or EN ISO 11925-2

(Figure 2.7)

Figure 2.7 Flame test according to DIN 4102-1 (Single-Flame Source Test (Ignitability Apparatus*,* EN ISO 11925-2)

Because the produced coating area was small, therefore, it was not possible to place the

specimens in the test chamber like regular specimens (with a size of 90 × 230 mm (wide

× length)). The size of the specimens made it also impossible to draw measuring marks

at 40 and 190 mm. Therefore, the first measuring mark (defining the position of the

flame) was drawn at 10 mm measured from the bottom edge of the specimen and that of

the propane flame at 20 mm (according to DIN 4102-1). The exposure time of samples to the flame of the Bunsen burner follows the standard.

The ignition time is one characteristic of the prepared PE and PS specimens. Therefore, the Bunsen burner was targeted to the specimen as long as it ignites the specimen (even though it took longer than 15 s to ignite the specimen). After ignition the burner was immediately removed. The focus was not on the spreading of flame only but also on the time to ignite and to flameout time.

To get an impression the first tests were carried out with the pure specimens without any fire retardant additives. Afterwards the same test (under the same conditions) was carried out with PE and PS samples coated with fire retardants or preventives layers

3. Results and discussion

3.1 Deposition of siloxane-like fire retardant layers

Farag, Z. R.; Krüger, S.; Hidde, G.; Schimanski, A.; Jäger, C.; Friedrich, Surface and Coatings Technology 2013, 228, 266-274.

Inorganic oxides layers are inflammable and therefore well suited for flame retardancy. Here, the known process of SiO_2 layer formation by plasma polymerization of hexamethlyldisiloxane (HMDSO) in presence of oxygen was used as first thin barrier towards flame exposure and as adhesion promoter for thick silicate layers. Water glass is such a well-known fire-retardant silicate, which can be applied in liquid phase and deposited by dipping or spraying.

3.1.1 Deposition kinetics of HMDSO

The deposition rate and the layer composition of SiO_2-like layers produced by the low-pressure plasma technique using $HMDSO/O_2$ mixtures with different stoichiometric ratios from 1:1 to the SiO_2-forming ratio of 1:12 were measured in dependence on plasma parameters. Series of experiments have been made to investigate the effect of $HMDSO/O_2$ ratio, pressure and input power on the plasma polymer deposition. Each parameter has been varied individually, while the other parameters were kept constant. $HMDSO/O_2$ was used in different molar ratios; 1:1, 1:3, 1:5, 1:7 and 1:12 at a pressure of 10 Pa and 100 W input power. Pure HMDSO (100%) was also plasma polymerized given for comparison [143-146].

Figure 3.1 represents the variation of the deposition rate of the plasma polymerized $HMDSO/O_2$ of different precursor ratios with plasma exposure time. The deposition

rates at different precursor mixtures were represented in Figure 3.2. The deposition rate of SiO_2 layers increase approximately linearly with increasing the percentage of O_2 gas.
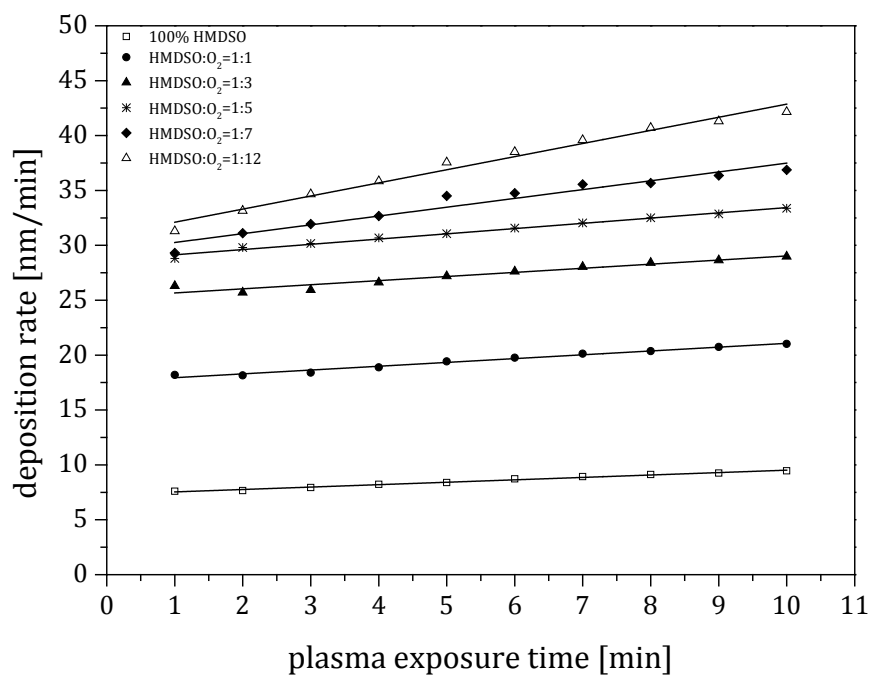
Figure 3.1 Variation of the deposition rate of the plasma polymerized HMDSO/O$_2$ with plasma exposure time
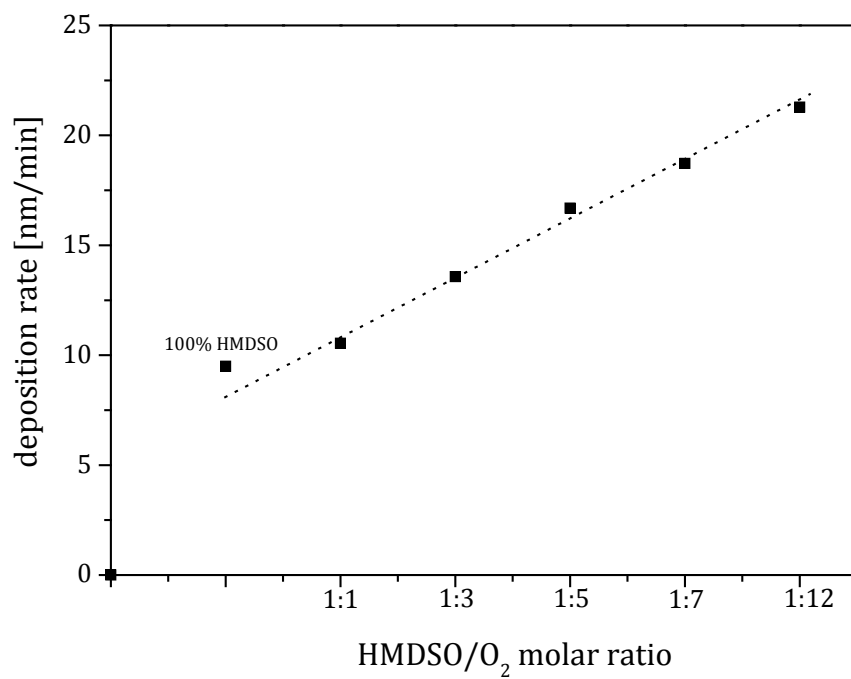
Figure 3.2 Deposition rates at different precursor mixtures

The deposition rate was expected to be constant; however, indeed it was linear but slightly increasing. The reason is not clear yet but this effect is very small. With higher oxygen introduction the deposition ratio is linearly growing. The polymer layer deposition of pure HMDSO by plasma polymerization is hindered because the absence of polymerizable double bonds. On the other hand the oxidation of silicon to silica is more easily. Thus, the deposition rate is maximum at highest oxygen addition.

Regarding to the FTIR-ATR data, the dilution of HMDSO by oxygen in the discharge led to changes in the chemical composition of the deposited film as shown in Figure 3.3 In this figure the spectra of plasma deposited layers for different HMDSO/O_2 ratios (10 Pa and 100 W input power), 100% HMDSO and the substrate spectrum are presented.
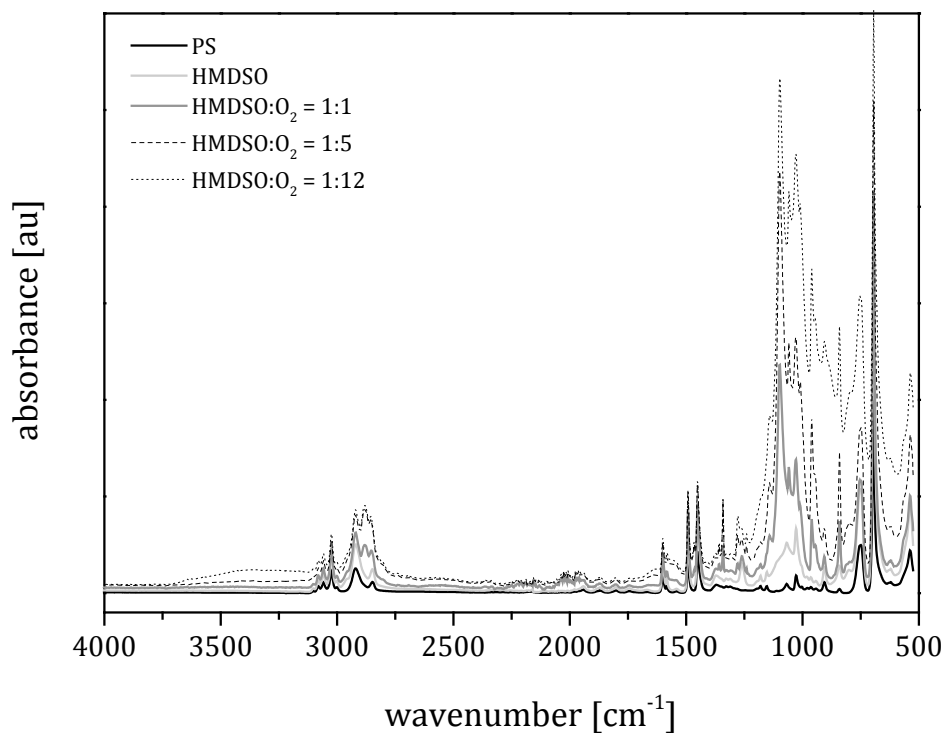
Figure 3.3 FTIR-ATR spectra of plasma polymerized SiO₂ layers at different HMDSO/O₂ ratios

The intense infrared absorbance at $\nu \approx 1027$ cm^{-1}was attributed to the Si\O\Si (and may be superposed by Si-O-C) asymmetric stretch vibration; this peak has also been assigned to Si-CH$_2$-Si bridging groups [147,148]. The addition of oxygen reduces strongly the intensity of hydrocarbon absorbance bands at $\approx$2960, 2920, 2890, 2850 and 839 cm^{-1} (Si(CH$_3$)$_3$, CH$_2$). The appearance of the silanol stretching signal was found at $\approx$3500 cm^{-1} slightly shifted by hydrogen bonds between Si-OH groups. Its intensity increased with the addition of oxygen. The –SiH stretching band at 2125 cm^{-1} is not observed for films deposited at these conditions. The bands at 1265 cm^{-1} (δCH$_3$), 865 (ρCH$_3$\Si\CH$_3$) and 840 cm^{-1} (ρSi(CH$_3$)$_3$) were successively eliminated. Bands at 1410, 1600 and 3060 cm^{-1} are indications for double bonds [149].

The hydrocarbon related bands diminished at oxygen addition to HMDSO (HMDSO: O$_2$ = 1:12) [150-152]. The addition of oxygen to HMDSO changes the composition from a more organic polymer-like to an inorganic quartz-like film. Oxygen addition to the plasma causes the removal of all CH$_3$ groups of HMDSO by gasification to CO, CO$_2$ and H$_2$O which increases the oxygen/carbon and oxygen/silicon ratios strongly. Thus, the intensity of the Si-O-Si band increases.

The XPS-measured O/C ratios in the deposited plasma polymers in dependence on the molar ratio of HMDSO: O$_2$ are shown in Figure 3.4. Increasing the oxygen content in HMDSO reaction mixture increase the at.% of O$_2$ and thus at.% of C decreases. So the O/C% is of small vlaue for the plasma polymerized pure HMDSO and increases gradually upto (HMDSO:O$_2$=1:12)
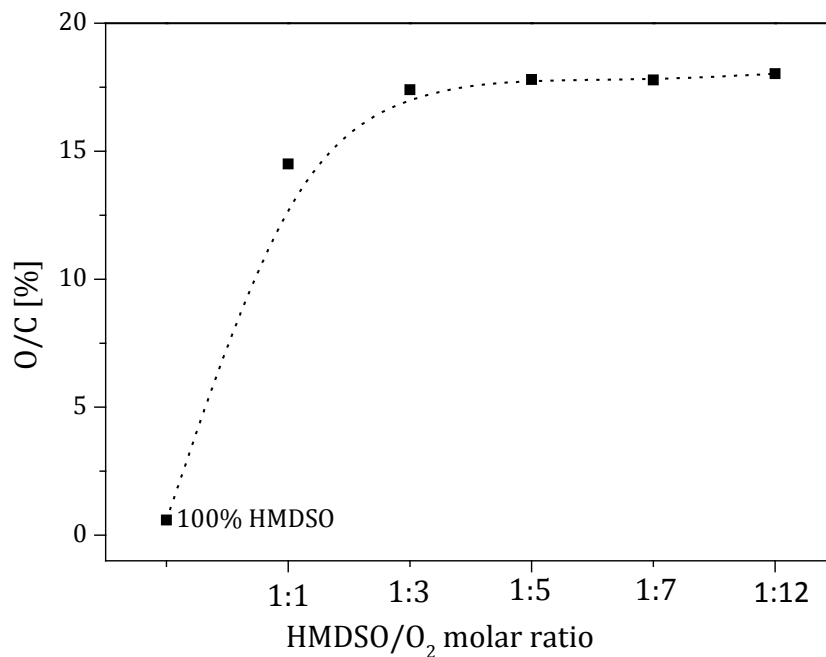
Figure 3.4 O/C ratio in the HMDSO deposits at different HMDSO/O₂ mixtures deposited at 10 Pa and 100 W

3.1.2 Influence of power and pressure

For studying the influence of power input on the deposition rate the HMDSO/O₂ precursor ratio was kept constant at 1:3 and the pressure was adjusted to each 10 Pa.

The rate of deposition was measured for power inputs of 20, 50, 70, 100 and 130 W.

Figure 3.5 represents the deposition rates in dependence on power.
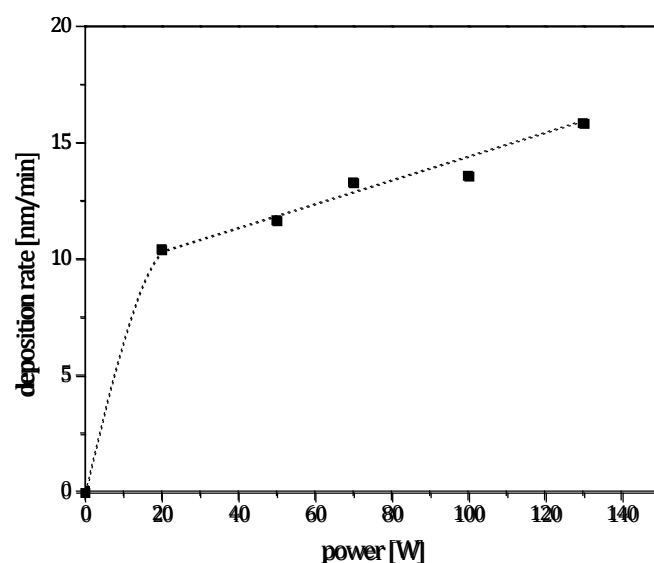
Figure 3.5 Layer thickness and deposition rates for different power input

FTIR-ATR analyses of these layers show that the power input has a significant effect on the chemical composition of the formed layers. Since HMDSO cannot polymerize chemically therefore at first hydrogen or methyl group abstraction have to be occur. Then, polymerizable fragments were produced. The higher the power input the more the yield in polymerizable fragments increase and therefore the deposition rate also increases. The IR spectra of HMDSO/O_2 at different wattage can be interpreted in the same way.

A new weak band for Si-O-Si at 1027 cm^{-1} appeared in addition to a broad absorbance band at 3400 cm^{-1} related to the stretching vibration of the Si-OH group. At higher wattage the intensity of all hydrocarbon peaks, such as Si-CH$_3$ at about 1250–1450 cm^{-1}, decreases and the films closely resemble stoichiometric SiO$_2$ (cf. Figure 3.6). A spectrum of pure SiO$_2$ was given for comparison [153,154].

Chapter 3: Results and discussion
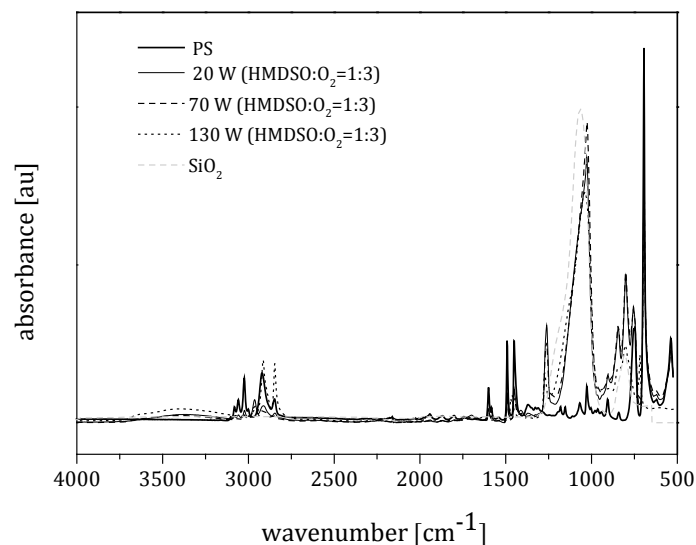
Figure 3.6 FTIR-ATR spectra of plasma polymerized SiO$_2$ layers at different input power

The effect of pressure on the deposition rate was studied by keeping the HMDSO/O$_2$ ratio and the power constant at 1:3 and 100 W respectively.

The pressure was varied from 10, 15, 20, 25 to 30 Pa. As shown in Figure 3.7 the rate of deposition increases with growing pressure.
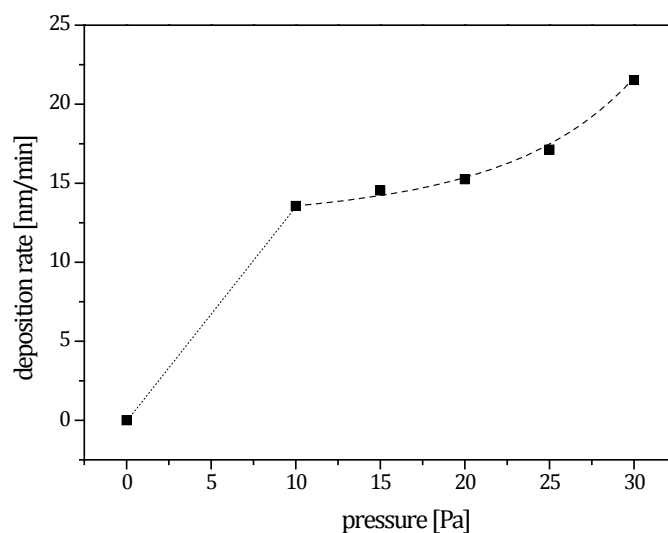
Figure 3.7 Deposition rates vs. pressure of precursor mixture

At high pressure the collision rate between the active species and the HMDSO molecules is higher, thus the deposition rate is also increased. However, the deposition rate did not increase proportionally to the number of HMDSO molecules (pressure) in the gas phase. Therefore, a loss in polymerization efficiency was found. The deposition rate normalized to the pressure (rate divided by pressure) decreases with growing pressure, i.e. the higher the concentration of HMDSO molecules in the gas phase with increasing pressure the HMDSO molecules cannot be transferred to a SiO_2 layer with the same efficiency as it is possible at low pressure. The reason is the lower energy transfer to the HMDSO molecules, less fragmentation and therefore lower deposition rates.

3.1.3 XPS measured chemical composition of plasma polymerized HMDSO/ O2 films

The XPS survey spectra of the samples prepared with pure (100%) HMDSO and with HMDSO: O_2 = 1:12 are shown in Figure 3.8. Four peaks were identified attributed to Si2p, Si2s, C1s and O1s. Using HMDSO: O_2 = 1:12 the C1s peak becomes absent.
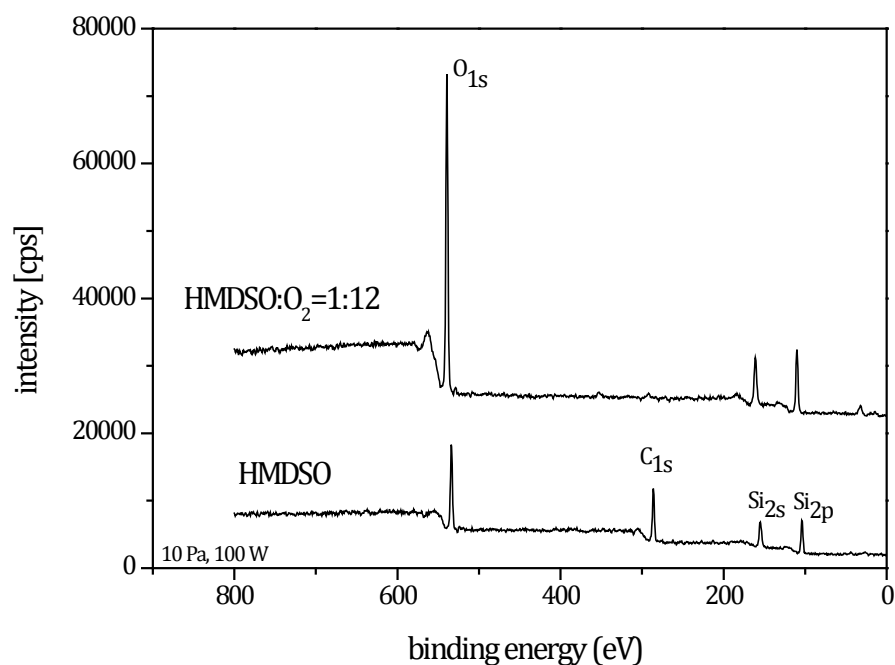
Figure 3.8 XPS spectra of films deposited from pure HMDSO and HMDSO: O_2=1:12

Figure 3.9 represents the O/Si and C/Si ratios, which were derived from XPS analysis as a function of the HMDSO/O_2 ratio.
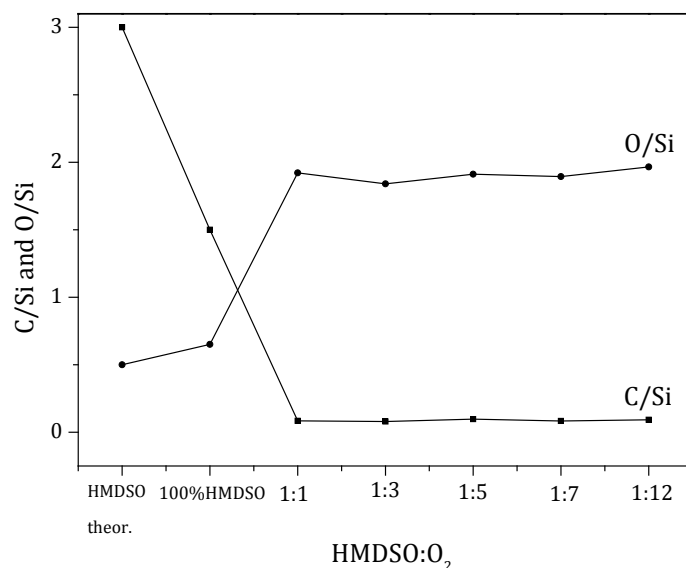
Figure 3.9 Effect of HMDSO/O₂ ratio on C/Si and O/Si ratio for HMDSO/O₂ films deposited at 10 Pa and 100 W

It is observed that increasing O_2 addition produces films with an elemental composition close to that of SiO_2 and nearly all CH_3 groups were removed as shown by absence of the C1s peak in the spectra shown in Figure 3.10. It can be summarized that the composition of HMDSO/O_2 layers is nearly independent on the precursor ratio also independent on pressure and wattage. Sub-stoichiometric SiO_2 layers were formed ($SiO_{1.8-1.9}$). These nearly carbon-free layers should be having best potential for flame retardancy. The comparison of the C1s peaks of pure plasma-deposited HMDSO without any additional oxidized carbon species at higher binding energy and that of HMDSO/O2 (1:12) confirm the nearly complete loss in carbon for HMDSO/O_2 system Figure 3.10.
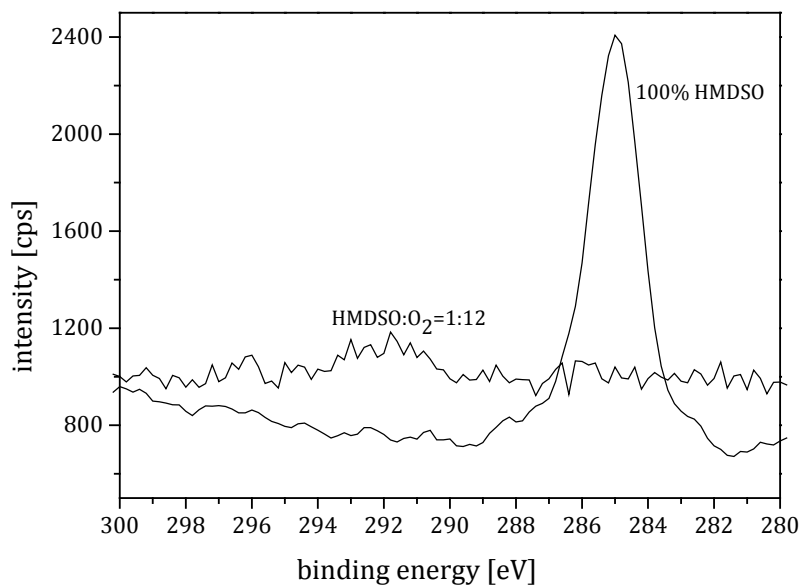
Figure 3.10 C1s peaks of HMDSO and HMDSO-O$_2$ (1:12) deposits (10 Pa, 100 W)

3.1.4 Elucidation of the structure using solid state NMR

Figure 3.11 represents the ^{29}Si spectrum of water glass is dominated by Q3 groups with contribution of silanols and Na$^+$ at 95 to 100 ppm and Q4 groups at −100 ppm as well as a few Q2 units present as shoulder at about −90 ppm.
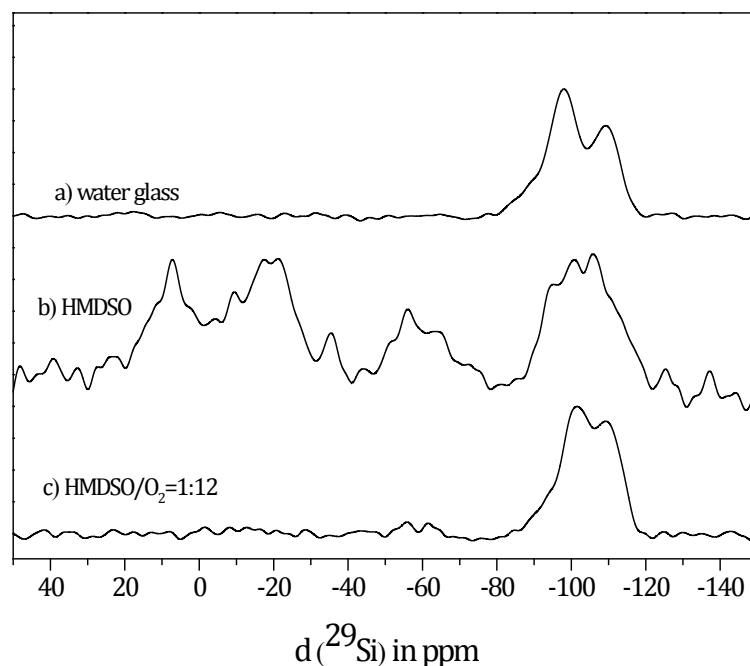
Figure 3.11 ^{29}Si NMR of a) Na silicate (water glass) b) HMDSO c) HMDSO: O_2=1:12

These signals are also found in the plasma deposited HMDSO/O_2 SiOx-like layer (sample c). Indeed, the silanol groups dominate. Pure HMDSO layers show a few T-groups, i.e. one Si\C bond / Si tetrahedral in the region around−60 ppm. It could be demonstrated that the addition of oxygen to HMDSO (HMDSO + 12 O_2) produces the SiO$_2$-like structure of the layer. Without oxygen addition Q groups are only partially formed. The ^{29}Si MAS-NMR spectrum of the HMDSO polymer shows additionally significant contributions of M- (around 8 ppm), D- (around −20 ppm) and the mentioned T-groups (at −60 ppm).

Thus, it could be confirmed that the proposed layer structures could be evidenced by ^{29}Si MAS NMR spectra.

3.1.5 Thermal behavior of SiOx layer coated polymers

The thick siloxane coated PE (1 μm HMDSO: O_2 = 1:12+ Na silicate/ water glass) were inspected by thermo-gravimetric analyses as well as the ones modified only with water glass. The results are shown in Figure 3.12 [PS substrates a) in presence of 1 μm ppSiO$_2$ base layer and b) without base layer] and [PE substrates c) in presence of 1 μm ppSiO$_2$ base layer and d) without base layer].
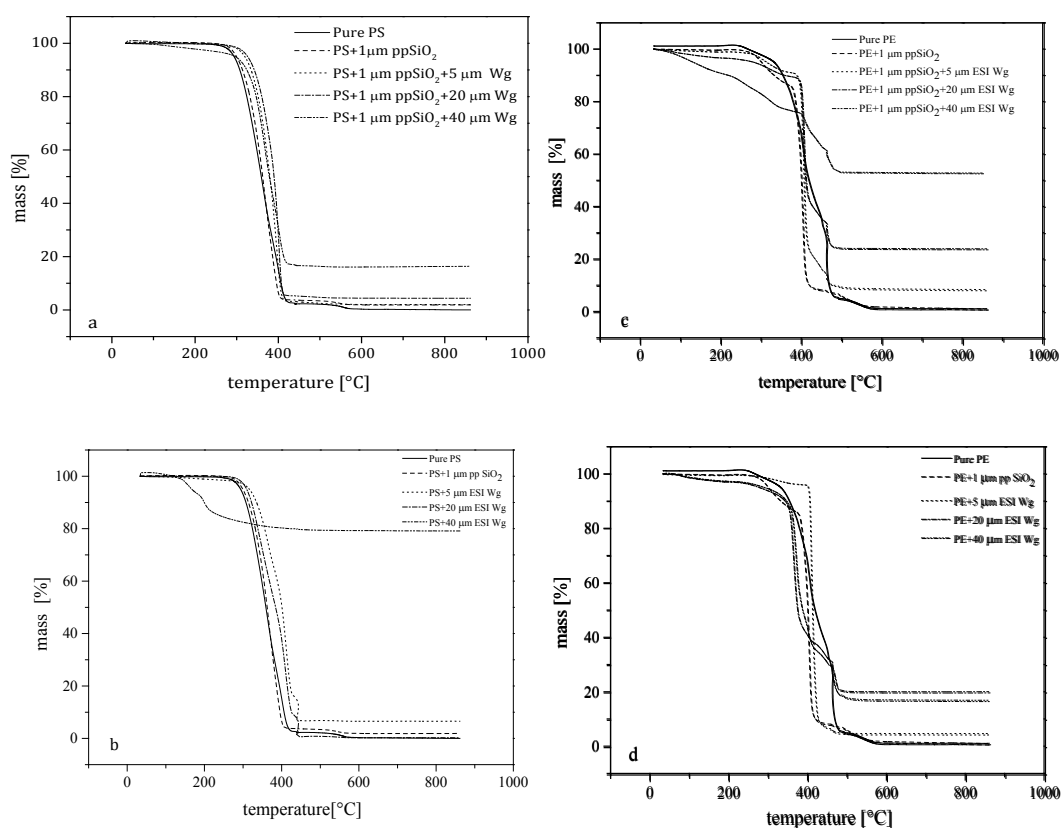
Figure 3.12 TGA curves of modified PS samples (a, b) and PE (c, d)

TGA curves shows that most of the samples begin to decompose at about 300°C and subsequently undergoes a destructive degradation up to ≈ 500°C with remaining different amounts of residue. The presence of water-glass (Wg) in all samples increases the remaining residue. The thermal stability of the polymer under study is not significantly changed besides the sample with the water glass layer of highest thickness.

It is assumed that residual water in the layers is the reason for some weight loss between 100 and 400°C. Water release may enhance the flame retardancy.

3.1.6 AFM measurements

The surface morphology of the SiO_2 films was studied by measuring atomic force spectroscopy AFM (Nanopics 2100), the thickness of the film was 200 nm.

The AFM scan of the $ppSiO_2$ (ppHMDSO: O_2=1:12) film and that of ppHMDSO without oxygen addition are represented in Figure 3.13.
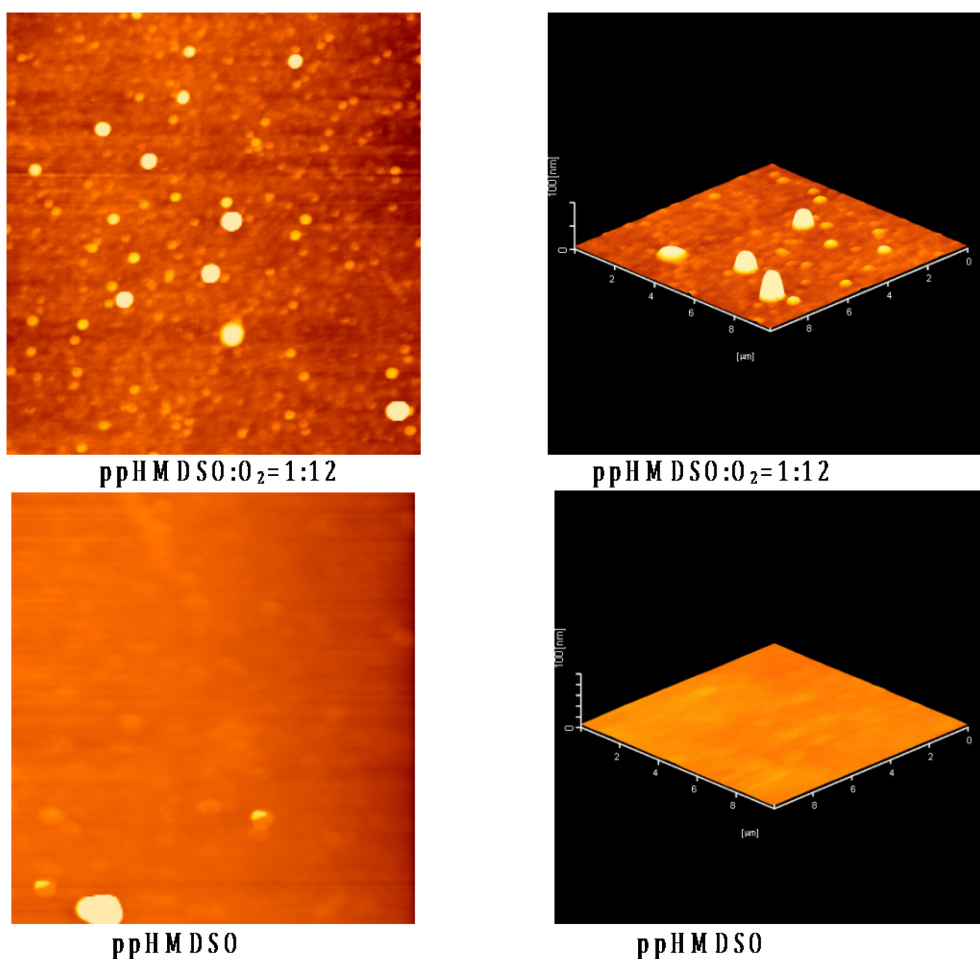
Figure 3.13 AFM micrographs of a SiO_2-like film (HMDSO: O_2=1:12) and ppHMDSO deposited under 100 W input power and 10 Pa

The scans show that the deposited layers are completely homogeneously in case of pure ppHMDSO. With addition of oxygen the topography is smooth but some agglomerates could be identified additionally.

Figure 3.14 represents micrographs of both ppSiO$_2$ (ppHMDSO:O$_2$=1:12) film and that of ppHMDSO without oxygen.

Si-wafer

ppHMDSO:O$_2$=1:12   ppHMDSO:O$_2$=1:12
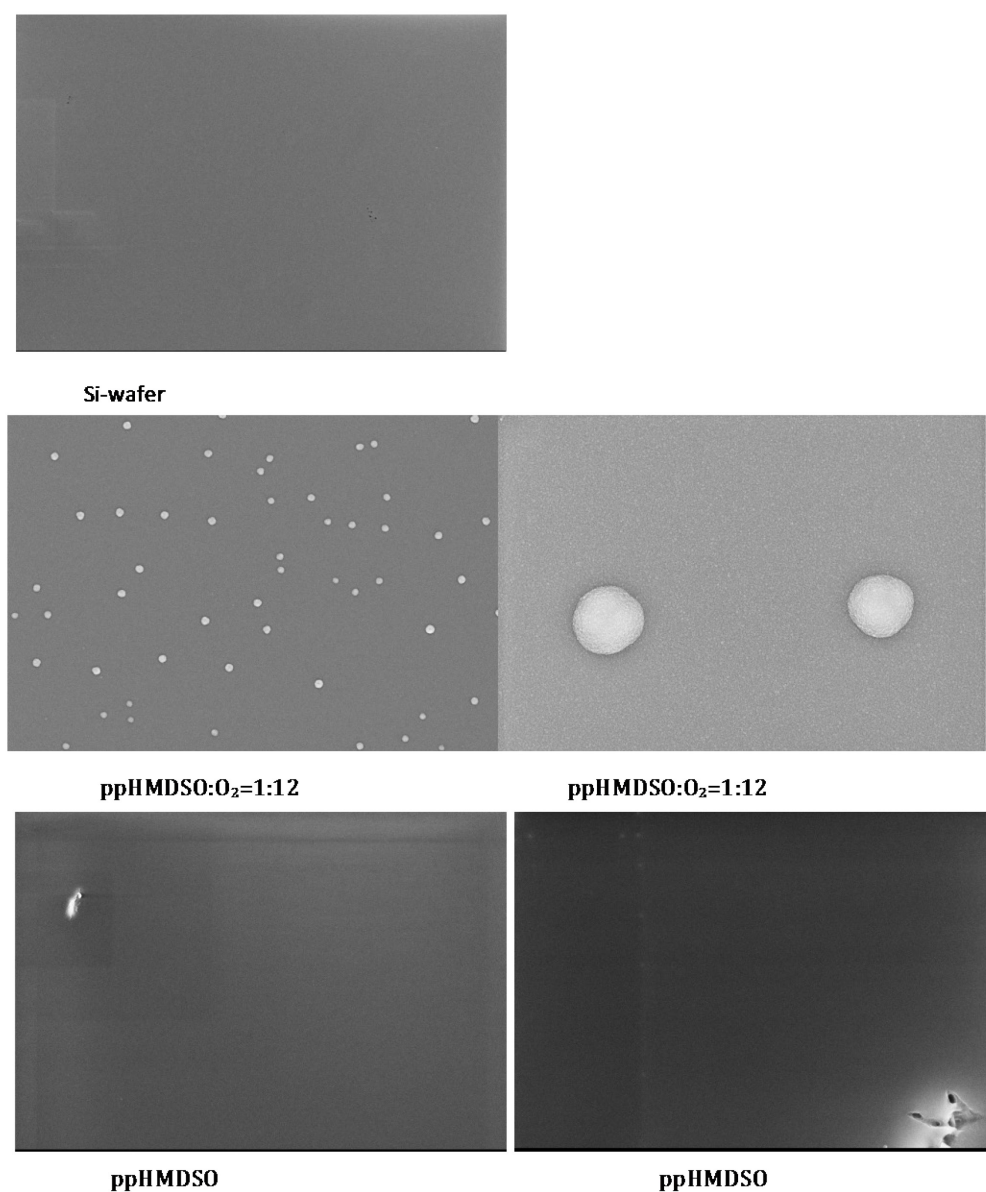
ppHMDSO   ppHMDSO

Figure 3.14 Scanning electron micrographs of a SiO$_2$-like film (HMDSO:O$_2$=1:12) and ppHMDSO deposited under 100 W input power and 10 Pa

SEM micrographs shows that for ppHMDSO deposited films the surface is uniform, smooth and free from pinholes, while for ppSiO$_2$-like films a rather uniform film is obtained with a few spherical micrometer dust particles scattered on the surface were observed [155, 156], the bright round spots being free-standing SiO$_2$ film over cavities etched in the polymer [157].

3.1.7 Adhesion measurements of coatings

The adhesion of the inorganic siloxane plasma polymer on PE or PS was measured using peel tests. The study was extended to investigate the effect of other plasma modifications of the substrate materials before the plasma deposition of the SiO$_2$ layer was performed. Either oxygen plasma exposure or deposition of a 0.1 µm thick allyl alcohol plasma polymer and oxygen plasma exposure + deposition 0.1 µm allyl alcohol plasma polymerized layers were investigated. The plasma oxidation of the polymer surface before deposition of the plasma polymerized siloxane layer enhances the peel strength additionally as seen in Figure 3.15.
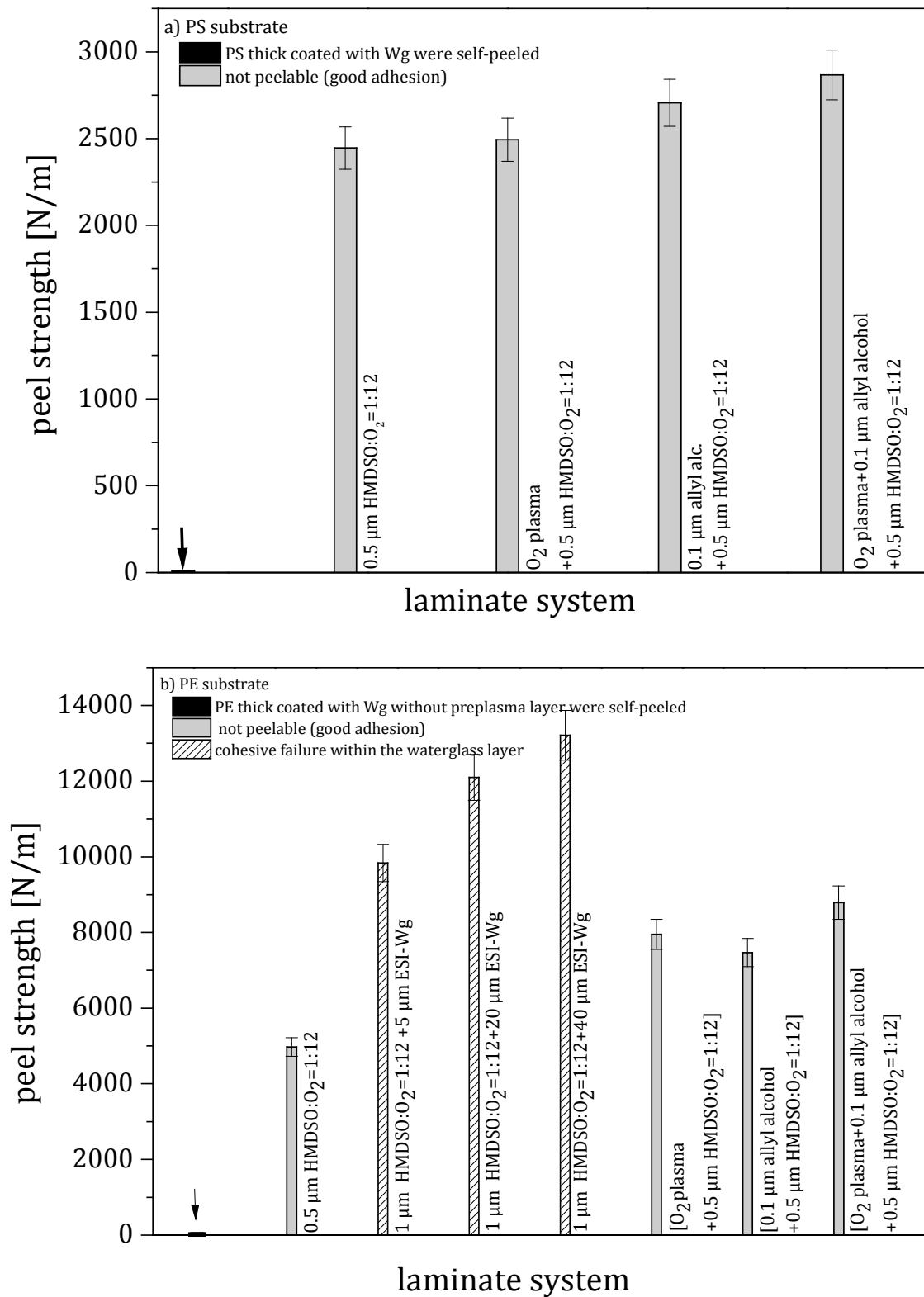
Figure 3.15 Peel strength of (a) PS/plasma-deposited SiO$_2$ layer (b) PE/ plasma-deposited SiO$_2$ layers + water glass

74

The peel strength of PS samples coated water glass either in with or without ppSiO$_2$ prelayer could not be measured because they are self-peeled also as PE samples coated with water glass without the additional (adhesion-promoting) plasma polymer layer. The peel strength values of plasma deposited HMDSO/O$_2$ and O$_2$-plasma + HMDSO/O$_2$ are in the same range as the samples without plasma pre-treatment as seen in Figure 3.15a, b. Additional coating with plasma polymerized ally alcohol slightly increases the peel strength further Figure 3.15a.

The results of coated PE samples showed strong improvement in the peel strength of water glass for the plasma modified samples in comparison to those without plasma modification as seen in Figure 3.15b. Self-peeling of the samples may be attributed to internal stress between the siloxane coating and the polymer substrate particularly at higher SiOx layer thickness and in absence of interactions at the interface water glass–polymer.

The sample modified with the pure HMDSO plasma polymer, without additional oxygen plasma exposure, does not adhere very well on PE. Pure oxygen plasma exposure generates a stronger oxidation of the PE surface and therefore more polar groups, which improves the adhesion between coating and PE [158]. In contrast the peel strength increased when HMDSO was polymerized in the plasma in presence of oxygen. It is noteworthy that in these cases also thick layers of water glass adhere very well. The reason may be due to the similarity of the structures of HMDSO/O$_2$ plasma polymer and water glass. Well adhesion is the indispensable precondition for improving the flame retardancy.

The XPS determined elemental compositions on both sides of the peeled PE modified with HMDSO/O_2 (1:12) plasma showed a peeling within the SiO_2 layer, alternating from interface-near to surface-near.

Additional coating with water-glass (5 µm) did not only improve the adhesive bond strength but also shift the locus of peeling into the polyethylene because of exclusive detection of carbon C1s on both peeled sides (82–99 at.% C-H= cohesive failure). The same was observed after deposition of 20 µm water glass on PE/SiO_2. However, a partial failure was also observed at the interface SiO_2/Na-silicate (water-glass). In the case of oxygen plasma pre-treatment of polyethylene and the additional insertion of 0.1 µm thick adhesion-promoting allyl alcohol plasma polymer film, and a second 0.5 µm thick SiO_2 (HMDSO/O_2 = 1:12) and the third 40 µm water-glass coating the peel front propagated through the water-glass coating preferably.

Optical microscopic pictures present differences between polymer and coating side after peeling were represented. Figure 3.16a represents PE sample thick coated with water-glass the polymer surface shows cohesive failure within the water-glass layer. On the other side, Figure 3.16b shows the surface of PS sample coated with pp (HMDSO:O_2=1:12) where the peel front propagates along the interface between the tape and the coated polymer surface.
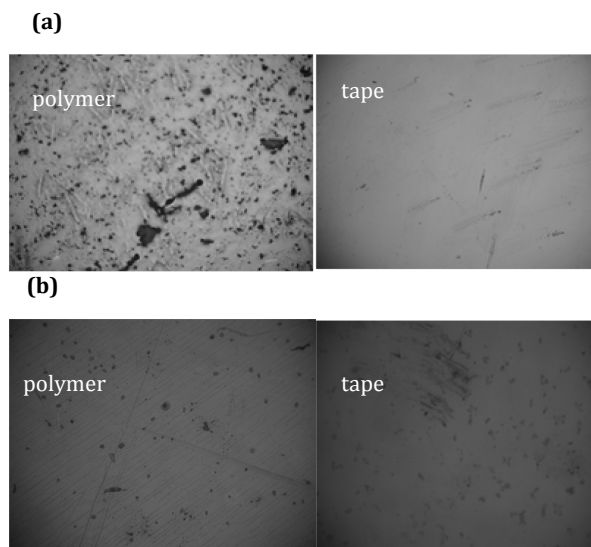
Figure 3.16 Optical microscopic picture of (a) PE and coating (HMDSO: O_2 =1:12) side after peeling (b) PS and coating (HMDSO: O_2 =1:12) side after peeling

XPS analysis of peeled surfaces of all types of polystyrene-SiO_2- water glass composites showed that peeling did not occur along its interface to SiO_2 because the characteristic shake up satellite of polystyrene was not found. The peeling was found to propagate between tape used for peeling and SiO_2 layer (0.5 µm) for samples with and without oxygen plasma pre-treatment or allyl alcohol plasma polymer deposition, thus, the full peel strength could not be measured. Optical micrographs confirm homogeneous peeling indicating failure between undestroyed, well-adhering coating and the tape seen in Figure 3.16b.

Thus, PE composites show cohesive failure within a near-surface layer, PS composites with SiO_2 were not peelable.

3.1.8 Contact angle

Table 3.1 represents the contact angles of the pure polymers and those after modification by exposure to the oxygen plasma also for coated HMDSO and HMDSO/O_2 = 1:12 samples. The contact angle of O_2 plasma exposed PE and PS were strongly reduced in comparison to the blanks ones. O_2 plasma changes the polymer surface from hydrophobic to hydrophilic character. The surface energy of plasma-oxidized polyethylene was increased by about 7 mN/m and that of polystyrene by about 18 mN/m. The HMDSO layer shows a very low surface energy (17 mN/m) but the addition of oxygen (HMDSO/O_2 = 1:12) increased it slightly to 24 mN/m as expected for a siloxane-like structure with a few silanol groups responsible for the polar contribution to the surface energy, which was also shown by the NMR experiments.

Table 3.1 Contact angles surface properties measurements

	Contact Angle[CA°]			Total Surface Energy [mN/m]	Disperse contribution [mN/m]	Polar contribution [mN/m]
	H_2O	EG	DIM			
PE	98	71	61	27,8	27,33	0,47
PE/O_2	79,7	47,4	53	34,11	28,6	5,51
PS	82,3	58,3	45,7	34,54	31,53	3,01
PS/O_2	40,6	30,4	36,3	52,63	23,32	29,32
HMDSO	103,1	90,3	75,3	17,83	17,06	0,76
HMDSO/O_2=1:12	84,7	68,3	67,2	24,87	18,67	6,2

*EG= Ethylene glycol
DIM= Diiodomethane

3.1.9 Flammability tests

Silicon and silicates are well known fire retardants and appear to work by a protective surface layer mechanism [159, 160]. Flammability tests according to DIN 4102-1 were used [161]. The presence of thick water-glass layers leads to significant improvements in the anti-fire behaviour of the modified polymers, while the complexity of a real fire situation makes it very difficult to predict the overall fire performance from laboratory tests. The results are summarized in Table 3.2.

Table 3.2 Flame test according to DIN 4102-1

Sample	Time to ignition [s]	Burning behavior
Pure PS	5	Dripping
PS + 1 μm HMDSO:O_2=1:12 + 5 μm Wg	8	Dripping after 23 s cracking could be heard
PS + 1 μm HMDSO:O_2=1:12 + 20 μm Wg	14	No dripping cracking could be heard
PS + 1 μm HMDSO:O_2=1:12 + 40 μm Wg	20	No dripping cracking could be heard
PS + 20 μm Wg	15	Sample turns white and cracking could be heard
PS + 40 μm Wg	20	Sample turns white and cracking could be heard
Pure PE	2	The flame tears at 5 s and then dripped at 8 s.
PE + 1 μm HMDSO:O_2=1:12 + 5 μm Wg	2	The sample burned with low flame, no dripping
PE + 1 μm HMDSO:O_2=1:12 + 20 μm Wg	5	No dripping
PE + 1 μm HMDSO:O_2=1:12 + 40 μm Wg	7	No dripping
PE + 20 μm Wg	10	No dripping
PE + 40 μm Wg	20	No dripping

The results reveal much progress in the thermal properties combined with significant improvement in flameout time and flame retardancy of all the samples coated with well-adherent layers of water glass. The visual observations of the flame tested samples showed that unlike pure polymers, which show dripping during flame test, a white residue is formed (probably attributed to SiO_2 and its partially hydrated forms) and a crackling was heard [162]. Figure 3.17 represents a sample before and after burning.

(a) **(b)** **(c)**
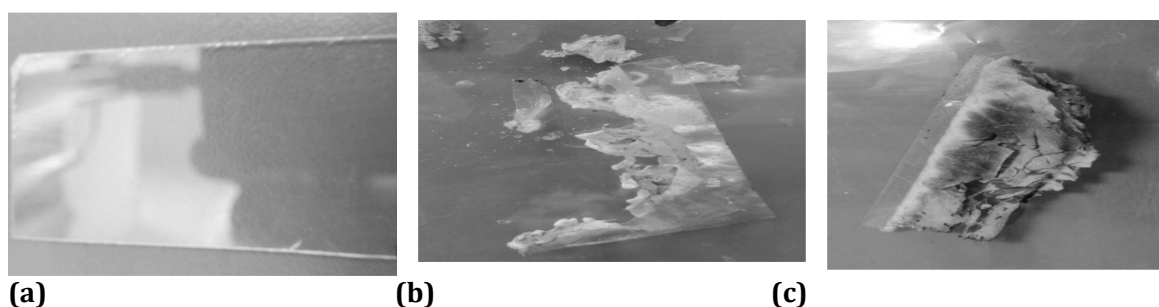
Figure 3.17 Sample coated with thick coated water-glass before burning (a) and after fire test (b,c)

All the samples take much more time to ignite if compared with the virgin uncoated polymers and the area where the flame hits the specimens turns white. PS and PE samples show no dripping and all PE samples keep its shape after burning. From both the flame tests and the TGA analysis can be concluded that well adhering coatings of polymers with siloxane-like layers of at least 40 μm thicknesses are required for promoting efficient flame retardancy. Without adhesion improving by $HMDSO/O_2$ intermediate layers or other plasma polymers or oxygen plasma pre-treatment the siloxane-like layers do not withdraw the internal stress produced by flaming.

3.1.10 Summary of results of SiO2 layers

SiO_2 films have been deposited on PS and PE substrate by plasma polymerization of HMDSO in presence of oxygen for improving the adhesion properties of SiO_2-like coatings onto polyolefins. The effect of different plasma parameters on deposition rate of HMDSO and elemental composition of the deposited films have been investigated in detail. The large carbon content in films deposited from pure HMDSO was efficiently reduced by the addition of oxygen to the plasma, which allows concluding the formation of silicon oxide like-layers with a composition of $SiO_{\sim 1.9}$. This dominant siloxane structure and the existence of silanol groups, important for adhesion promotion, were evidenced by NMR and FTIR-ATR. Additionally, coatings with water-glass layers without pre-treatment were not effective but in combination with the plasma-promoting HMDSO–SiO_2 layers these layers great fire-retardant potential. The adhesion, thermal and fire retardant properties of such plasma deposited and SiO_2-like coatings were studied.

Well-adherent layers could be produced by combination of plasma coating and subsequent deposition of water glass by dipping into solutions of it. The locus of peeling of such thick multi-layers was found to be within the SiO_2/Na-silicate (water-glass) layer for PE. PS composites with plasma deposited intermediate $SiO_{\sim 1.9}$ layers could not be peeled. The fire retardancy was significantly changed by the siloxane-like layer but high significance needs layer thickness of at least 40 μm. Details of flame mechanism and the role of cracks in the layer are planned to be investigated.

3.2 Deposition of N-rich fire retardant layer

3.2.1 General demands of well-adherent fire-retardant melamine polymer layers by plasma polymerization and dip-coating

Zeinab R. Farag, Jörg F. Friedrich, Simone Krüger, Journal of Adhesion Science and Technology, **2014***, 28(21), 2113-2132.*

N-rich compounds can release nitrogen or ammonia in case of flaming which act diluting and condensing under char formation. Melamine and its resins are successful examples of fire-retardants. Melamine is also able to form ionic bonds to polyphosphates, another efficient flame retardant. Released ammonia reacts to water and N-oxides in the flame under scavenging oxygen within the flame. To fulfill such action the melamine resin coating should have a proper adhesion to the polyolefins, here accomplished by plasma polymer deposition of adhesion-promoting layers onto the polymer substrate as interlayer between the polyolefins and the melamine resin.

3.2.2 Plasma polymerization of allylamine and allyl alcohol

100 nm of adhesion promoting layers of plasma polymerized allylamine (ppAAm) or allyl alcohol (ppAAl) films were deposited onto polyethylene and polystyrene substrates. The mass of the deposited polymers has linearly grown with deposition time as shown in Figure 3.18; the deposition rate was constant for all the time.
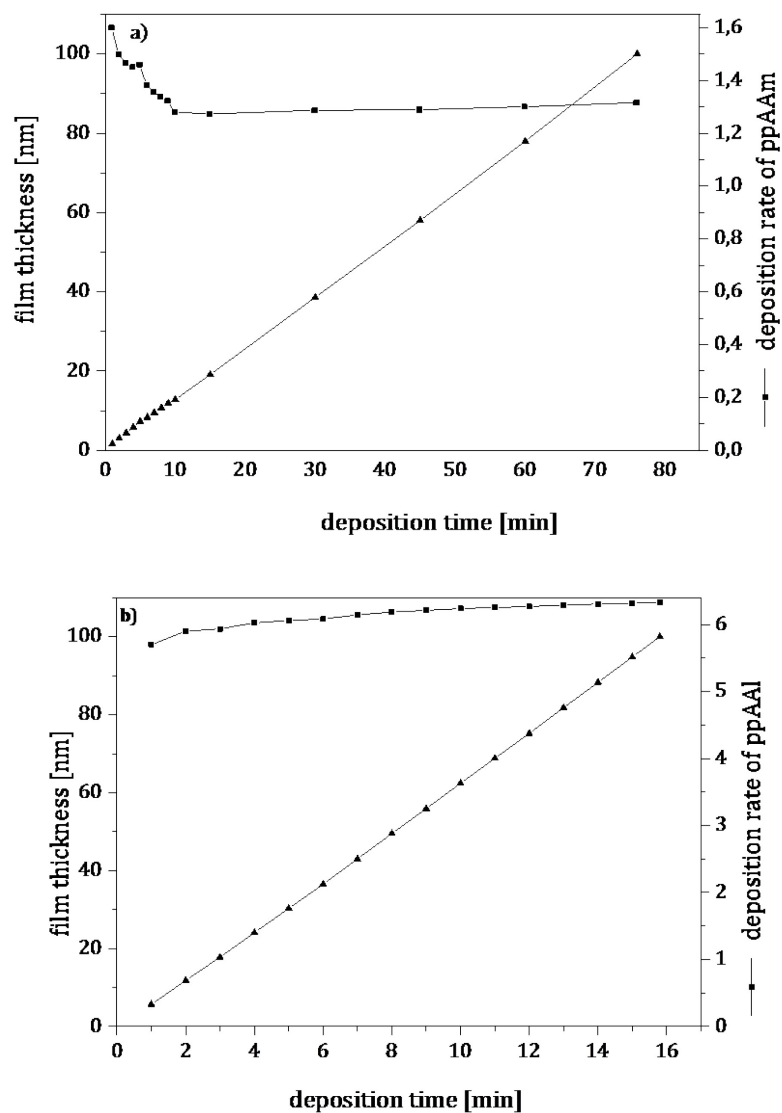
Figure 3.18 Deposition rates of a) ppAAm and b) ppAAl (100 W, 10 Pa, 0.1 duty cycle, and 10³ Hz repetition frequency of pulsed plasma)

3.2.3 Characterization of plasma-deposited poly(allylamine) and poly(allyl alcohol) layers

The chemical structure and elemental composition of the deposited ppAAm and ppAAl layers was investigated using FTIR-ATR and XPS.

After derivatization with pentafluorobenzaldehyde (PFBA) the number of free amino groups in the ppAAm layer amounts 10-12% NH_2/C, i.e. 1/3 of the theoretical concentration in a regularly structured ppAAm.

Figure 3.19 represent the FTIR-ATR spectra of ppAAm and ppAAl deposited on PS and PE, respectively. A strong and broad absorption band was observed in the region of 3500–3100 cm^{-1} which can be assigned to the N-H stretching vibrations of amino groups consisting of asymmetric (3368 cm^{-1}) and symmetric (3290 cm^{-1}) ones. The second important band appears around 1660 cm^{-1} and can be attributed to the bending mode of amides ($v_{C=O}$, "amide I") which should be principally absent. However, a side-reaction may be the reason for it. Primary amine groups are situated around 1610 cm^{-1} (δ_{N-H}, scissor, "amide II"). The band at 1072 cm^{-1} is attributed to the C-N stretching vibration and that at 810 cm^{-1} to the NH_2 wagging mode. No peaks appear in the 2100 – 2250 cm^{-1} region which indicates the absence of nitrile (-C≡N) or isonitrile ($-N^+≡C^-$) groups. The OH stretching vibration bands are expected to overlap by the neighboring amine peaks around 3500 cm^{-1} [163]. The presence of C=O groups is evident by appearance of its absorption near 1700 cm^{-1} ($v_{C=O}$). On the other side, the deposited ppAAl layers show a stretching absorption band at ≈3370 cm^{-1} corresponding to OH groups.
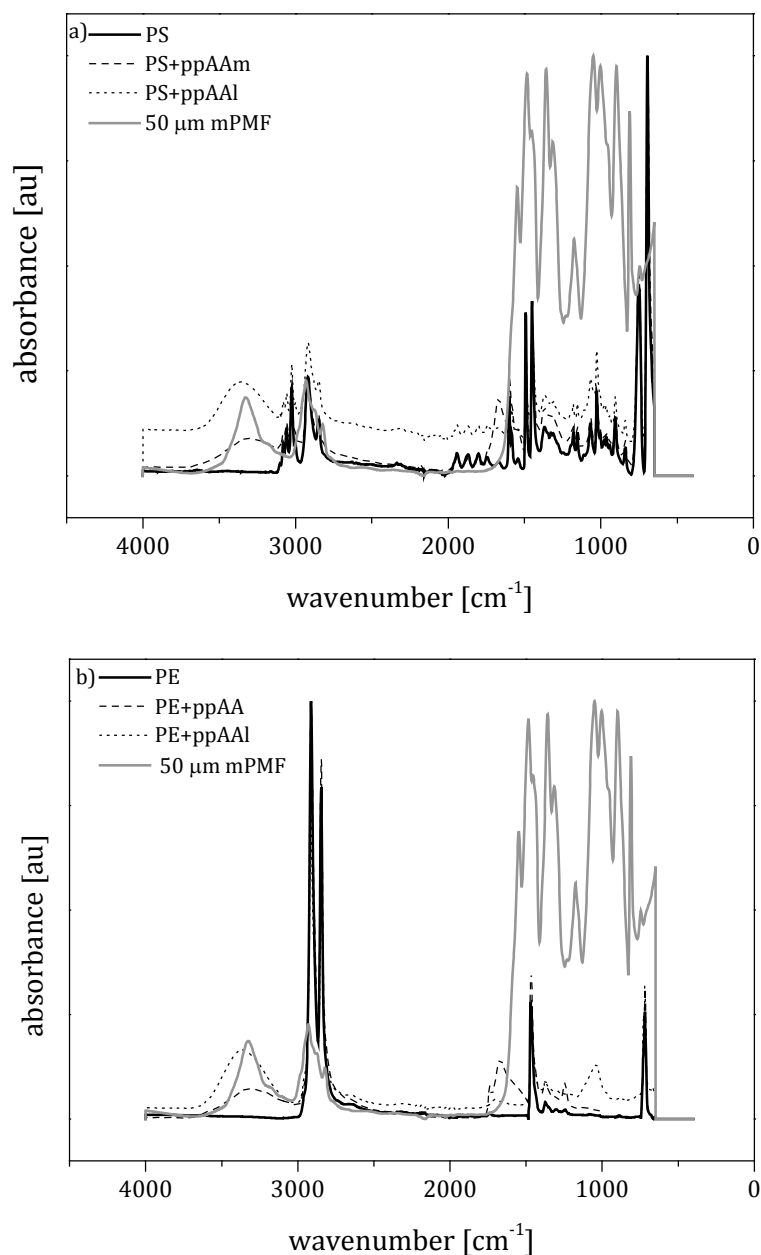
Figure 3.19 FTIR-ATR spectra of ppAAm and ppAAl deposited onto a) PS and b) PE

In order to see how the mPMF top layer is bonded to the adhesion-promoting ppAAm or ppAAl interlayers thick mPMF coated PE and PS samples were washed two times ultrasonically for 15 min each in 1-butanol to dissolve the non-bonded mPMF, followed by ethanol extraction to remove residual 1-butanol. After drying FTIR-ATR and XPS

analyses were performed. The spectral analysis after extraction shows that the melamine nucleus could not be completely extracted because the melamine-characteristic hetero cycle was still present. Figure 3.20 shows a N 1s peak in the XPS spectrum of a extensively washed (extracted) polymer sample coated with mPMF and ppAAl as primer; XPS spectra of mPMF with ppAAl and of the extraction product is also given. In case of significant remained mPMF resin, it was interpreted as strong, probably chemical fixation to the polymer surface. Without primer layer mPMF could be extracted completely.
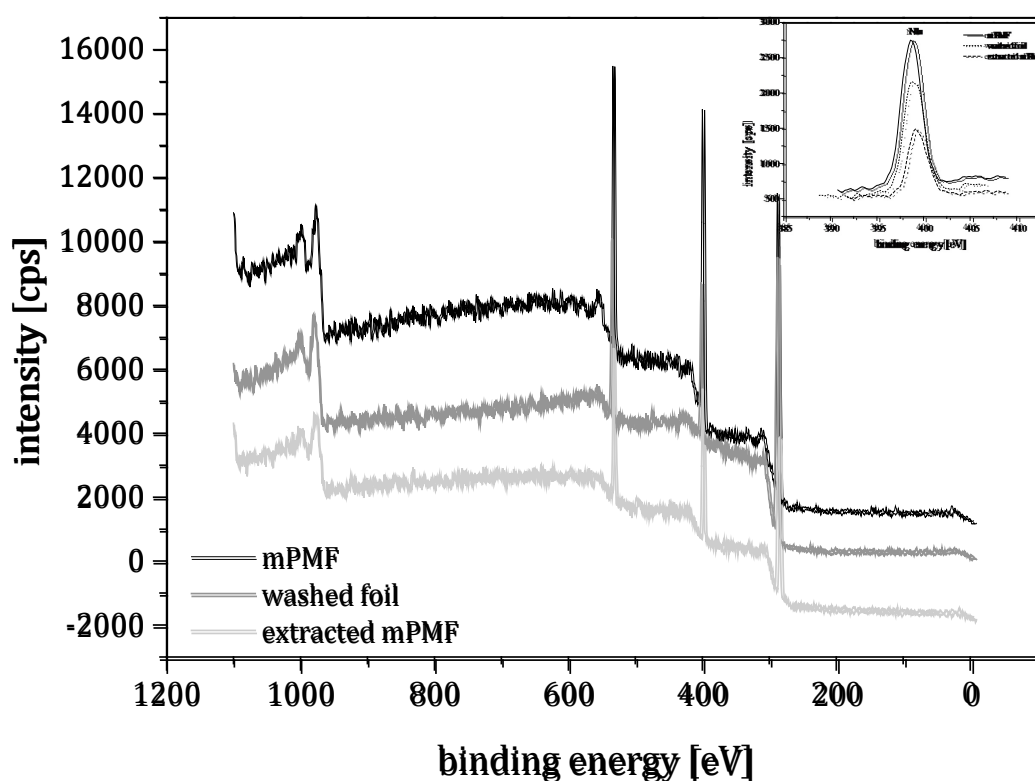
Figure 3.20 XPS of the extraction product of thick coated polymer pre-treated with ppAAl

The tentative chemical mechanism of chemical bonding of mPMF is presented in Figure 3.21.
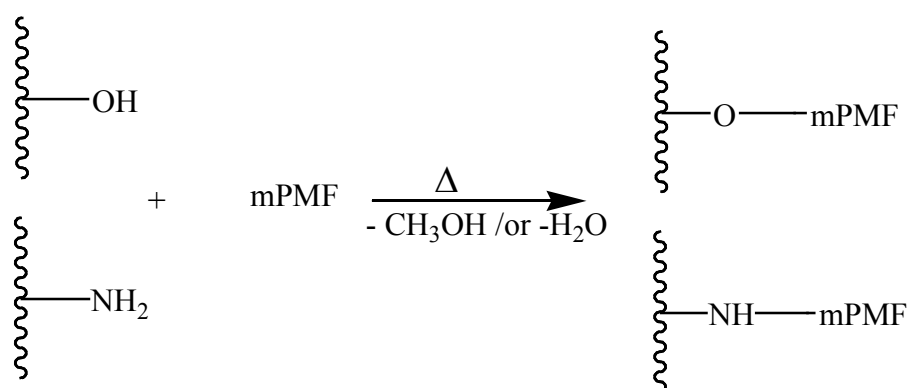
Figure 3.21 Chemical bonding between mPMF and ppAAm and ppAAl pre-treated polymers

The XPS elementary analysis presented in Figure 3.22 shows the ppAAm and of the product of ppAAm after derivatization with pentafluorobenzaldehyde (PFBA). Oxygen atoms which are not present in the monomer are probably incorporated in the polymer from residual oxygen in the deposition chamber and by oxidation reaction of C radical sites after exposure to the ambient atmosphere.
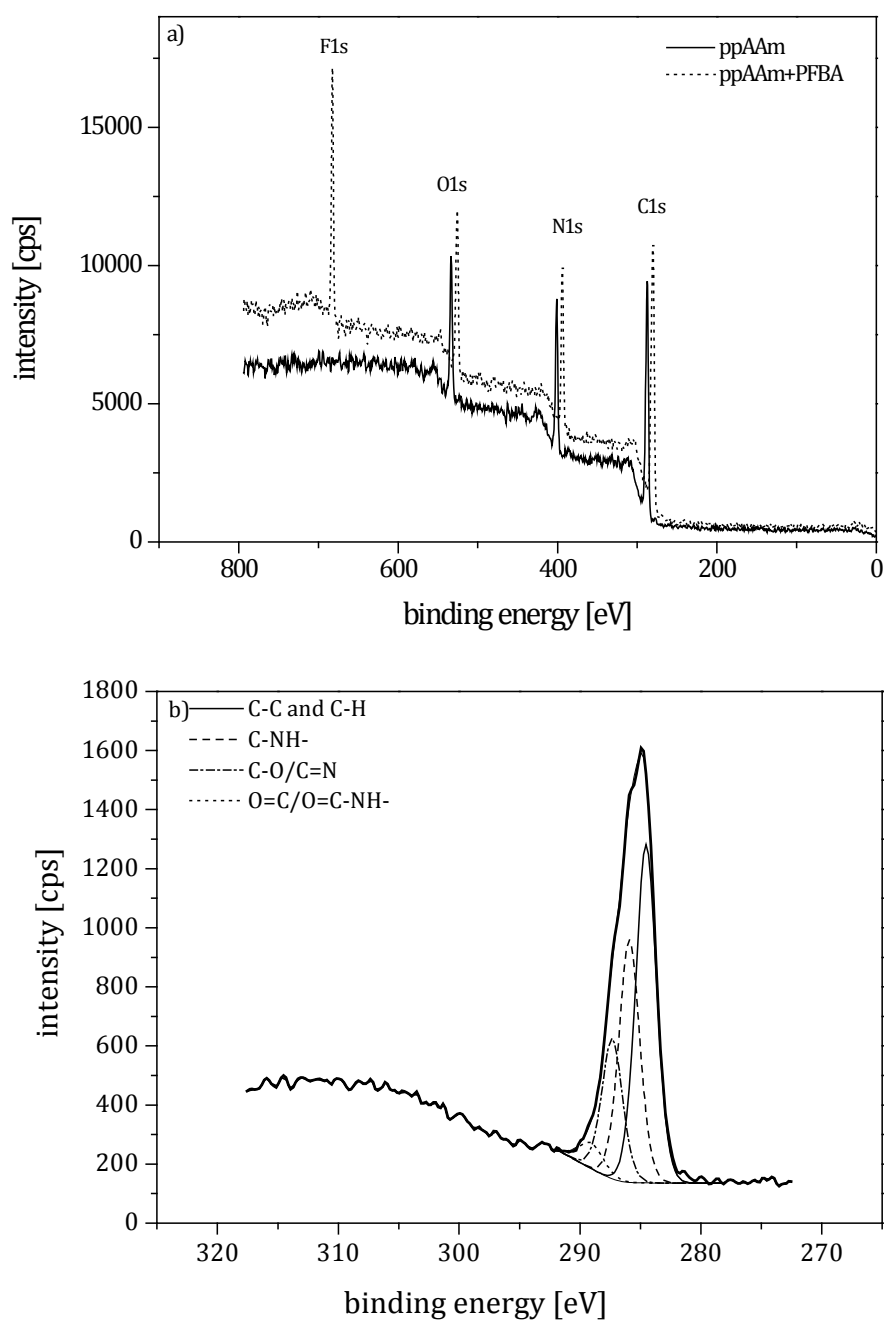
Figure 3.22 XPS of a) ppAAm and the derivatized PFBA b) decomposition of C 1s of ppAAm

Survey scan XPS spectra show the C1s, O1s, and N1s peaks as well as after derivatization of primary amino groups with PFBA the F 1s peak Figure 3.22a.

Figure 3.22b shows the fitting of the C 1s peak into C- C, C-H bonds at 284.7 eV [163, 164], C-NH$_2$ groups at 285.9 eV, superposed by C-O features (undesired post-plasma side

reaction with oxygen from air) at 286.5 eV, and carbonyl (C=O) and/or amide (O=C-NH-) groups at 287.8 eV.

The chemical environments of N atom on the polymer surface can be derived from N 1s peak fitting as shown in Figure 3.23. The high resolution N1s spectrum is fitted into three components: the low energy component at 398.2 eV is assigned to >C=N-, -C≡N or –NH$_2$ groups, while the peak at a binding energy 399.3 eV is assigned to the amide group (CO-NH-) and the peak at 400.3 eV is due to the protonated amine (-NH$_3^+$) [165, 166].
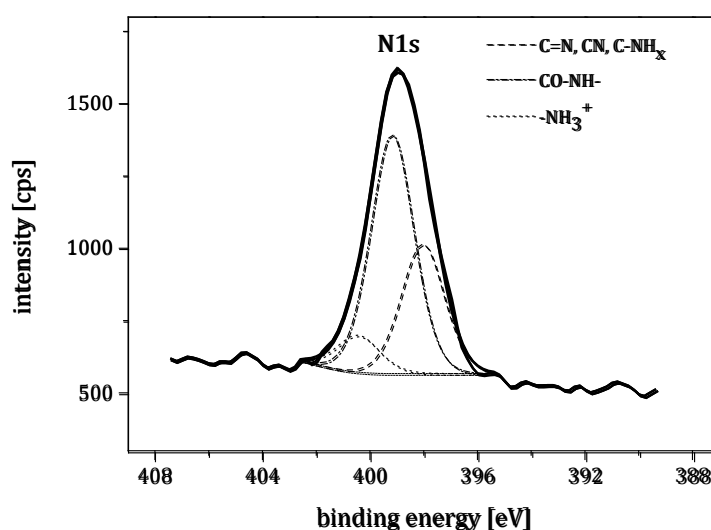
Figure 3.23 Fitted N 1s peak of ppAAm

The XPS survey scan of ppAAl and the derivatized reaction product with triflouro acetic acid anhydride TFAA are represented in Figure 3.24a. fitting of C1s peak of ppAAl shows C- C, C-H at 284.7 eV, C-O at 286.3 eV, C=O at 287.5 eV, and carboxyl (COOH) at 289 eV [167] as seen in Figure 3.24b.
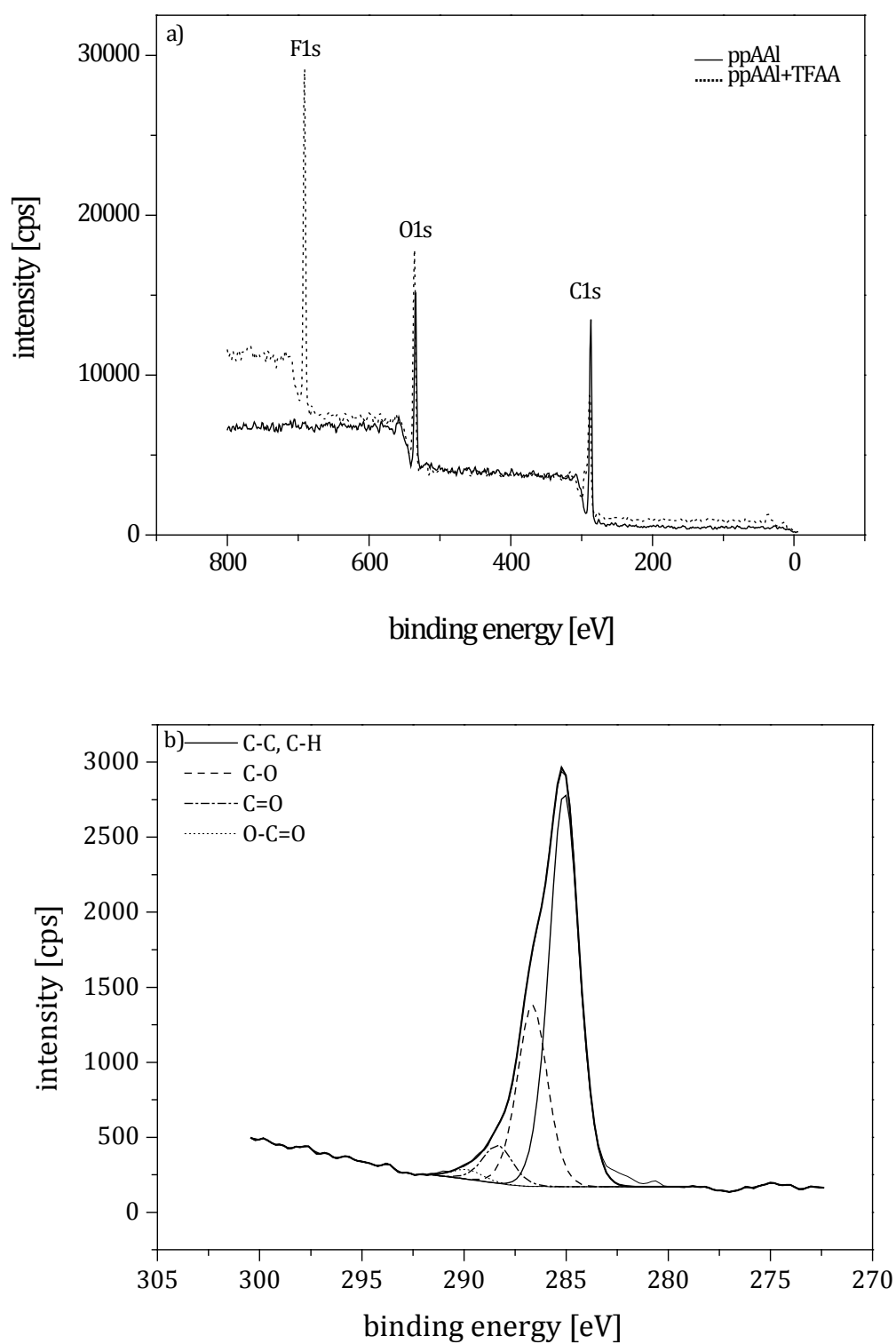
Figure 3.24 XPS of a) ppAAl and the derivatized TFAA b) decomposition of C 1s of ppAAl

3.2.4 Preparation and characterization of the thick melamine-formaldehyde layer

Here, 100 nm thick ppAAm or ppAAl plasma polymer layers were used as adhesion promoting primers for additional coating of thick flame retardants layers made from melamine formaldehyde, which should be deposited simply by dipping. Thus, thicker layers of methylated poly (melamine-co-formaldehyde) with thicknesses of 10-50 µm were deposited onto PS and PE pre-coated with ppAAm or ppAAl layers.

Figure 3.19 have always represented the IR spectra of the plasma- and dip-coated PS and PE polymers as discussed before. The XPS C1s and N1s peaks of the deposited mPMF layer are represented in Figure 3.25 [168].
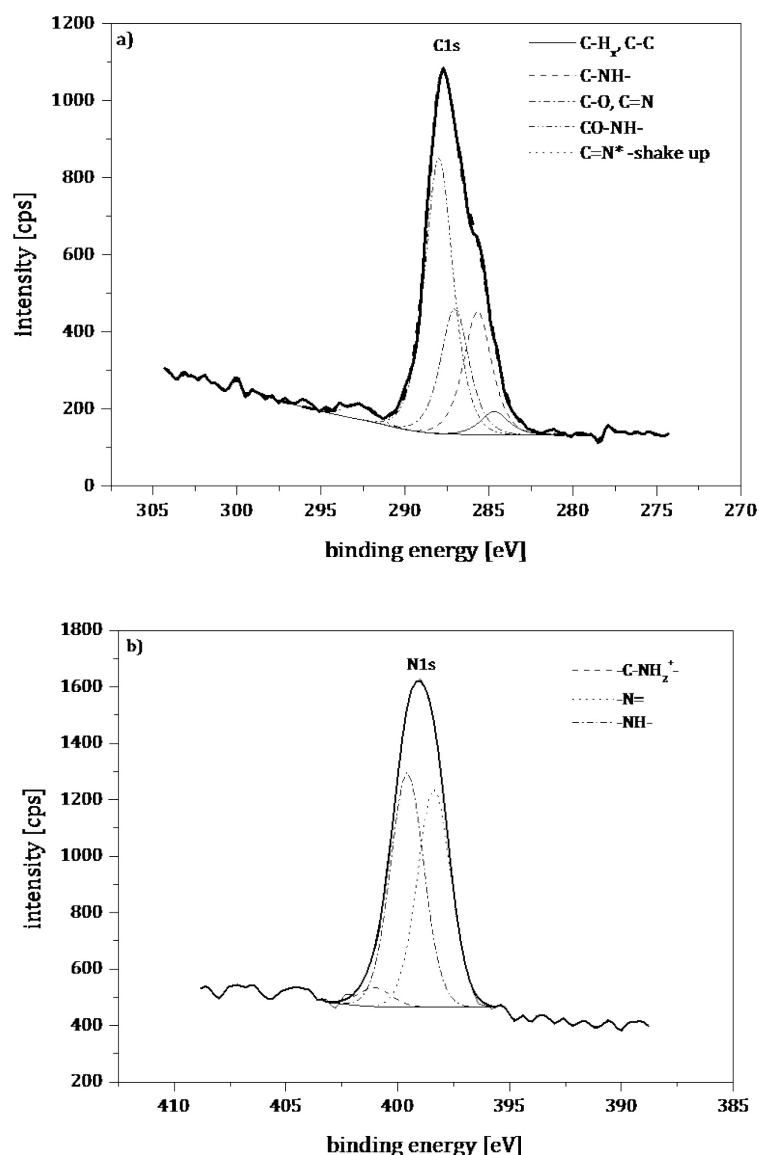
Figure 3.25 XPS of mPMF a) C 1s and b) N 1s peaks

C-C, C-H species with a binding energy of 284.7 eV were found, C-NH- at 285.7 eV, C-O and C=N- at 286.3 eV, CO-NH- and N=C-N at 287.3 eV and O-C=O at 288.0–289.0 eV. The N 1s peak was attributed to =N-, NH- and NH_2 at 399.7 eV and amide groups ($CO-NH_x$) and/or protonated amino groups ($-NH_2^+-$, $-NH_3^+$) at 400.7 eV. It should be added that the O1s peak could be fitted into 3 components N-C=O ($CO-NH_x$) at 531.2 eV, >C=O and at 532.5 eV as well as O=C-$\underline{O}$ at 533.6 eV following XPS measurements on melamine-

formaldehyde resins [169]. It could be shown that all these peaks could be found again in the thick mPMF coating.

3.2.5 Peel strength of the deposited layers

The peel strengths of mPMF and (ppAAm, ppAAl) layers on PE and PS were also investigated Figure 3.26. The substrate polymers were first modified with oxygen plasma, then thin coated with ppAAm or ppAAl as adhesion promoters and finally covered with a thick mPMF layer by repeated dipping into mPMF solutions. It should be reminded that the peel test measures the peel strength of the double-faced adhesive tape during its removing from the mPMF layer. Either it sticks parts of the coating and indicates interface or cohesive failures or it peels from the mPMF without any failure of the laminate.
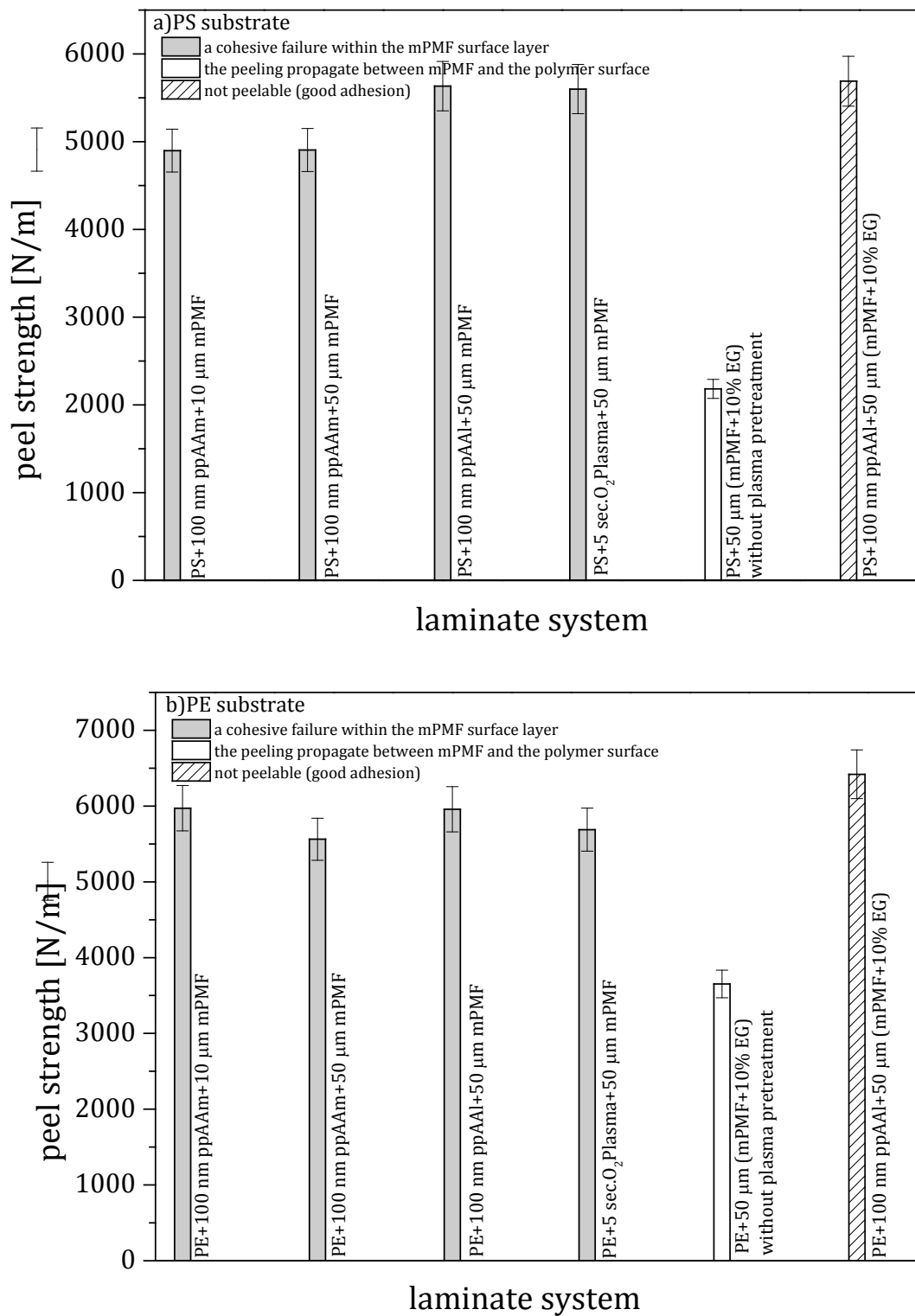
Figure 3.26 Peel strength of a) PS and b) PE coated with mPMF layers

The peel strength of PS samples after preliminary exposure of the polymer foils to the O_2 plasma or deposition of 100 nm ppAAl increases the peeling strength as seen in Figure 3.26a.

Coated PE samples showed also improvement in peel strength of the deposited layers if compared with that's of polymer foils coated with mPMF without plasma pretreatment. Marginal lowering in the peel strength of PE sample modified with ppAAm and 50 μm mPMF may be attributed to the accurateness of measurement. Modification of the surface with oxygen plasma or ppAAl pre-layer improves the adhesive bond strength slightly.

The XPS determined elemental compositions on both sides of the peeled surfaces of all types of polymer composites showed in each case a cohesive failure within the mPMF surface layer, i.e. the cohesive strength of the melamine copolymer decides the peel strength. Besides XPS results; micrographs confirm also peeling within the mPMF layer.

In order to avoid the cohesive failing within the mPMF layer in the PE-mPMF and PS-mPMF systems and therefore to improve the adhesion mPMF was additionally crosslinked. For this purpose a solution of mPMF and 10% of ethylene glycol (EG) as crosslinker was heated for 2 h at 80°C and then immediately used for dipping before gelation.

A significant improvement in the peeling strength was observed by this procedure as shown in Figure 3.26. Moreover, XPS analysis of the peeled PE and PS samples, which were thick-coated with mPMF + 10% EG, shows no residual nitrogen on the surface of peeled tape, i.e., the tape was peeled from the laminate, the cohesion properties of the melamine layer were improved, and the laminate remains intact. Now, the peel front has propagated along the interface of coating and tape as shown by XPS analysis Figure 3.27,

It represents the N1s peak of the surface of the peeled laminate as well as of the peeled tape. It is evident that no residual mPMF was remained on the tape.
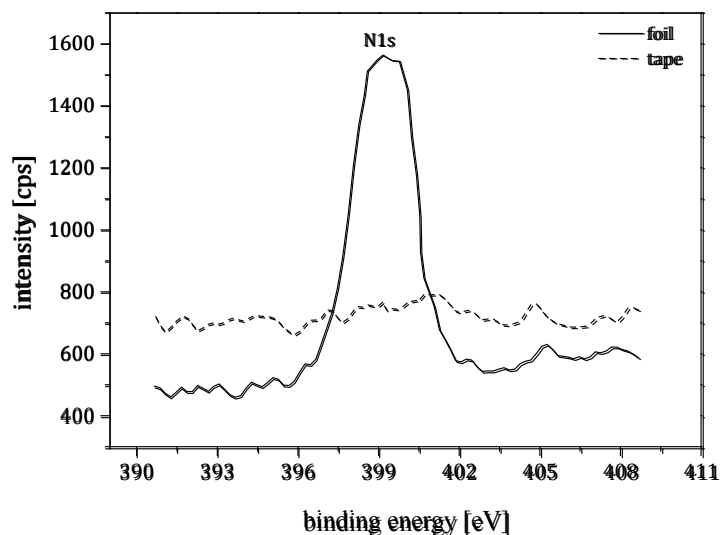
Figure 3.27 N 1s peaks of peeled PE laminate consisting of the PE substrate which was coated with (mPMF + 10% EG), showing the XPS analysis of the peeled tape and laminate foil sides

considering optical micrographs of peeled tape and coating surfaces after peeling the same conclusion can be drawn inspecting the differences between the coating with mPMF and mPMF + 10% EG as presented in (Figure 3.28).
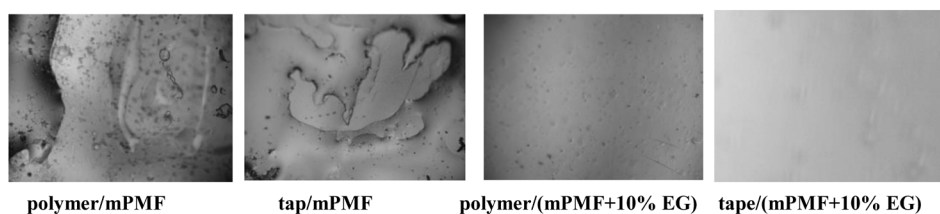
Figure 3.28 Optical microscopic pictures of mPMF and mPMF/10% EG thick layers

3.2.6 Thermal behavior of poly melamine layer coated polymers

The thick mPMF coated polymer composites as well as the pristine polymer substrates were inspected also by TG analyses as shown in Figure 3.29.
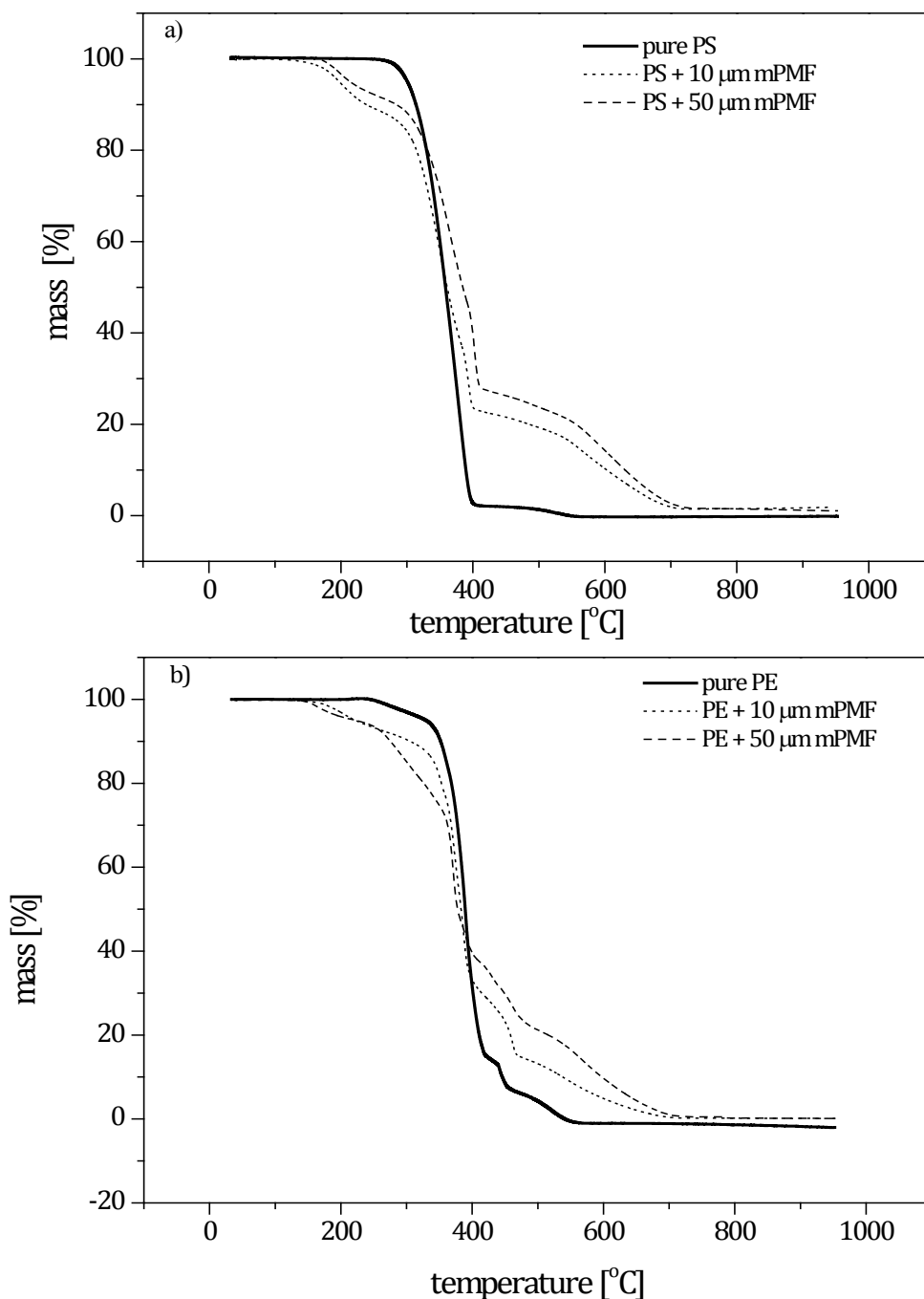
Figure 3.29 TGA of a) PS and b) PE laminates

TGA curves show that unlike the pure polymers, which starts to decompose at about 300°C, the polymer composites starts to decompose at lower temperature. On the other hand TGA curves reflect also an improvement in thermal resistivity accompanied by lowering the weight loss at higher temperature in combination with increasing of the remaining residue.

Derived from the TGA thermograms four degradation ranges could be defined for the polymer composites [170]. The first is in the range of 150°C up to ≈200°C this weight loss is due to the removal of water, the second is in the range of 200-350°C which corresponds to the elimination of formaldehyde. From 350°C near to 400°C there is the scission of the methylene bridges which are stable up to 350°C. Finally and beyond 400°C the thermal degradation of the triazine ring begins [170]. These interpretations were determined by analysis of the emitted gases during the heating-up of samples using FTIR spectroscopy.

This stabilizing effect of melamine resin coatings may be attributed to the barrier effect of the deposited mPMF layers towards oxygen and to the char formation. Moreover, the emission of such inert diluent gases as ammonia supports the fire retardancy of such coating too.

It is evident considering the FTIR spectra of the gaseous decomposition products depicted in Figure 3.30 (red line) that the emission of ammonia at about 398°C is significant.
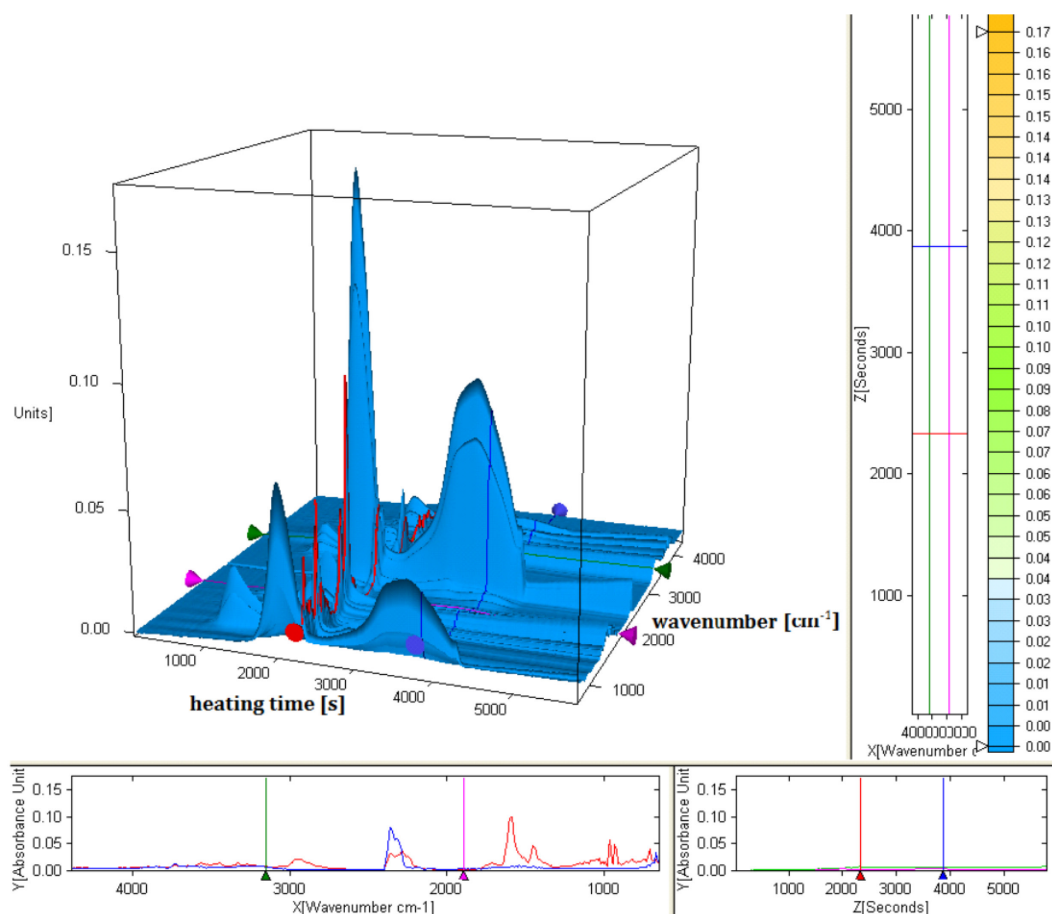
Figure 3.30 FTIR spectra of the emitted (NH₃) gas during thermo-gravimetric test of PS thick coated with mPMF

3.2.7 Flammability tests

The fire behavior of building materials were assessed according to DIN 4102-1 again [161]. Generally, the presence of thick mPMF layers lead to significant improvements in the anti-fire behavior of the modified polymers. However, the complexity of a real fire situation makes it very difficult to predict non-ambiguously the overall fire performance from laboratory tests. Nevertheless, the laboratory tests give a useful hint and tendency to expect flame retardancy. The results are summarized in Table 3.3.

Table 3.3 Flame test results of the modified PS and PS samples

Sample	Time to ignition [s]	Burning behavior
Pure PS	Ignited too fast in 0.5 s	Dripping
PS +10 µm mPMF	2	Completely burned after 3s In 20s Dripping without burning Flame out after 32 s
PS +50 µm mPMF	2	Dripping without burning Flame out after 36 s
Pure PE	2	The flame tears at 5 s then dripped at 8 s
PE + 10 µm mPMF	4	Burned with high flame No dripping Flame out after 45 s
PE +50 µm mPMF	4	No dripping Flame out after 56 s

The results show an improvement in the fire-retardant properties of the modified samples. The visual observations of the flame tested samples showed that pure polymers show dripping and fast burning during flame test while PS composites dripped only after a long time without burning. PE composites showed no dripping and large improvement of the flame out time. Figure 3.31 represents a coated polymer sample before and after flame test. Nevertheless, effective flame retardancy requires thicker mPMF layers or additional thick inorganic layers. 50 µmPMF layers alone achieve not the demanded fire barrier.
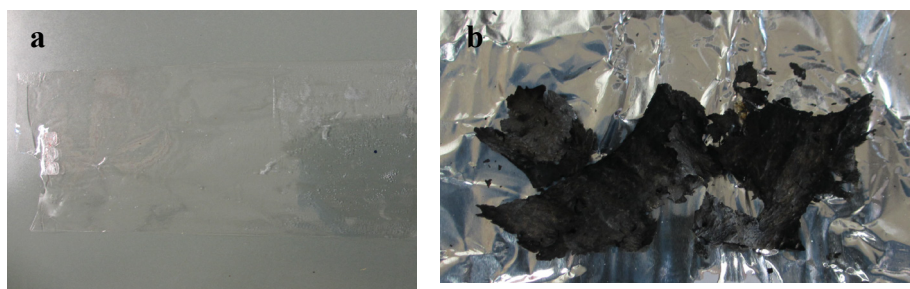
Figure 3.31 A thick-coated mPMF sample pre-coated with ppAAl a) before and b) after burning

The preliminary modification of the polymer surface either with oxygen plasma, ppAAm or ppAAl had no significant influence on the results of fire tests as expected. Their introduction was owing to improving the adhesion of coatings.

3.2.8 Summary of results of mPMF layers

Thick coating (10-50 µm) with melamine pre-polymers and crosslinked melamine resins using plasma polymer as adhesion promoters had a positive effect on flame retardancy of polystyrene as well as polyethylene. Using different kinds of PE and PS plasma pretreatment and plasma polymer coating strongly adherent fire-resistant coatings could be manufactured as peel-strength results had shown. It could be achieved that different thermal expansion coefficients of coating and polymer substrates were balanced by the deposited thin plasma polymers. At direct exposure to flames no thermal-initiated peeling or cracking of mPMF coatings were observed. Moreover, it seems to be evidenced that chemical bonds between pretreated polymer substrate, plasma polymer, and melamine resin contribute to the peel or lift-off resistance of the flame-resistant coatings during flame exposure.

3.3 Cured melamine systems as thick fire-retardant layers

3.3.1 Aim of curing the resin coating

To increase the mechanical stability of melamine resins as thick coating on polyolefins, as described in the foregoing Section, the resins were cured thus withdrawing better the stress of flaming. The cured and crosslinked layers have an improved mechanical stability and hinder more efficiently the oxygen transport to the polyolefin substrates. Melamine resins possess a high concentration of secondary amino groups ($-NH-CH_2OR$ groups) which are able to be cured at low temperature under strongly acidic conditions [171] using different amine or hydroxyl crosslinkers. The characteristic condensation reaction proceeds via an imino group intermediate [130,172]. Analogous reactions are proposed for the curing of the melamine resin and the co-condensation with hydroxyl containing polymers [173].

Melamine resins are normally unreactive and need high curing temperatures; they react with alkyds, saturated polyesters with high concentration of hydroxyl groups [171]. Some of melamine resins are highly responsive to acid catalysts, keeping the curing temperature below 100°C [170, 174-176]. Curing agents used in these experiments were ethylene glycol (EG), urea and pentaerythritol (PER) which is mainly used as a char former in intumescent flame retardants [177, 178].

3.3.2 Coating preparation

The polyolefin substrates were exposed to oxygen plasma first. Subsequently, 100 nm of plasma polymerized allyl alcohol (ppAAl) film were deposited as adhesion-promoting interlayer. Thick melamine resin layers were deposited by dipping into melamine resin solutions enriched with the crosslinking agent before the thickening of mixture begins.

3.3.3 Characterization of the cured melamine layers

Different curing processes of melamine resin coatings (50 μm) were used. Figure 3.32 represents the FTIR-ATR spectra of the differently cured poly(melamine-co-formaldehyde) resins with many similarities to the uncured melamine resin coatings as discussed in the foregoing Section. The FTIR-ATR spectra shows a strong and broad absorption band in the region of 3500–3100 cm^{-1}, that can be assigned to the N-H stretching vibrations of amino groups consisting of the asymmetric (3368 cm^{-1}) and the symmetric (3290 cm^{-1}) ones. The second important band appears around 1560 cm^{-1} and can be attributed to the triazine-ring stretching band of melamine. The OH stretching vibration bands are expected to overlap by the neighboring amine peaks around 3500 cm^{-1}.
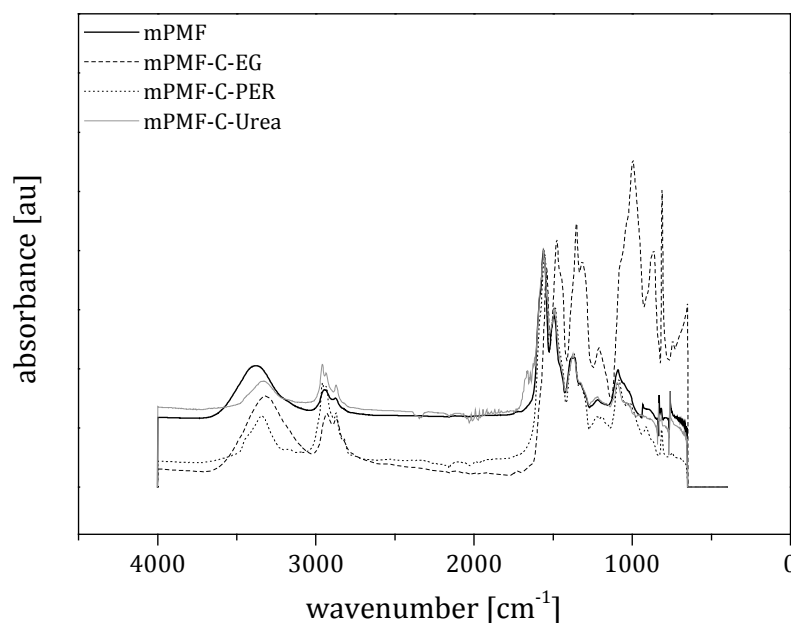
Figure 3.32 FTIR-ATR spectra of the cured Poly(melamine –co-formaldehyde) systems (EG-ethylene glycol; Urea-urea; PER-pentaerythritol)

Using urea the introduction of the carbonyl group at about 1700 cm^{-1} is obvious. On the other hand the intensity of the NH stretching band is decreased as expected after curing. Considering the pentaerythritol hardened coating the increase in the O-H stretching is remarkable as also seen when using ethylene glycol.

The XPS of the cured mPMF layers are represented in Figure 3.33.
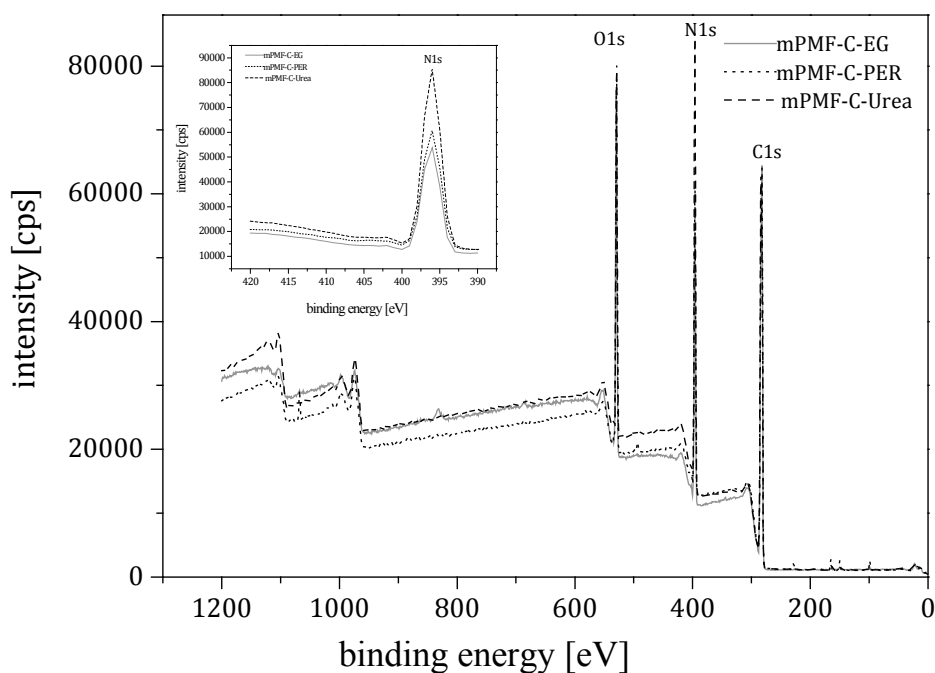
Figure 3.33 XPS of cured Poly(melamine –co-formaldehyde) polymers (EG-ethylene glycol; Urea-urea; PER-pentaerythritol)

It shows the increase in the at.% of N in the mPMF-C-Urea if compared with EG and PER cured polymers.

3.3.4 Peeling strength of the deposited layers

The peel strengths of virgin polymers, coated with mPMF before and after curing were measured Figure 3.34.
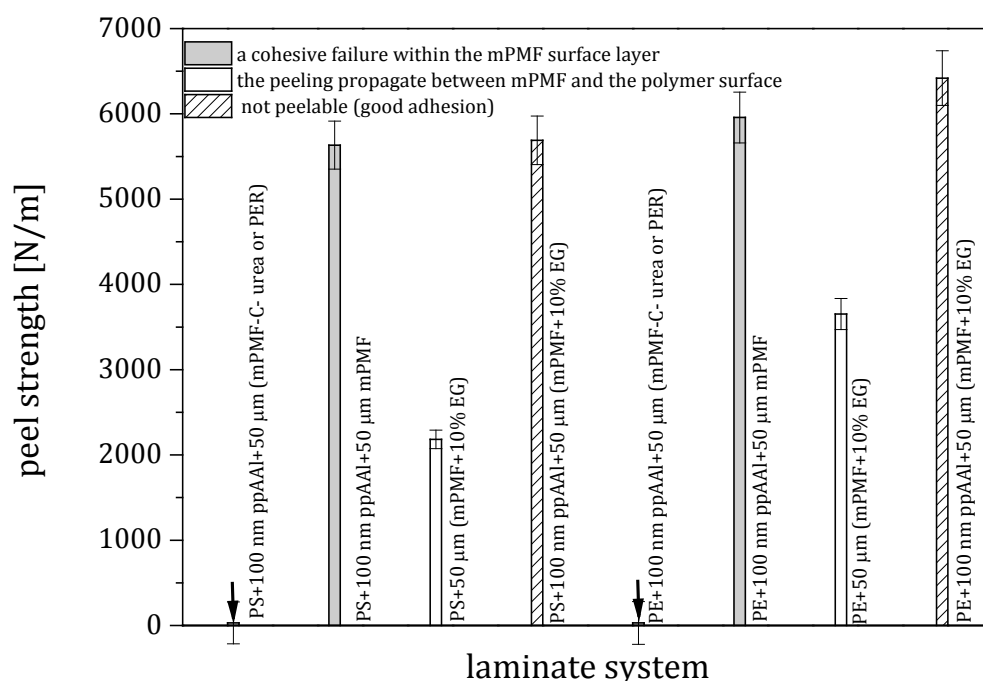
Figure 3.34 Comparison of peel strength results of a) PS and b) PE coated mPMF systems before and after curing

The polymer substrates were first thin coated with ppAAl as adhesion promoter and then covered with a thick Cured poly(melamine-co-formaldehyde) layer.

The XPS analysis of peeled mPMF coated specimens showed in each case a cohesive failure within the mPMF surface layer on both peeled surfaces of the laminate system, i.e. the cohesive strength of the melamine copolymer itself has decided the peel strength.

Curing such melamine polymer with EG, PER or urea was performed in order to improve the adhesion and to avoid the cohesive failing within the mPMF layer in the laminate systems. Thus, indeed, an improvement in the peeling strength was observed as shown in Figure 3.34. Additionally XPS analysis of the two peeled sides of the thick (mPMF-cured-EG) coated PE and PS laminates did not show any residual nitrogen on the peeled surfaces as seen in Figure 3.35 i.e., the cured mPMF coating has improved cohesive strength, remains intact and peeling was impossible from now on. Now, the peel front has propagated along the interface of coating and tape.
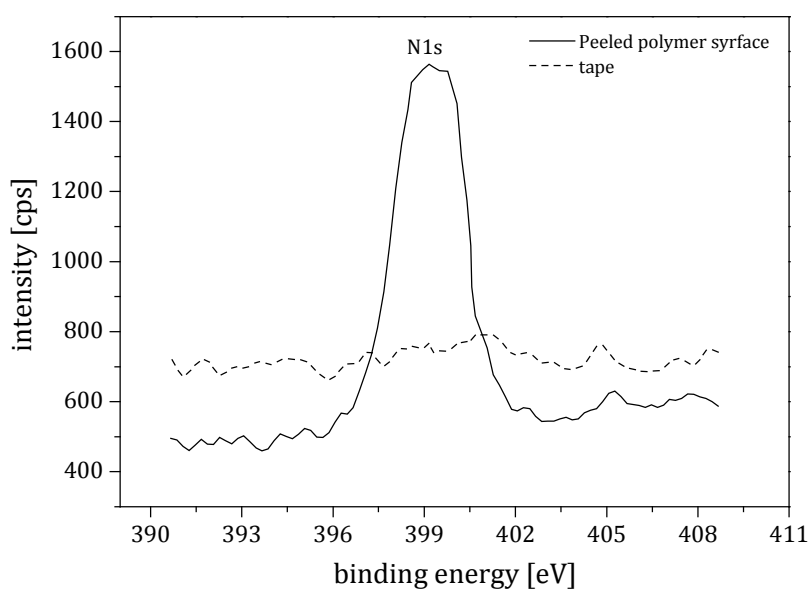
Figure 3.35 XPS of peeled mPMF cured with ethylene glycol

Figure 3.35 represents the N1s peaks of the peeled surfaces of the EG-cured laminate (laminate and tape). It is evident that no residual mPMF was remained on the tape.

On the other hand, PS and PE laminate systems thick coated with mPMF cured with PER or urea were self-peeled. It is assumed that contraction during the hardening process provokes self-peeling.

3.3.5 Thermal behavior of poly melamine layer coated polymers

Cured and non-cured mPMF thick coated polymer composites as well as the pristine polymer substrates were inspected also by thermo-gravimetric analyses as shown in Figure 3.36.
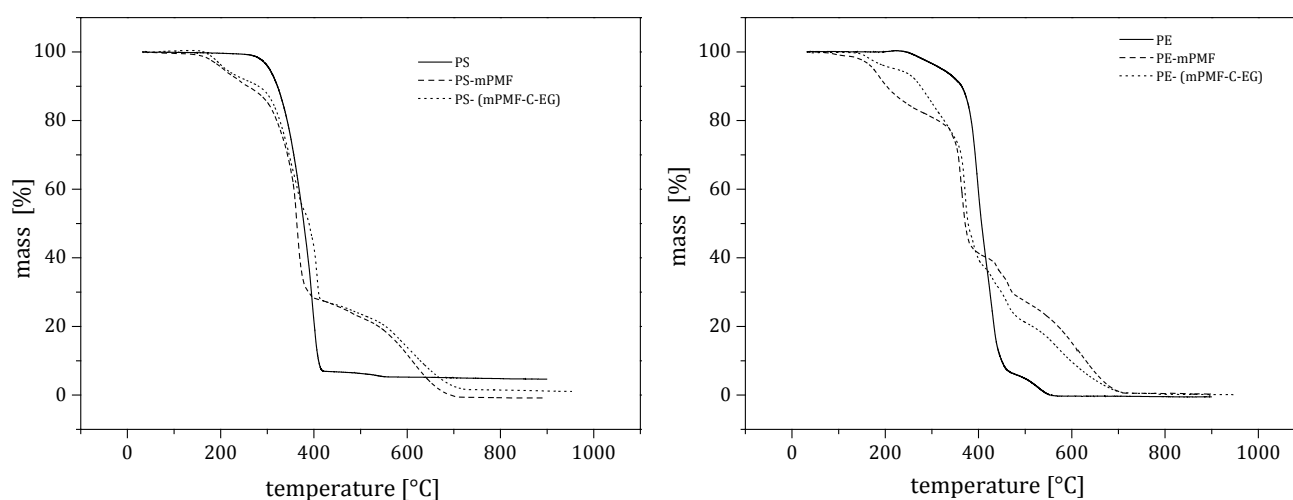
Figure 3.36 TGA of PS and PE thick-coated with cured mPMF systems

TGA curves show that unlike the pure polymers, which start to decompose at about 300°C, the polymer composites decomposed at lower temperature. TGA curves reflect an improvement in thermal resistivity accompanied by lowering the weight loss at higher temperature in combination with increasing the fraction of remaining residue.

3.3.6 Flammability tests with cured mPMF coatings

The fire behavior of thick cured mPMF layers as well as the virgin polymers was measured. The results show a significant improvement in the anti-fire behavior of the modified polymers. However, the complexity of a real fire situation makes it very difficult to predict non-ambiguously the overall fire performance from laboratory tests. Nevertheless, the laboratory tests give a useful hint to flame retardancy. The results are summarized in Table 3.4.

Table 3.4 Flame test results of PS and PE samples coated with cured mPMF

Sample	Time to ignition [s]	Burning behavior
Pure PS	Ignited too fast in 0.5 s	Dripping Completely burned after 3s
PS +50 μm mPMF	2	Dripping without burning
PS +50 μm mPMF-cured-EG	4	No dripping Burned with low flame fire spread slowly Charring
PS +50 μm mPMF-cured-PER	6	No dripping Charring
PS +50 μm mPMF-cured-Urea	7	No dripping Charring
Pure PE	2	The flame tears at 5 s then dripped at 8 s
PE +50 μm mPMF	4	No dripping
PE+50 μm mPMF-cured-EG	6	No dripping Burned with low flame, fire spread slowly Charring
PE+50 μm mPMF-cured-PER	12	No dripping Charring
PE+50 μm mPMF-cured-Urea	5	No dripping Charring

The results show an improvement in the fire retardant properties of the modified samples. The visual observations of the flame tested samples showed that unlike the pure polymers, which show dripping and fast burning during flame test, thick coated PS and PE samples show no dripping and large improvement of the flame out time.

Curing the melamine pre-polymer improves the fire retardant properties further as evident from Table 4. It shows that all the PS and PE thick coated systems with cured melamine layers exhibit no dripping, char formation, and improvement in ignition time of the samples. Samples coated with mPMF-cured-EG burned with low flame and the fire spread slowly during the test. Figure 3.37 represents photographs of coated polymer samples after flame test.

mPMF   mPMF-cured-EG   mPMF-cured-urea   mPMF-cured-PER
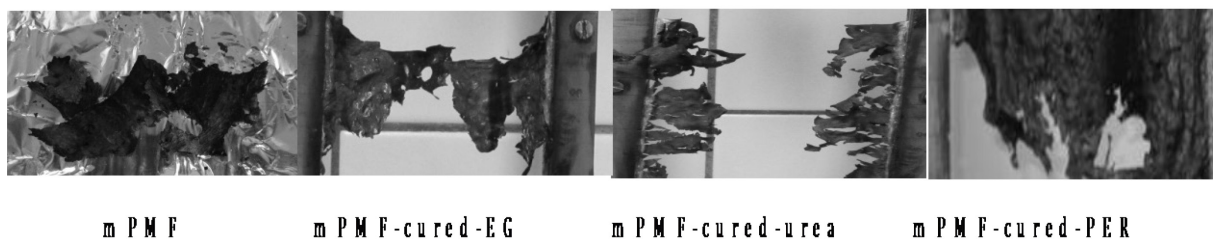
Figure 3.37 Polymer samples thick coated with cured mPMF systems after single flame source test

3.3.7 Conclusion to improvement of fire-retardancy by curing the melamine coatings

Thick coatings with cured melamine resins using plasma polymer as adhesion promoters have a positive effect on flame retardancy of polystyrene as well as polyethylene. Moreover, it seems to be evidenced that chemical bonds between pretreated polymer substrate, plasma polymer, melamine resin and in the bulk of melamine resin (intermolecular crosslinking) contribute to the peel or lift-off resistance of the flame-resistant coatings during flame exposure, at least in case of crosslinking with ethylene glycol.

3.4 Deposition of polyphosphate fire retardant layers

3.4.1 Motivation of using polyphosphates

Surface treatment of polymers is one of the easiest and efficient methods used for covering the surface of the polymer by flame-retardant coatings [179,180]. In addition, it has many advantages: it does not affect the intrinsic bulk properties of the materials such as mechanical properties; they are usually easily processed (in a small scale) and also applicable on several materials such as, polymers, textiles, and wood [181-183]. An additional protection layer on the surface or processed fire retardant additives can be used to prevent the spread of the fire or at least retard it [184].

The range of phosphorous based fire retardants are extremely wide including phosphates, phosphonates , phosphines and red phosphourous. Polyphosphates and ammonium polyphosphates are often used inorganic fire retardants. Thermal degradation of polyphosphates results in the release of ammonia and phosphoric acid forming further inflammable products and char as well as ultraphosphates and polyphosphoric acid with a highly crosslinked structure and release of water, carbon dioxide etc. [98, 185] Figure 3.38.

Figure 3.38 shows chemical structures of crosslinking and char formation during the combustion of polyphosphates, including Ammonium polyphosphate, with reactions releasing $-NH_3$ and $-H_2O$ under heat (Δ), leading to thermal decomposition, crosslinking, and char formation.
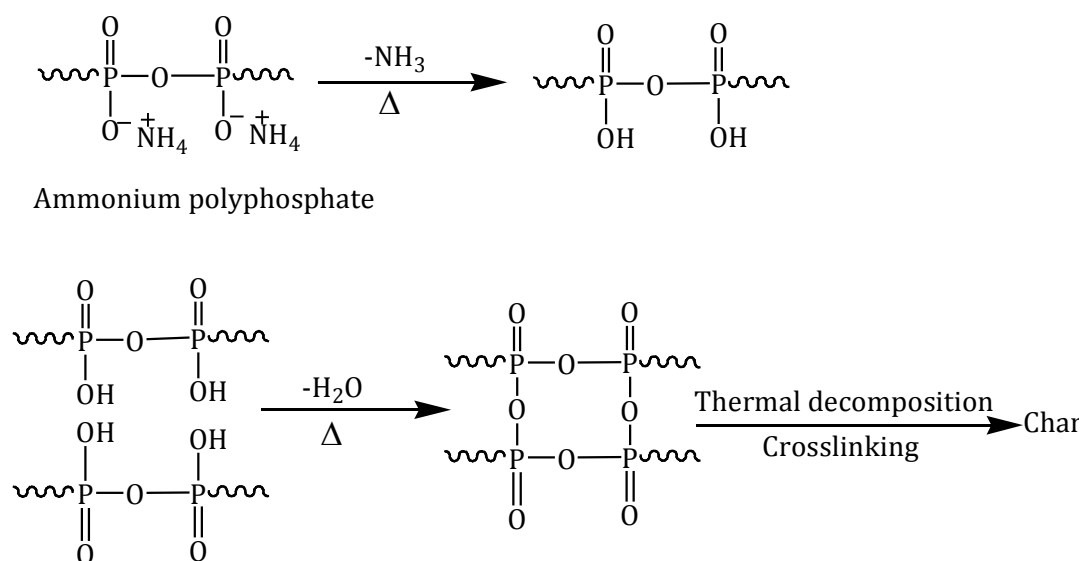
Figure 3.38 Crosslinking and char formation during the combustion of polyphosphates

In this work novel approaches were used to deposit fire retardant layers such as plasma technology and layer–by-layer technique (LbL). As always before, a layer of 50-100 nm of plasma polymerized (allylamine) ppAAm was deposited as adhesion promoter [186] for both PS and PE.

In LbL technique a solid substrate is dipped into polycation and polyanion solutions to form polyelectrolyte multilayer films (PEM). Recently, this method was developed to treat the polymer surface with intumescent flame retardant coatings to reduce their flammability [187-190].

In this work, fire protection of PS and PE using LbL intumescent coating were studied. This intumescent coating consists of alternating polyallylamine. hydrochloride (PAH) (charged positively) and sodium polyphosphates (PSP) (charged negatively) deposited on PS and PE Figure 3.39. The polymers were modified with 20 and 40 bilayers (PAH-PSP)n without spoiling the intrinsic properties of the modified polymers [190].

Sodium polyphosphate

PSP

Poly (allylamine.hydrochloride)

PAH
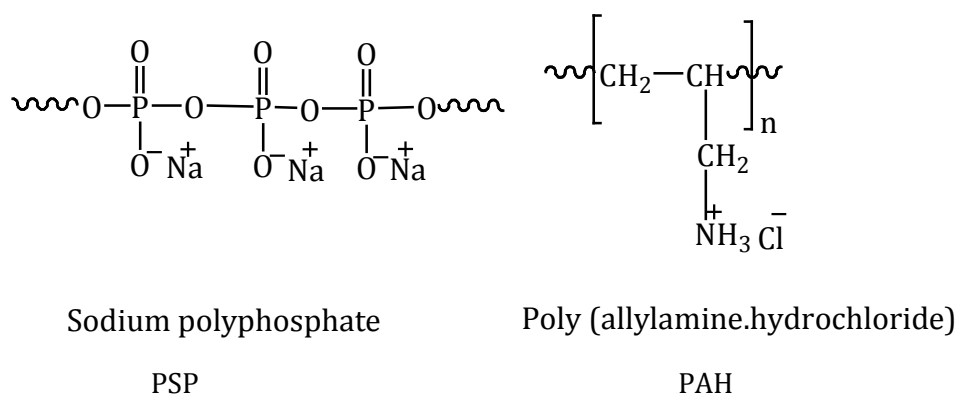
Figure 3.39 Chemical structure of sodium polyphosphate PSP and poly (allylamine hydrochloride) PAH

The thickness, morphology, topography, thermal stability, peeling test as well as fire performance have been assessed and presented.

3. 4.2 Topographic characterization of the deposited (PAH-PSP)n layers

The thickness of the films has been measured on silicon wafer as model substrate pre-coated with a 50 nm thick ppAAm layer. The thickness of the subsequently deposited polyallylamine-polyphosphates assemblies (PAH-PSP) with 20 or 40 bi-layers (BL) is presented in Figure 3.40. The thickness of a deposited 20 BL is sample is approximately about 700 nm and that of 40-BL sample 1 μm.
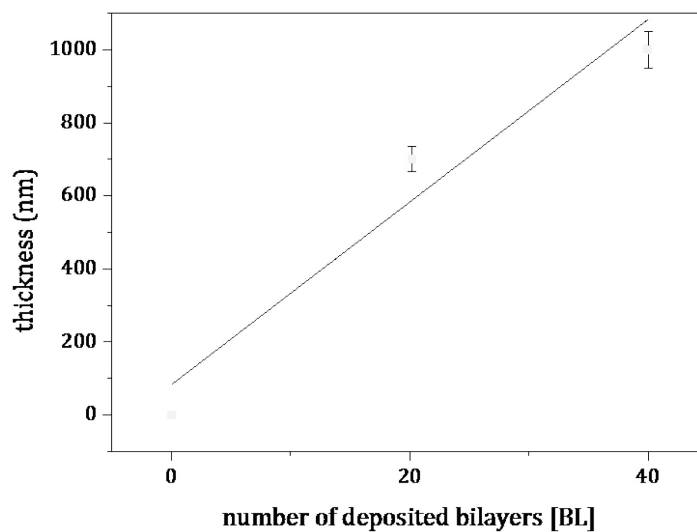
Figure 3.40 Thickness as a function of the number of the deposited (PAH-PSP)n bi-layers

The topography of a 40 BL (PAH-PSP) layers, deposited on silicon wafer, was studied by AFM as shown Figure 3.41. The surface appeared to be homogenous, smooth, and regular.
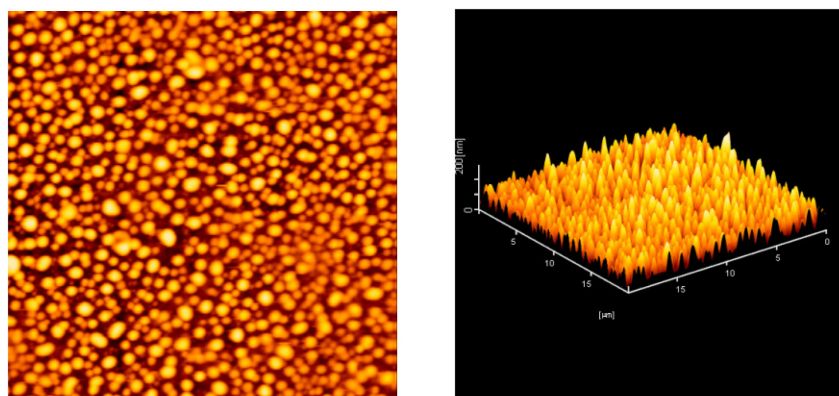
Figure 3.41 AFM surface images (20 x 20 μm²) of 40 BL deposited on silicon wafer

3.4.3 FTIR-ATR measurements

FTIR-ATR spectra of the modified PS and PE samples coated with 50 nm ppAAm layer followed by depositrion of 40 BL of PAH-PSP were presented in Figure 3.42. The IR spectra of ppAAm deposited on PS and PE have been discussed in detail before.
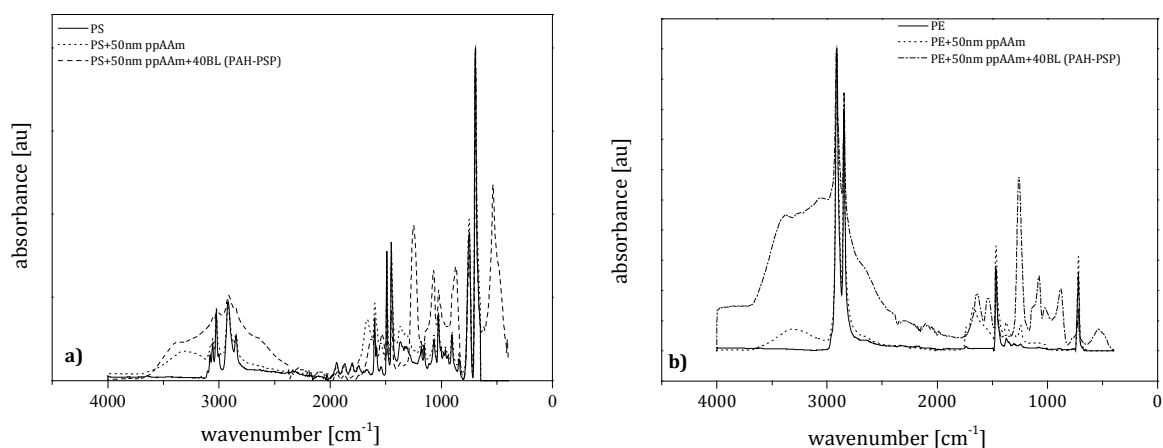
Figure 3.42 FTIR-ATR spectra of a) PS and b) PE modified either with ppAAm or with ppAAm-(PAH-PSP)

For a (PAH-PSP) coated polymer a characteristic band at 3449 cm^{-1} was attributed to –NH$_2$ and –OH groups stretching vibration; and the band at 1650 cm^{-1} to amide I. The peak at 1250 cm^{-1} is characteristic for PSP.

3.4.4 XPS results

The XPS of a 40 BL PAH-PSP is represented in Figure 3.43. The identified peaks correspond to C1s, O1s, N1s and P2p were found at 285, 533, 399, and 135 eV, respectively.
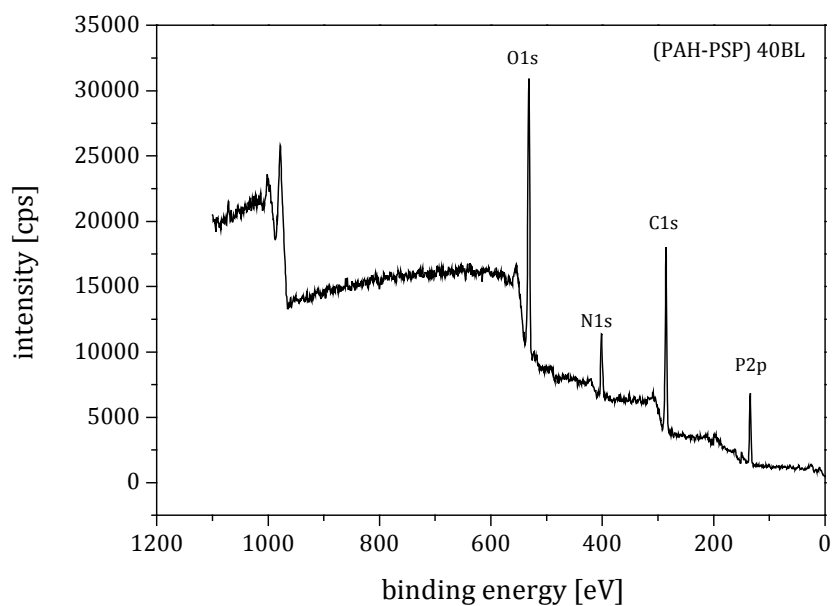
Figure 3.43 XPS of (PAH-PSP) layers

3.4.5 Peel strength measurements of the deposited layers

In this test the peel strength of the 40 BL (PAH-PSP) layers deposited onto the polymer substrate was measured Figure 3.44. The substrate polymers were modified first with ppAAm as adhesion promoting layer.
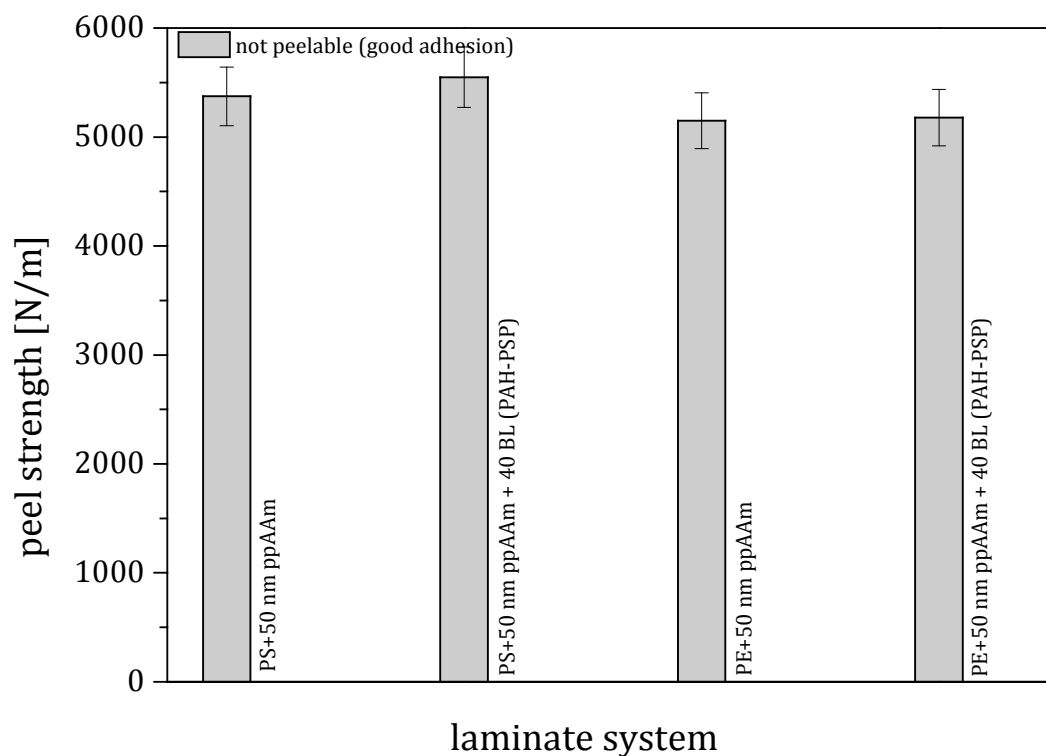
Figure 3.44 Peel strength of a) PS and b) PE coated with (PAH-PSP) bi-layers

The peel strengths of samples modified with ppAAm were in the same range as those of the pure polymers samples coated with PAH-PSP layers.

The XPS inspection of the peeled PE and PS samples with XPS accentuated that the peel front has propagated in each case along the interface of coating and tape. Figure 3.45 represents the P2p peak of the surface of the polymer; on the other hand, the tape did not show phosphorous.
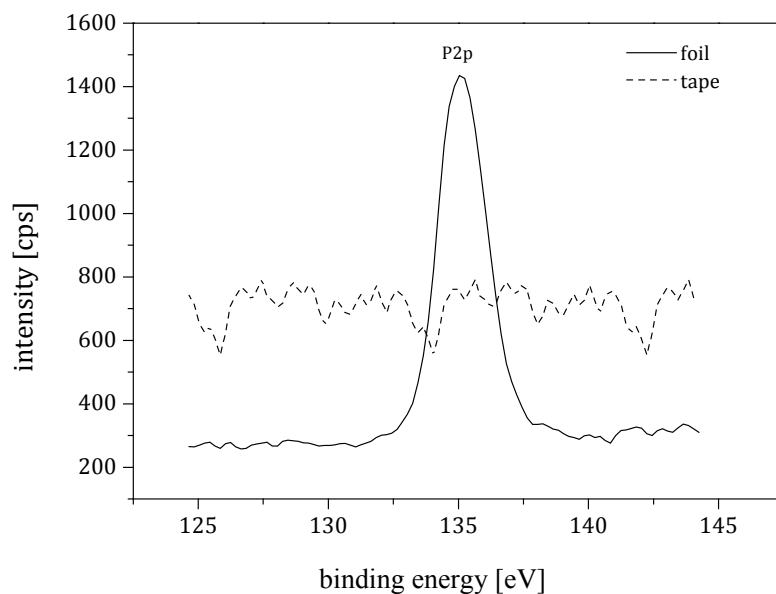
Figure 3.45 XPS of peeled (PAH-PSP) layers

3.4.6 Thermal behavior of (PAH-PSP) coated polymers

Phosphate-coated polymer samples as well as the pristine polymer substrates were inspected also by thermo-gravimetric analyses as shown in Figure 3.46.
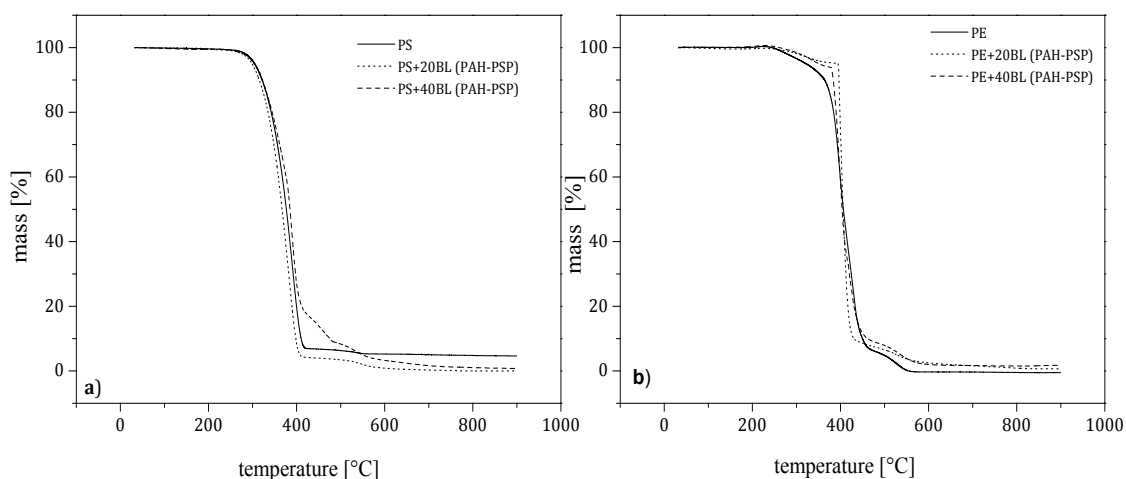
Figure 3.46 TGA of a) PS and b) PE coated with 40 BL of (PAH-PSP) after preliminary deposition of ppAAm

TGA curves confirm enhancement of thermal stability of coated polymers compared to that of the pure polymers. This effect is ascribed to the shielding effect of the PAH-PSP layer system, which act as a physical protective barrier on the surface of both PS and PE. TGA curves reflect slight improvement in thermal resistivity. This stabilizing effect may be attributed to the barrier effect of the coated layers, which accompanied to the crosslinking of the released phosphoric acid to form ultraphosphates and release of water.

3.4.7 Flammability tests

The visual observations of the flame tested samples showed that unlike pure polymers, which ignited rapidly with dripping, the 40 BL coated PS sample ignited also fast but without dripping, and for PE drips little pit adding to improvement in the flameout time for coated PS and PE. This may be attributed to the low thickness of the fire retardant coverage (in the nm scale).

Proceeding work will be done to deposit much more thick (PAH-PSP) layers combined with studying of the peel strength of the thick deposited layers.

3.4.8 Conclusions to the adhesion of thick polyphosphate layers on polyolefins and their efficiency in flame-retarding

A fire retardant layer consisting of a (polyallylamine-polyphosphates) assembly has been deposited on plasma polymer interlayer on poly(styrene) and poly(ethylene) surfaces.

The surface was modified with (PAH-PSP) coatings of 20 or 40 bilayers without affecting the intrinsic properties as shown by nearly unchanged thermal properties. The characterization of the deposited layers was performed using FTIR-ATR, XPS, and AFM. The peeling strength of a sample coated with 40 BLs was measured followed by inspection of the two peeled surfaces with XPS. It has shown that any peeling of the coating was absent.

General conclusion:

In this work:

- Preparation of thick well adherent fire retardant layers onto PS and PE surface. Surface treatment doesn't modify the bulk properties of materials and it could be applied over a wide range of materials.

- Different techniques were used to prepare such thick layers and to promote strong adhesion between the non-polar polymer substrate and the coating. Coatings have to withdraw high temperatures at exposure to flame without self-peeling.

- Combinations of two deposition techniques were optimum. Generally, plasma pre-treatment were used to deposit a basecoat responsible for maximal adhesion to the polymer. This basecoat was 0.1 to 1.0 μm thick.

- Subsequent simple dipping into coating solution or by spraying it was used for the deposited layers thicknesses ranged from of 10 to 50 μm.

- The deposited layers were characterized by different analytical methods such as X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) in the Attenulated Total Reflectance mode (ATR), Thermal Gravimetric Analysis (TGA) as well as by 90° peel strength measurement, fire test (according to DIN 4102-1) etc.

Different types of flame retarding coating materials were used:

- For deposition of inorganic fire retardants, precursors or materials forming siloxane-like structures were used.

General conclusion:

- Thin siloxane prelayers were deposited by low-pressure plasma polymerization of hexamethyldisiloxane (HMDSO) in presence of oxygen, thus, siloxane structures dominate and also silanol groups are at the surface, which are important for adhesion promotion, were evidenced by NMR and FTIR-ATR.

- Alternatively, additional SiO_2 layers (water-glass) were deposited by combination of a pyrolytic method (Silicoater process) for adhesion promotion, then, dipping into Na-silicate solution for deposition of SiO_x layers.

- The adhesion measurements shows that well-adherent layers could be produced by combination of plasma coating and subsequent deposition of water glass by dipping into water-glass.

- Thermal and fire retardant properties of such SiO_2-like coatings was significantly changed; details of flame mechanism and the role of cracks in the layer are planned to be investigated.

Second type of fire retardants are melamine precursors:

- Methylated poly(melamine-co-formaldehyde) is used as precursor to deposit N-rich fire retardant layers.

- Thick coating (10-50 μm) with melamine pre-polymers and crosslinked melamine resins using ppAAm or ppAAl plasma polymers as adhesion promoters.

124

General conclusion:

- Peeling tests showed that a cohesive failure within the mPMF layers. So, to increase the mechanical stability of melamine resins as thick coating on polyolefins, the resins were cured thus withdrawing the stress of flaming.

- The cured and crosslinked layers have an improved mechanical stability and hinder more efficiently the oxygen transport to the polyolefin substrates.

- Thick coating with cured melamine resins has a positive effect on flame retardancy of polystyrene as well as polyethylene. Moreover, evidence of chemical bonds between pretreated polymer substrate, plasma polymer, melamine resin and in the bulk of melamine resin (intermolecular crosslinking) was proved.

Another type of fire retardants is polyphosphate

- A fire retardant layer consisting of a (polyallylamine-polyphosphates) assembly has been deposited on plasma polymer interlayer on poly(styrene) and poly(ethylene) surfaces.

- 20 to 40 BL of (PAH-PSP) coatings were deposited and characterized.

Advantage of such coatings is the safe and cheap use of technical polymers as construction material and the safe protection of surface at pronounced. Also, these coatings can be prepared easily, rapidly and with good properties by more simple methods working at atmospheric pressure.

In future, these techniques should be further developed and tested, combinations of the coatings will be deposited and tested (water-glass, melamine precursors and

General conclusion:

polyphosphates), and also application of melamine pre-polymers in combination with paints will be tested to be applied in automotive industry.

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136

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146

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6- Zeinab R. Farag, Jörg F. Friedrich, Simone Krüger. Deposition of intumescent fire retardant layer of poly(allylamine) and polyphosphates) on poly(styrene) and poly(ethylene) using plasma technology and Layer-by-Layer technique, Submitted to Plasma Processes and Polymers, in progress.