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IN SITU PREPARATION OF NHFR POLYAMIDES

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Abstract

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PhD Course in Industrial Chemistry, XXIII cycle
Final Report on the of the PhD Research project

In situ preparation of Non Halogenated flame retardant polyamides

Introduction

The research project starts with the goal of using the knowledge developed during the years by our research group, applying it to a current problem in the field of macromolecular research: the development of halogen-free flame retardant materials. Since 1930 poly-halogenated aromatic compounds (chlorine-based in the first time, bromine-based in a second one) have been used as flame retardant; but with the growing attention to health care, toxicity in human body^[1] and bioaccumulation in the environment^[2] have been evidenced. Step by step^[3] national and supranational organization have prohibited at first the use of poly-chlorinated molecules and in a second time the use of some of the brominated ones, pushing the research to the development of alternative products with a less environmental impact, named NHFR (Non Halogenated Flame Retardant).

The insertion of flame retardants in a polymeric matrix can be achieved with two processes, each one with peculiar advantages and disadvantages:

- *Compounding* is a mixing process of the product (additive) that brings the desired property to the melt polymeric matrix. It is a physical mixing that leads compatibility problems between matrix and additive, caused by dimensional non homogeneity and different values of surface tension (difference between organic and inorganic materials); these problems can lead to the aggregation of the additive during the compounding process and migration phenomena during time. On the other and compounding has the advantage to be a versatile process, based on semi empirical studies, that brings results in short time.
- *Copolymerization* is a process that can give peculiar properties to the polymeric matrix, when the comonomer has elements that bring the desired property, appropriate reactive groups to be inserted in the macromolecular chain and thermal stability in synthesis conditions. This process involves the disadvantage of needing more important investments than compounding both regarding scientific knowledge and time to obtain the desired result. In spite of the difficulties in the development, it has the advantage to insert the property in the main chain, making it intrinsic in the material, building up a chemical bond between the comonomer and the structural unit of the polymer, eliminating the problems of migration and low compatibility typical of compounded materials. It has the potentiality to develop materials completely new that can be object of intellectual property.

The insertion of a molecule by copolymerization causes a modification in the chain regularity with effects on the polymer's crystallinity. To deepen this aspect, a part of the research project has been conducted in the centre of research of Rhodia in Lyon, France, in the context of the European Program for the training activity of PhD students. The training time lasted 5 months and during this period the knowledge on the synthesis and the characterization of polyamide-based copolymer was improved.

Material choice

In this research project the work was focused on the development of flame retardant polyamides by using two different approaches: the copolymerization with phosphor-containing molecules (one of the most promising class of NHFR) and the insertion of surface-modified mineral nanoparticles (another class of NHFR with high potential interest). The choice of polyamide is owed to the fact that an high amount of this material needs flame retardant property, considering its use in moulded manufactured articles with application in risk conditions (electric covering, control units..) and its use in the production of fibre (carpeting, drapery..) that should need a specific flame retardant material (obtainable by copolymerization because compounded materials aren't usable) that doesn't exist on the market (while there is an example of a PET FR^[4]). Regarding intellectual property there are some patents^[5] on the use of a minimal quantity of phosphor-based comonomers in copolymerization with nylon 66; however at the beginning of the PhD, there weren't on the market polymeric materials obtained according to these patents. Polyamide 6 has been chosen because it is a commodity obtained by polymerization of an α -amino acid; this kind of polymerization gives less problems in comparison with a polycondensation of a diacid and a diamine (i.e gelification problems), allowing a better study of copolymerization.

Copolymerization

The first way is the use of a phosphor-containing comonomer: 2 carboxyethyl (phenyl) phosphinic acid (CEPP). This molecule (Fig.1) is used as additive in some polyamide-based polymers and as comonomer in the production of a PET FR^[4]; our goal is to insert it in the polyamide via copolymerization using the knowledge on the modification of the macromolecular architecture field, where our research group has wide experience.

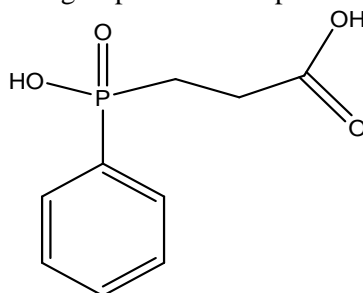


Figure 1: 2 carboxyethyl (phenyl) phosphinic acid (CEPP)

Nanocomposite preparation

As explained before, the second way is the insertion, during the polymerization, of mineral spherical (nanosilica) or lamellar (montmorillonite) nanoparticles, with surface modification obtained using silanes (terminated with aliphatic chain or aminic groups); high surface area of the mineral at nanometric level permits to obtain a good dispersion in the polymeric matrix with an enhanced effect of the properties carried, as the flame retardancy^[6]. The insertion in situ ad the research of the best conditions of surface modification have as goals the maximum homogeneity of the resulting nanocomposite.

Materials obtained via copolymerization

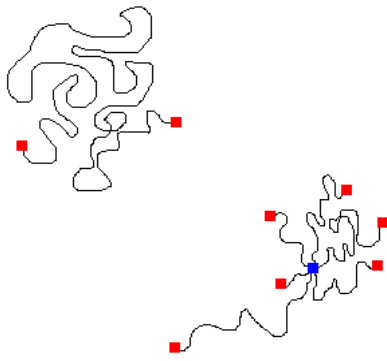
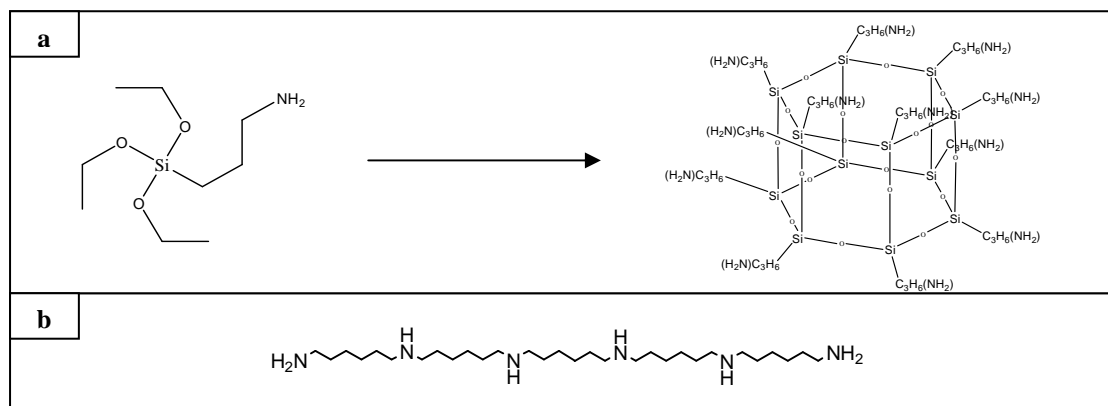


Figure 2: Linear Polymer vs star shaped one. In red are marked linker point for the CEPP, in blu the star shaping molecule

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comonomer permits to obtain a polymer with a number of branches equal to the functionality of the central molecule, maintaining an higher value of molecular weight in comparison with the linear polymer (Fig.2).

Among multifunctional molecule tested as comonomers, best results have been obtained by the self-condensation product of the 3 aminopropyl-triethoxy-silane, and an hexafunctional polyamine called HBHT (hexafunctional bis-hexamethylene-triamine) (Fig 3.a and 3.b).

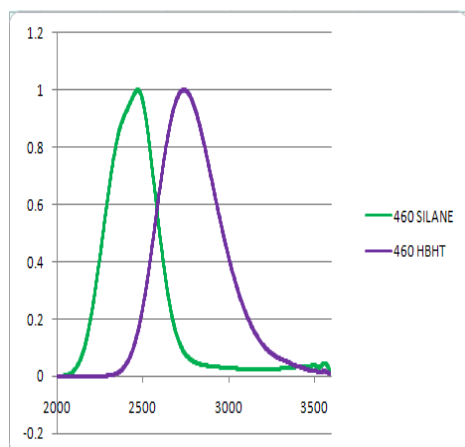


The condensation of the silane is a process described in literature^[8], that carries to the formation of the so-called POSS (Polyhedral Oligomeric Silsesquioxanes); one example of is reported in figure 3.a. These products are formed by a cage of Si-O bond in the central part and a series of organic pendants in the external part. The result of the condensation in our conditions is a statistical mixture of molecules, whose degree of condensation can be calculated by titration of the equivalent molecular weight of the repetitive unit.

HBHT is a tail product of the distillation of the hexamethylenediamine (HMDA), one of the monomers of the polyamide 6,6. BHT (bis-hexamethylenetriamine) is usually obtained by this distillation process as sideproduct, but if the ammonolise reaction that brings from HMDA to BHT is carried on for a longer time, molecules with higher molecular weight and higher functionality can be obtained. The interest in the use of this molecule is caused by the thermal stability in polymerization condition, the high value of functionality that brings to star shaped polymers with higher fluidity than the linear ones^[9], and its origin as side product of the distillation of a HMDA (1 million of ton/year).

Using these two molecules, different polyamide 6-based polycondensation products have been synthesized, studying the behavior of the synthesis reaction in the presence of two chain regulators: a multifunctional molecule and a monofunctional one with complementary reactive group.

This kind of copolymerization inserts a series of variables in the statistical process of condensation that prevents a behavior's prediction using the mathematical models developed^[10].



By using POSS as star shaping molecule, polymers with high number of amino terminal groups and high molecular weight (compared with the ones of linear polymer and star shaped ones synthesized by using HBHT), have been obtained. Figure 4 reports SEC curves of two polymers obtained using HBHT (violet curve) and POSS (green curve), synthesized with the goal to obtain the same number of amino terminal groups: it is possible to observe that the hydrodynamic volume (referable to the molecular weight) is higher in the case of the POSS containing material. Molecular weight data, obtained by a calibration in linear nylon 6 equivalent, are reported in table 1.

Figure 4: SEC curve for the matrix 460 obtained with POSS and HBHT

Terminal NH ₂ (meq/Kg)	POSS		HBHT	
	M _n	d	M _n	d
460	15907	1,45	4177	1,53
255	15380	1,85	5350	1,83
160	25493	1,94	8832	1,68

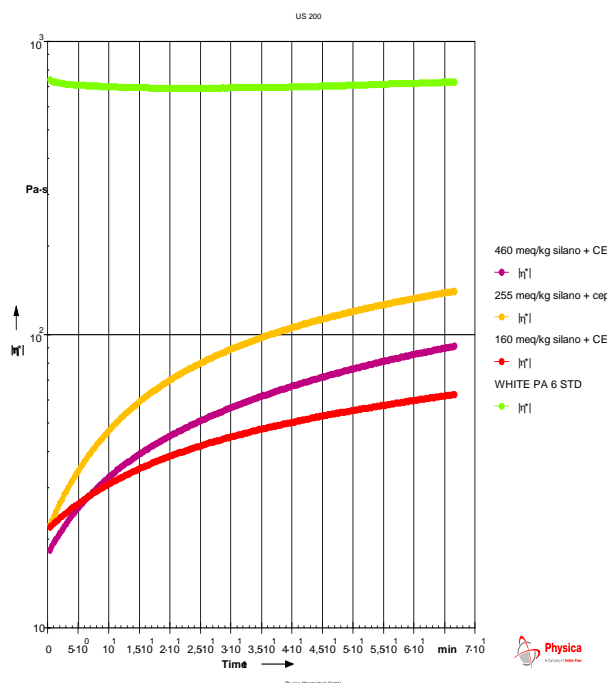
Table 1: Molecular weight data of star shaped polymers containing POSS and HBHT

A comment is needed in relation to the data of molecular weight presented in this work obtained through SEC analysis: this technique determines the molecular weight of a polymer measuring its retention time in the chromatographic apparatus (related to its hydrodynamic volume) and correlating it through a calibration made with polymers with known molecular weight. In our case the calibration is obtained with nylon 6 linear polymers that have a dependence of the hydrodynamic volume from the molecular weight different from the one of the star shaped polymers. For these ones the dependence is related to a series of variables (number of branches of the star, chain length..) that make impossible to build up a calibration system that can be able to give absolute values. However these data can be considered valid for an internal comparison of polymers with this molecular architecture.

The behavior of the copolymerization in presence of two comonomers (multifunctional amino and monofunctional acid) has been investigated. Using benzoic acid as monofunctional chain ender in the amount necessary to balance the excess of amino groups introduced with the multifunctional, a series of polymers have been obtained, having lower molecular weight than the correspondent ones obtained without benzoic acid.

A series of polymeric materials with CEPP replacing benzoic acid have been synthesized, to evaluate the behavior of monofunctional chain ender of the phosphor-containing molecule. Polymers with CEPP have lower molecular weight in comparison with materials containing benzoic acid, both when using POSS and HBHT; this means that CEPP is not only a chain ender but also that its presence disturbs the polymerization process.

Moreover it has been evidenced a particular interaction between CEPP and POSS with effects on the viscosity of the material over time (Fig. 5).



In the figure the rheological behavior of the materials containing CEPP and POSS is reported (complex viscosity in the log scale of the ordinate versus time) using as reference a sample of an industrial polyamide 6^[11]. Viscosity values are lower in our samples in comparison to the ones of the standard (typical behavior of star shaped polymer), but this value increase during the time, sign of a further reactivity. This increase is owed to a cross linking phenomenon caused by the reaction of the -POOH groups of the CEPP with the -OH groups unreacted of the POSS. It must be remembered that the POSS is a non completely reacted product and the POOH group of the CEPP is able to create stable bonds with OH group. This behavior isn't remarkable in any other material synthesized.

Figure 5: Increasing of viscosity in POSS-CEPP polymers

Nanocomposites materials

The second way followed to develop halogen-free flame retardant materials is the synthesis of nanocomposites materials; different amounts of mineral nanoparticle have been added to polyamide 6 with or without surface modification.

The two classes of nanoparticle used are very different:

- Nanosilica: is a material based on Si-O bonds, minced to nanometric dimension. Particles have spherical shape
- Montmorillonite (industrial name Cloisite): is a mineral particle, lamellar shaped, with ammonium ions, having C₁-C₁₈ aliphatic chain, inserted between lamellae; the ions represent 40% of the weight of the material. General chemical formula of the inorganic component of this material is (Na,Ca)_{0,3}(Al,Mg)₂Si₄O₁₀(OH)₂·n(H₂O).

Inorganic particles have been modified on the surface through a reaction with silanes, because the addition of mineral particle (inorganic) to a polymeric matrix (organic) gives problems of dispersion caused by different surface tension of these two species. Silanes are a class of chemical products with both an organic and an inorganic portion, that work as a compatibilizer, reacting in a first time with the nanoparticle (grafting process, fig.6) and in a second one with the polymeric matrix (in situ polymerization), if the organic portion brings an appropriate reactive group.

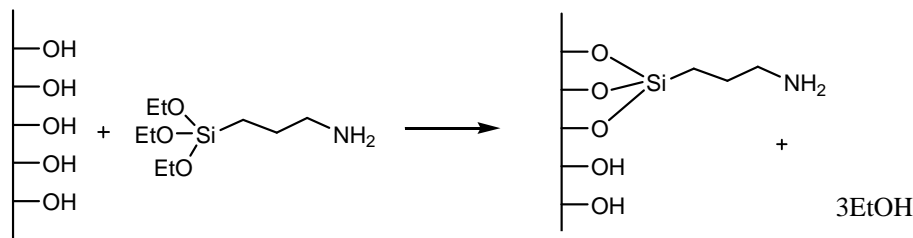


Figure 6: Grafting reaction with 3-aminopropyl-triethoxy-silane

The reaction yield in the case of silane with amino terminal groups can be followed by acid/base titration; table 2 reports the results for the graft process in the case of nanosilica and montmorillonite grafted with 3-aminopropyl-triethoxy-silane.

Name of Nanoparticle	Meq NH ₂ /Kg theoretical	Meq NH ₂ /Kg measured	% grafting theoretical	% grafting effective
Nanosilice 2%	246	148	2	1.2
Nanosilice 7,5%	833	671	7.5	5.6
Nanosilice 15%	1667	1287	15	10.7
Nanosilice 35%	3890	2447	35	20.3
Cloisite 2%	246	241	2	2.0
Cloisite 7.5%	833	485	7.5	4.0
Cloisite 15%	1667	942	15	7.8
Cloisite 35%	3890	3053	35	25.3

Table 2: Effective grafting % of nanoparticle with 3-aminopropyl-triethoxy-silane

When the grafting process is conducted on a nanoparticle organized in defined structure (in example lamellae composing the cloisite) it is possible to measure the effect of the grafting process on this structure, by measuring in the XRD (X-Ray Diffraction) the modification of the inter-lamellae distance (Fig.7).

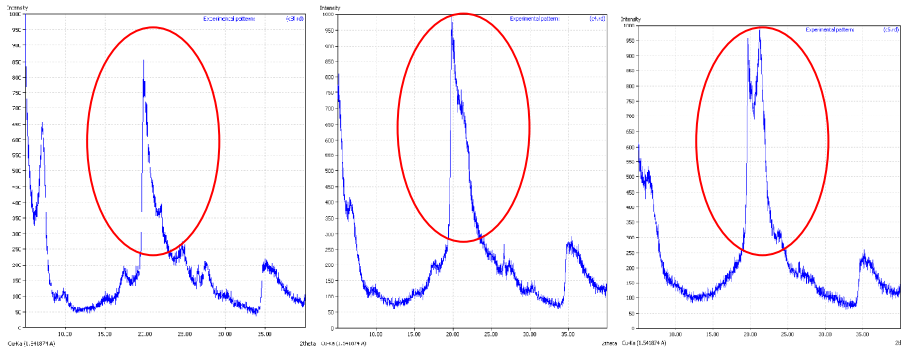


Figure 7: Modification of XRD spectra of cloisite a) pure, b) 20% silane C-16 e c) 40 % silane C-16

The silane is inserted on the lamella surface and changes the interlamellae distance; nanoparticles, covered by organic material, lose the ionic energy that gives the position of a lamella respect to another promoting the exfoliation in the polymeric matrix during the polymerization. In the reported case, the effect is strong because the silane considered is composed with an aliphatic chain C-16, and increases in increasing the amount of the graft. Nanocomposite materials with different ratio nanoparticle/polymer has been prepared; these materials have been characterized with DSC, SEC, titration of terminal groups, rheology and in some cases also with SEM spectroscopy (Fig.8)

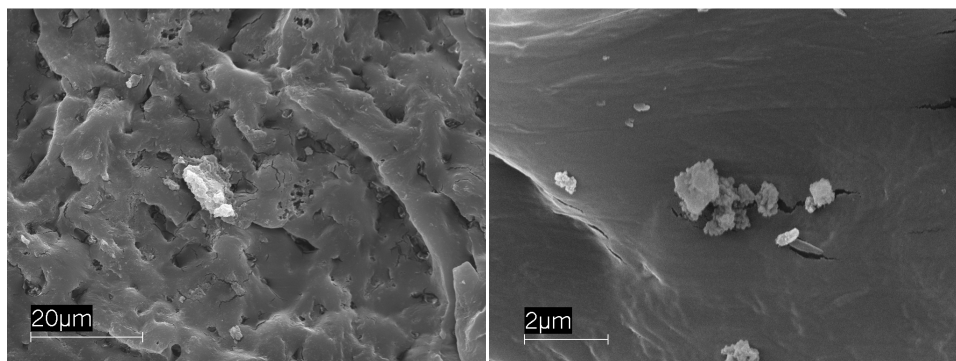


Figure 8: Two nanocomposites polyamide 6-based containing 1% (dx) e il 5% (sx) of nanosilica grafted with 15% of 3 aminopropylsilane

By comparing the two picture is possible to observe that the lower the amount of grafted nanosilica inserted the lower the tendency to the aggregation causing the formation of less compact structures; also using higher magnification a bigger surface area for the contact with the polymeric matrix is evidenced.

Tests of thermal stability and flame retardancy

While in the industrial field the flame retardancy is evaluated through tests universally recognized that give a certification for the material (i.e. UL94), in the scientific field and especially on a laboratory scale, the most common technique is the evaluation of thermal stability through DSC and the loss of weight with temperature through thermo-gravimetric analysis (TGA) ^[12]. Thermal stability of the materials has been evaluated through thermogravimetric analysis coupled with IR spectroscopy of the formed volatile materials; the result is that the degradation curve of the synthesized material that can be compared with the one on the pure polyamide 6, and the 3D spectra obtained by the series of the IR spectra registered during the analysis (Fig.9).

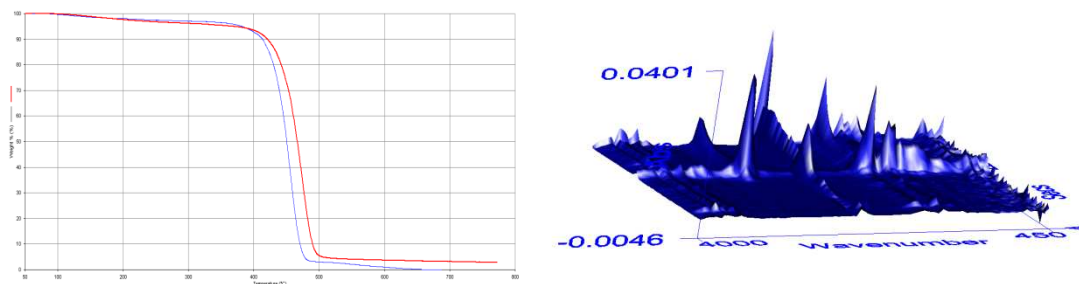


Figure 9: Curve of the loss of weight compared with PA6 (a) and series of IR spectra of degradation products (b) of nanocomposite nylon 6- 5% Cloisite grafted 35% 3-propylamminosilane

TGA curve shows temperatures and rates of evolution of combustible vapors that feed the combustion process; the series of the IR spectra shows the structure of the vapors evolved during the degradation, giving information on the amount of water present and the mechanism of the degradation (in the case of polyamide 6 our analysis confirms the unzipping process of thermal degradation).

In the case of the CEPP-containing polymers, a synthesis of great quantity of material (500-1000g) has been performed to evaluate the data through the cone calorimeter analysis. All three materials have give a good result of Rate of Heat Release (RHR), confirming their flame retardancy.

The RHR value, in fact, is the most important of the data obtained by the cone calorimeter analysis, because it shows the rate of the combustion and the tendency to spread it.

Conclusions:

In conclusion, during the PhD research the problem of the flame retardancy in polyamides has been evaluated, following ways of development not successfully used by others yet. The problem was handled using the scientific knowledge of our research group in polymeric field, obtaining either important results at scientific level and polymeric materials and with a high potential in industrial development. During the PhD course neither scientific publication nor patent claiming the rising of results similar of our ones have appeared.

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CHAPTER 1: The combustion process in polymeric materials

Introduction

Combustion is a chemical-physical process that consists in the thermo-oxidative degradation of a matter defined “combustible” (that can be in any physical state: solid, liquid or gas) in the presence of a combustive agent (usually air or oxygen in the atmosphere) producing light, heat and volatiles (CO₂, CO, fumes) or not volatiles products (charred residue).

A generic representation of the combustion reaction can be the following one:

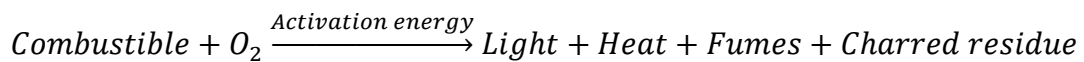


Figure 1: The combustion process

This is the most general definition that collects all the forms of combustion, even if they can presents several different aspects: for example the amount of charred residue is related to the carbon content of the combustible and fumes composition to the chemical composition of the combustible and to the ratio combustible/combustive agent; as a matter of fact, if oxygen concentration in the combustion zone is high enough to oxidize all the organic matter, the process is called “complete oxidation” and all the organic matter is transformed in CO₂; if, on the contrary, the oxygen concentration is not high enough, the process is called “partial oxidation” and the main product is carbon monoxide.

This difference is very important since the toxicity level of the two gases is very different, considering that also at low concentration CO molecule is able to bond the hemoglobin site dedicated to oxygen transportation for cellular respiration, causing a risk for the survival of exposed subjects (a concentration in the air of 2000-4000 ppm causes the death in 15 minutes, after loss of conscience)^[1].

The combustion process in polymeric materials

When combustion occurs in a polymer, the process is composed by a series of chemical and physical mechanisms that take place in two different physical phases: the gas one and the condensed one. Matter and energy are exchanged between these two phases, following the Figure 2:

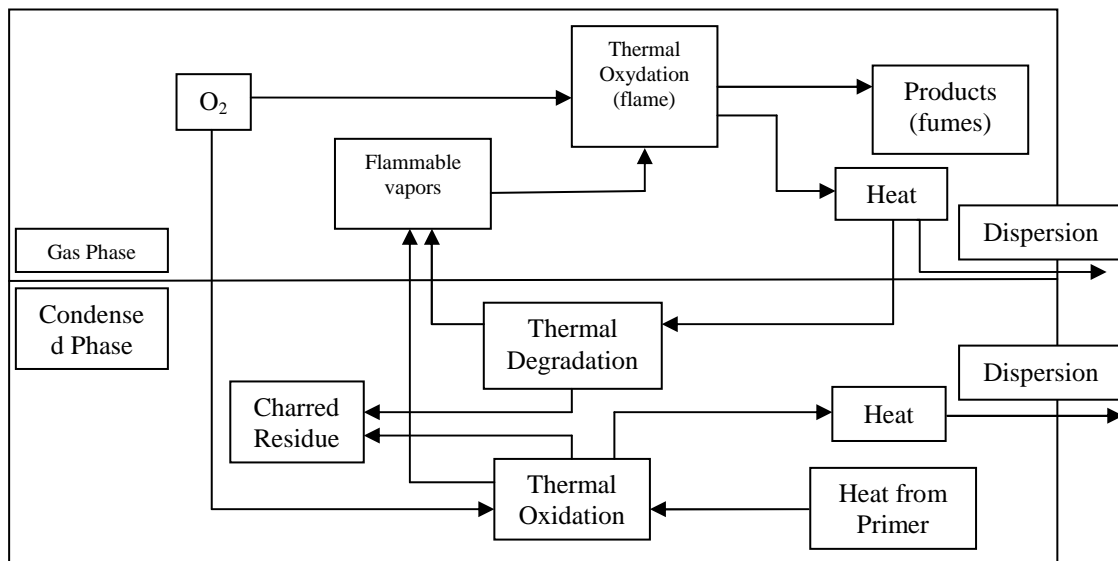


Figure 2: The combustion process in polymeric materials

The condensed phase is composed by the polymeric material in the solid state, while the gas phase is the atmosphere in which the polymer is placed, that might be enriched by the vapors emitted by the polymers and is the place of development of the flame.

The base skeleton of the combustion process is composed by two elements: the polymer in condensed phase and the flame in gas phase; between these two elements, there is a matter transfer that is directed from the condensed phase to the gas one and an energy transfer going to the opposite direction. In this way a circle is obtained, where the volatiles compounds are burned, emitting heat that decomposes new matter that burns and so on. As long as the energy emitted is high enough to maintain a degradation kinetic that furnishes combustible vapors to maintain the flame, the process is autofeeded^[2].

However combustion process in a polymeric material is not spontaneous, needing to be started through an external source of energy. The role of this source of energy (called “primer”) is, on one side, to cause the thermal degradation of the polymer that develops volatile products in a concentration that is comprised in the flammable limits and, on the other side, to cause the increase of temperature of the gas phase until a temperature higher than the self burning temperature of the gases is reached.

As shown in Figure 2, the combustion process in polymeric materials carries a series of secondary passages, that can be determinant on the process, modifying the conditions of development until, in some cases, the stop of the process. An example is the formation of charred residue on the polymer in condensed phase: this process leads to a carbon-rich coat of inert matter deposited on the polymeric material that makes it harder to exchange energy and matter between the two physical phases, causing the end of the combustion process.

Another important secondary process of the combustion of polymeric materials is fumes development; also if this process isn't involved in the propagation of the combustion (if is excluded that fumes transmit heat helping this propagation), it is very important for the safety of the subjects exposed to the phenomenon. The two most important parameters in fumes analysis are toxicity and opacity: usually in fact, fumes produced by the combustion are highly toxic and kill people earlier than the flame, while the analysis of the causes of death during a fire shows that the opacity of the fumes is the responsible of the disorientation of the subject exposed so they cannot find an exit from the risk zone.

Different phases of the fire

Fire is the macroscopic phenomenon that corresponds to the combustion process and, even if an accurate analysis of this event is not the objective of this work, a brief explanation of the phenomenon is useful to understand the effects of the chemical substances studied in this work on the materials.

The development of the fire process passes through some steps, in which the entity of the process changes:

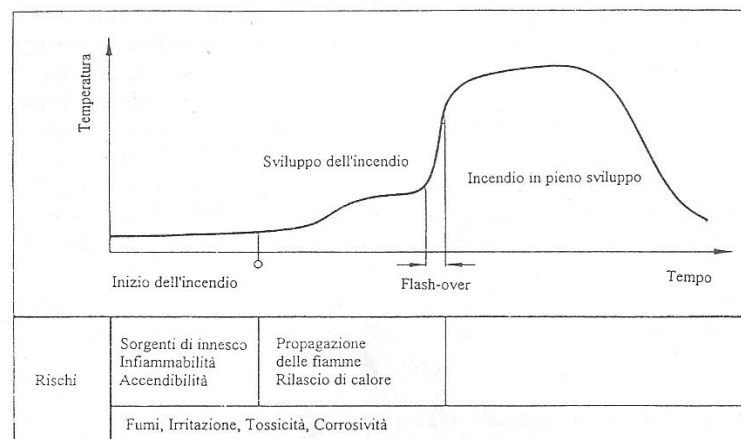


Figure 3: The Fire event

It is possible to see in the Figure 3 the variation of temperature with the time during a fire, at the beginning of the process, a low temperature profile is maintained, and most part of the energy produced is absorbed by the propagation phenomenon; only during this phase substances called “flame retardant” can enter in action to slow or block the combustion process, because energies involved are still low and the effect of flame retardancy can play a determinant role.

After the propagation phase, combustion process reaches a level of heat release that cannot be controlled; the phase called “flash over” starts, coming just before the maximum development of the fire. When the flash over phase starts, no flame retardants can have an appreciable effect on the combustion process.

Polymer's thermal degradation

The thermal degradation of a polymeric material is one of the most important steps of the combustion process regarding these materials because it produces the volatiles products that feed the flame.

The term “degradation” is used in the polymeric field to identify all the processes that lead to a modification of chemical and physical properties of the material; it is not necessary a massive action of these processes to obtain an high loss of the properties: it can be considered, for example, that the scission of the 0,1% of the chemical bond in the main chain of a polystyrene with $M_n = 1000000$ of Dalton causes the reduction to 100000 Dalton^[3].

The degradation of a polymer can be performed through chemical agents (i.e: acids, bases, water, oxygen..) or through physical agents (in example, light, heat, UV beams..). The behavior of the polymer in response to a degradation process isn't deductible by the chemistry of the ideal chain: in fact in the real chain there are errors or imperfections that act as weak points and that determine the degradation behavior of the polymer: for example, a chain of polyethylene, containing weaks point formed during the polymerization process degrades through the same mechanism of the model compound esadecane, but at 200°C lower, because this molecule hasn't weak points.

The depolymerization reactions are divided in two groups that correspond, in the inverse sense, to the two groups of polymer synthesis reactions: depolymerization by polyaddition and statistical step by step polymerization.

Radical depolymerization

As the name suggests, this kind of depolymerization proceeds through the formation of radical species that are obtained by the homolytic scission of a chemical bond through thermal degradation.

This process mainly involves polymers composed by long hydrocarbon chains that don't contains functional groups on the main chain (otherwise preferable target of degradation); the process passes through three main phases:

Start: The breaking of the chemical bond causes the formation of two radical molecules

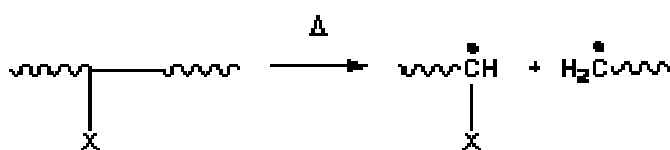


Figure 4: Start reaction in radical depolymerization

Propagation: it occurs through 3 main mechanisms: depropagation, intra-molecular transfer and inter-molecular transfer, presented in the following Figures:

Depropagation

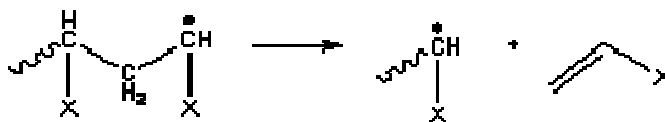


Figure 5: Depropagation reaction in radical depolymerization

Intra-molecular transfer

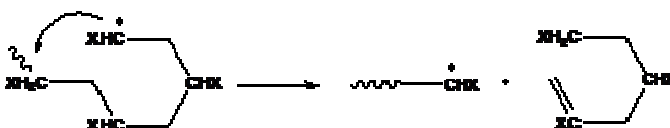


Figure 6: Intra-Molecular transfer reaction in radical depolymerization

Inter-molecular transfer

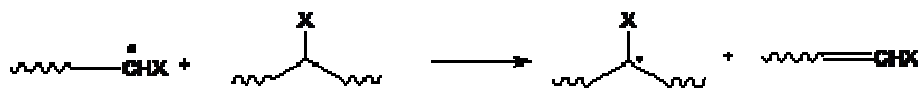


Figure 7: Inter-Molecular transfer reaction in radical depolymerization

Ending: as in the case of radical polymerization, the reaction ends in the case of coupling of two radicals or through disproportionation.

The relation between the three kinetics of the reaction of propagation is what determines the degradation product obtained: when the depropagation reaction dominant, the main product obtained is the monomer and the reaction is called “unzipping reaction” (reminding to the effect obtained when a zip is open); if the most important reaction is the intra-molecular transfer, main products are oligomers with low number of repetitive unit (3,4,5) because these are the species that are eliminated; finally, if the dominant reaction is the inter-molecular transfer, degradation products are macromolecular chains with statistical molecular weight that decreases during time.

Degradation reaction through statistical scission

Statistical scission of a bond in a macromolecular chain doesn't involve only the cited mechanisms of homolytic scission in the radical depolymerization but also the case of depolymerization by hydrolysis in polyester and polyamides; in this kind of polymers all bonds between repetitive units are equal, therefore they have the same probability to be broken.

This depolymerization process results in a loss of molecular weight during time, that is predictable through a kinetic analysis: if x_0 is the polymerization's degree at zero time, the polymerization degree after a time "t" is in relation with the first one through the relation 1.1:

$$x_t = \frac{x_0}{s + 1}$$

where "s" is the average number of scissions on a macromolecular chain that can be evidenced as in the 1.2:

$$s = \frac{x_0}{x_t} - 1$$

if the scission process follows a first order kinetic, the scission rate is calculated by the 1.3:

$$-\frac{dN_t}{dt} = kN_t$$

From equation 1.3 is possible to predict the decrease of the molecular weight of a polymer subject to this kind of degradation process during time considering the amount of bonds that can be broken in the chain.

These equations are valid independently from the molecular weight of the polymer and refers to a distribution of molecular weight that changes during the time.

The thermogravimetric analysis (TGA) of a polymeric material can give indications on its behavior regarding thermal degradation, giving data on the temperature, mechanism and rate of the process. This analysis is usually coupled with spectroscopic analysis as mass spectroscopy, where the molecular weight of the degradation products is analyzed, or IR spectroscopy where the absorbance of IR spectra of products is obtained.

The risk factor connected to the combustion process

Combustion process in modern society represents an increasing risk for human safety: the presence of a lot of people in a building that containing an high amount of polymeric materials potentially combustible is normal.

Combustion process involves a development of heat that causes an increase of temperature up to levels that cause the carbonization of organic tissues, the consumption of atmospheric oxygen necessary for the respiration, and fumes emission that are toxic and prevent with their opacity the possibility to left the fire.

For these concerns the research of chemical products that inserted into the polymeric materials can slow the development of the combustion, is one of the principal targets in the field of polymers.

National and supranational laws rule the flame retardancy of polymeric materials with high attention and with parameters in continue evolution both regarding the flammability of the final products and regarding the toxicity of the materials used as flame retardants.

Flame retardancy theory

A flame retardant is a substance that can slow one or more passages of the combustion process of a polymeric material (the scheme of the main transfers during the combustion of polymeric materials is reported in the figure 8)

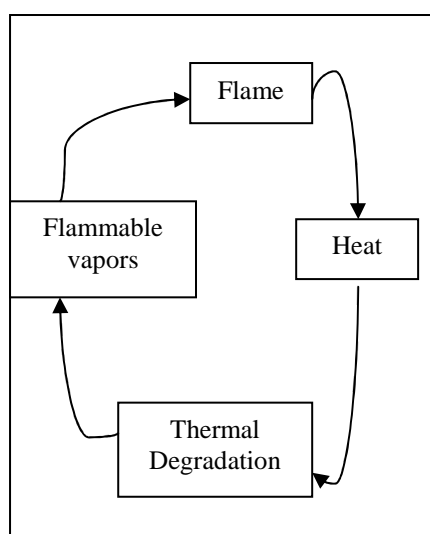


Figure 8: Main transfers in combustion of polymeric materials

Flame retardants can be elements or molecules, having organic or inorganic nature, can act in gas or condensed phase, through a chemical or physical mechanism. In this paragraph the main aspects of the flame retardant's action will be considered; for a detailed description of the action of single flame retardants, please refer to chapter 2 (halogenated flame retardant) and 3 (non halogenated flame retardant).

Flame retardants operating in condensed phase

The key passage of the process in the condensed phase is the thermal degradation of the polymer that emits volatile products that are the principal feed of the flame:

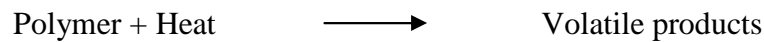


Figure 9: Reaction in condensed phase

Any substance that is able to slow the heat transfer from the gas phase to the condensed one or the matter transfer in the inverse direction or that can slow the degradation process of the polymeric material is considered a flame retardant that acts in the condensed phase.

Flame retardants operating in gas phase

In the gas phase the most important element in the combustion process is the flame; processes that feed it are the key passages on the kinetic of the combustion therefore retarding them the entire process can be slowed.

Flame retardants that act in gas phases are substances that are introduced in the polymeric material (in the condensed phase) and that are transformed during the thermal degradation to furnish inert gases or radical species that intercept hydrogen and hydroxide radicals feeding the flame, slowing the process.

Flame retardants that act through chemical mechanism

This kind of flame retardants is composed by substances that, in degradation conditions, form chemically reactive species that are able to disturb the processes of flame feeding and heat transferring. The most common example is the formation of stable radical species that are able to intercept hydrogen and hydroxide radicals that feed the flame, substituting them slowing the feeding process. These species are thermodynamically more stable than hydrogen and hydroxide radicals therefore slower to furnish energy; another example is the formation of charred coating on the polymeric material obtained through dehydration of carbon rich molecules. This coating (called “char”) slows the passage of the matter from the polymer to the flame and the passage of heat in the opposite direction.

Flame retardants that act through physical mechanism

These flame retardants, during the thermal degradation of the polymeric material, decompose with emission of substances that change the conditions of the environment where combustion occurs, making it less favorable. The most common processes are the development of a inert gas that dilutes the concentration of the combustible products in the gas phase slowing the rate of the reaction of combustion, and the decomposition through endothermic reaction that takes away heat from the environment, slowing the reaching of the ignition temperature.

Flame retardants usually act through a series of the above mentioned mechanism, other ones need to be coupled to obtain a synergic effect that permits to reach better results with low amount of flame retardant.

Flame retardant tests

Consequences on public safety and on the environment that can be caused by the combustion of polymeric materials, push national and supranational legislation to an high attention about the materials that are to be used in the common applications.

In the case of polymeric materials, the combustion process is not easily analyzable as for example in the case of the gases, where the flammability is only defined through the limits of concentration in air or oxygen and the temperature of self ignition. In the case of polymeric materials, many factors are involved, as the shape of the object, the environment of the combustion, the kind and the position of the primer.

For these concerns, during the years a series of scientific tests have been optimized, with the goal to predict the behavior of a determined material or of the object that are produced with these materials during combustion.

These tests vary from the ones that study the behavior of the polymeric material in controlled combustion conditions (rate of heat release, O₂ necessary to develop and self-feed the combustion process), to the ones that analyze the behavior of a manufacture (i.e. an armchair containing desired material is burnt).

There are also tests consisting in the burning of an entire building to study the behavior in the real scale; although this test furnish data on the real behavior of a polymeric material in the application condition, the environment conditions are very variable (atmospheric conditions, presence and dimension of the primer) and influence the result of the test.

In this work the most important tests that study the behavior of the polymeric material evaluating it in controlled condition of shaping and environment will be explained; in particular tests that are universally recognized as the most representative of the flammability of polymeric materials will be treated:

- UL 94
- LOI
- Cone Calorimeter Test

UL 94 Test^[4]

The UL 94 is a test performed by the Underwriters Laboratory to furnish a preliminary analysis of the flammability of a polymeric material; there are three kind of tests that are distinguished for the shape and the position of the sample during the analysis: *horizontal test*, *vertical test* and test on *thin materials*.

Vertical test UL 94V

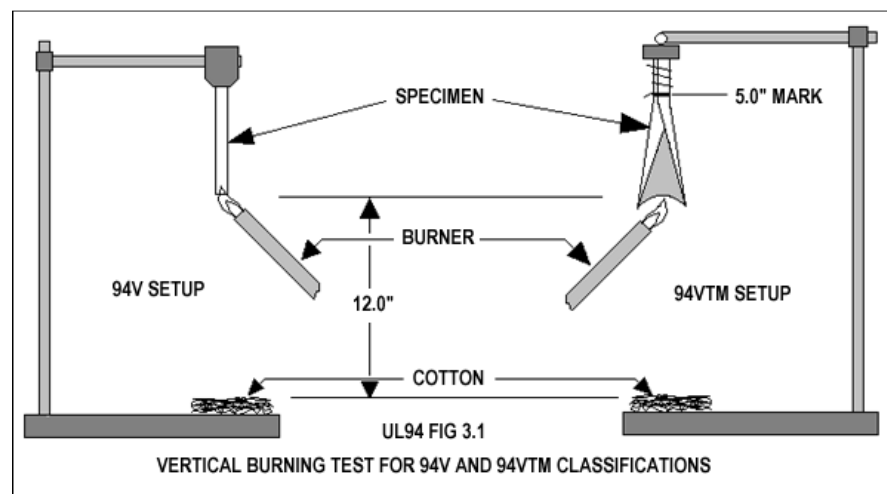


Figure 10: UL 94 V and UL 94 TM apparatus

This test is used to evaluate the flammability of pieces that are used in common applications and that are subjected to the risk of combustion as part of white goods, switchers and so on.

The test consists in the burning with a little fire a sample (127 x 12,7 x 3,2 or 1,6 or 0,8 mm) placed as represented in figure 1. The fire is applied twice for 10 seconds; between the two appliances the sample must self-extinguish the fire.

UL 94 divides polymeric materials in three classes:

- 94V-2: sample burns for a maximum time of 30 seconds after both the two applications; the glowing is stops in a maximum time of 60 seconds. Moreover drops of melt can ignite the cotton placed under the sample (see figure 1)
- 94V-1: results are the same than in case of 94V-2 classification except for the ignition of the cotton that in this classification is not permitted
- 94V-0: sample burns for a maximum time of 10 seconds and 30 seconds is the maximum time allowed for the glowing. The cotton isn't ignited.

Horizontal Burning UL94HB

This test is the easier to be passed and usually materials that pass the vertical burning test are automatically considered good for the horizontal test. In this test the sample (127 x 12,7 x 3 mm) is maintained in horizontal position and there are two signs that indicates the distance of 25,4 mm to the end of the sample as shown in figure 2.

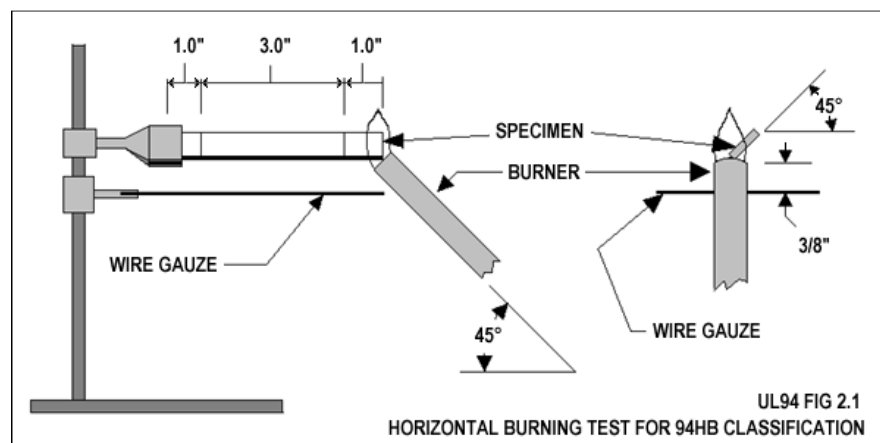


Figure 11: UL 94 HB apparatus

A little fire is applied for 30 seconds or until the fire reaches the sign at 25,4 mm. The test is passed if the fire needs more than 60 seconds to consume 76,2 mm of the sample. The test is performed on three samples. If one of them fails the target, the test is performed on three other samples, and all of them must reach the target to obtain the certification.

Vertical test on thin materials UL94VTM

In this test materials that are thin gauge or very flexible and may distort, flex or shrink during the UL94V test are analyzed: this test is different from the UL94V for three reasons:

- Dimension of the sample are 203.2 x 50.8 mm
- Material is rolled on a cylinder (12,7 mm diameter) and blocked on one side, when the cylinder is removed, the film assumes a cone shape as shown in the right side of the figure 1.
- Two application of the little fire have the duration of 3 seconds instead of 10.

Classification obtained is the same that in case of UL94V test, even if empirical data show that the same material tested with these two test is classified in an better class through the UL94TM test. If a material can be used to both two testes, this one is preferred because in this case an higher classification is obtained.

LOI- Low Oxygen Index (ASTM D-2863)

This test is developed by the ASTM (American Society of Testing Materials) to give a numeric value about the tendency of a polymeric material to sustain the flame in controlled conditions; this test doesn't give data on the combustion of the polymeric material in real conditions, but is a measure of its intrinsic flammability.

The advantage of this test is that it can be performed with a little amount of material (low cost test) and in controlled conditions; these characteristics make the LOI to be one of the most important tests worldwide recognized for the study of the behavior of flame retardants, the efficiency of their mechanisms, and their comparison in the combustion process.

In the following figure (figure 3) a typical tester is presented. It has a small camera, where the sample is placed, and the combustion process is studied varying the oxygen percentage.



Figure 12: LOI apparatus

During the test the “oxygen index” is measured (it is indicated through several acronyms as OI “Oxygen Index, LOI “Low Oxygen Index”, COI “critical oxygen index”) meaning the minimum concentration of oxygen in a nitrogen-oxygen mixture that is able to maintain the combustion during time.

The test is performed through the ignition with a little light that is removed when the material is able to maintain the combustion; after this, the minimum concentration of oxygen that permits the self-sustaining of the combustion is determined.

The LOI is measured as:

$$LOI = \frac{[OI_{cr}]}{[OI_{cr}] + [N_2]}$$

where $[OI_{cr}]$ means the amount of oxygen in the controlled atmosphere when the condition for the self-sustaining combustion are reached, while $[N_2]$ is the nitrogen concentration. The effect caused by the use of a flame retardant is measured as the increment of the LOI in the new material.

Considering that in the atmospheric air 20,95% of oxygen is contained, all materials that have a LOI lower than this value have a great probability to self-sustain the flame if ignited; if the LOI value is higher, the material can have the behavior of self-extinguishing material.

Cone Calorimeter

This instrument^[5] (that take the name from the heater that is cone-shaped) is the most complete for the study of the flammability of a polymeric material. It was invented by the American scientists of the NIST (National Institute of Standards and Technologies) and determines the rate of heat release (RHR) of a material subjected at a combustion process. Now its use is regularized through a series of standards described in the ISO 5660-1:1993. Figure 13 presents a classical cone calorimeter:



Figure 13: Cone Calorimeter apparatus

The test is performed in the following way: the sample is heated through irradiation from the cone heater with a controlled flux of heat (25-35-50-75 kW/m²); to obtain a complete certification of the ISO standard the test must be performed three times for each flux of heating. Vapors developed by thermal degradation are ignited by a spark and fumes produced by the combustion process are collected and analyzed.

This instrument has dimensions higher than testers for the LOI or UL94 tests, but this is due to the series of modules that composes the tester and the series of factors that are analyzed during the test:

- *RHR* (rate of heat release): is the most important parameter measured by the cone calorimeter analysis; it determines increase of temperature in the environment, the rate of the combustion and the rate of propagation
- *Fume's density*: it is measured by the attenuation of a laser beam; it is a parameter that determines the disorientation of the subjects in the case of combustion
- *Fume's toxicity*: toxicity of the fumes is measured, moreover is possible to connect specific modules for the analysis of the CO or CO₂ concentration.
- *Fume's temperature*: is an important parameter because this parameters can determine the propagation of the heat, therefore the propagation of the fire.

Complete final report is composed by the value of:

- Time to ignition (s)
- Total Heat Release (MJ/m²)
- Maximum rate of heat release (kW/m²)
- Average rate of heat release after 180 and 300 seconds (kW/m²)
- Maximum temperature reached (MJ/kg)
- Average production of the fumes (m²/s)
- CO production (g)

Moreover following results are graphically reported, showing the value reported during the time:

- Rate of heat release (kW/m²)
- Fume's production (m²/s)
- Rate of HCN and CO production (g/s)
- Mass of the sample during the analysis (g/s)

CHAPTER 2: (HFRs) Halogenated Flame Retardants

Introduction

Halogenated flame retardants have been the first kind of flame retardants used by the industry of plastic manufactures and until now their efficiency has not been reached by product.

Aromatic compounds with high halogen content (in example polychlorobiphenyls-PCBs and polybromodiphenylethers-PBDEs), act during the combustion of the polymeric material through a series of steps that slow the flame development:

- *In the gas phase:* these compounds intercept hydrogen and hydroxide radicals substituting them with bromine and chlorine radicals that are heavier and more stable and therefore in slower feeding the flame
- *In the condensed phase:* they form hydrohalic acid during the combustion; this acid in contact with the polymeric material dehydrates it giving a carbon-rich coating called "char". The char is a coating with high content of carbon that covers the polymeric material, slowing the passages of matter and energy at the inter-phase.

The history of the halogenated flame retardants

PCBs – Poly-Chloro-Biphenyls

The first halogenated flame retardants produced on industrial scale has been in the '30s were molecules with biphenilic skeleton and variable amount of chlorine atoms bonded. In the 1929 Monsanto industries bought the production plant of PCBs from Swann Chemical company; PCBs was a mix of bi-phenyl based molecules with an amount of chlorine atom for each molecule variable from 1 to 10.

The generic formula of these compounds is $C_{12}H_{10-x}Cl_x$ and is graphically reported in the Figure 14:

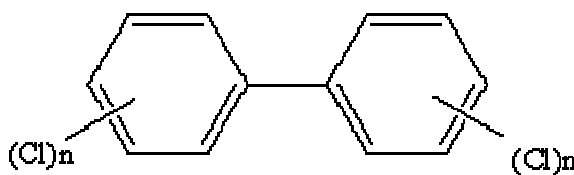


Figure 14: PCBs General Formula

Is possible to obtain 209 different molecules basing on the amount and the position of the chlorine atoms on the biphenilic skeleton ; these molecules are called “congeners” and they are ordinate from the number 1 to 209 through the so called BZ series, that was invented by Ballschmiter e Zell. 130 of these congeners have been found in the mix produced.

The PCBs production grew as an answer to the increasing request of flame retarded polymeric materials for application in the electric and electronic field, and from 1937^[6] the concern on the toxicity of polychlorinated molecules was investigated.

PCBs production has continued until different legislations, because of their toxicity, banned their production and utilization. This happened in 1972 in Japan, 1977 in the USA, and between 1976 and 1984 in several national legislation of the EU.

The total amount of PCBs produced is estimated in 1'500'000 ton, starting from 1930's until the end of 20th century; the region with the maximum amount of PCBs produced is the USA, where the Monsanto produced, between 1929 and 1977, 600'000 ton of material, followed by Europe with a production of 450'000 ton and then by Japan and URSS (Figure 15)^[7].

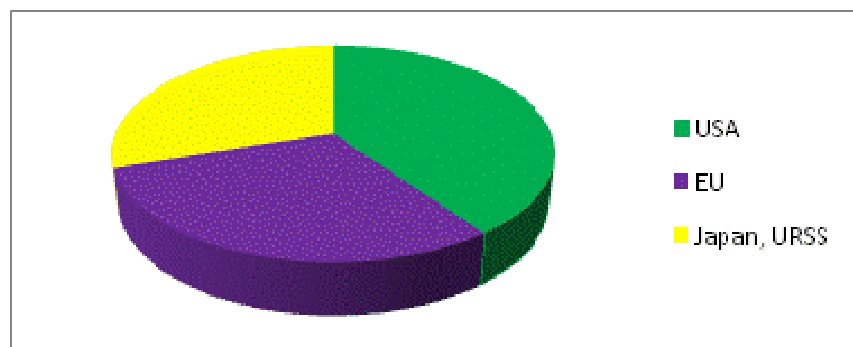


Figure 15: PCBs Production in the world

Some data are not available (production in Poland and East Germany during the beginning of the Cold war).

PBDEs - Poli-Bromo-Diphenyl-Ethers

Polychlorinated molecules as flame retardants were abandoned during the 1970's; a valid alternative has been found in the polybrominated molecules. Among them, one of the most important group is the one of poly-bromo-diphenyl-ethers (PBDEs).

They are molecules structurally similar to the PCBs, the differences are the ether bridge between the two aromatic rings and the presence of bromine atoms replacing chlorine atoms.

The general formula for these molecules is $C_{12}H_{10-x}Br_xO$ and their structure is presented in the Figure 16:

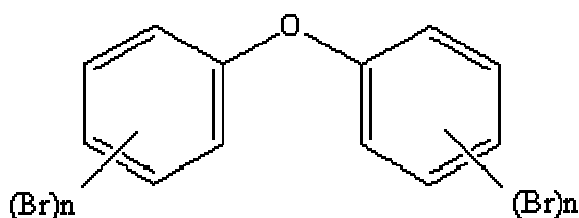


Figure 16: PBDEs General Formula

Also in this case, considering the variable amount and position of bromine atoms a series of 209 congeners is found. They are divided in congeners with low amount of bromine content (less than 5 bromine atoms for molecule) and high amount of bromine content (more than 5 bromine atoms for molecule). While the first ones are considered the most dangerous from a toxicological point of view, the molecules with the highest production volumes are penta/octa/deca- BDEs. Also in this case the amount of bromine content is an average value, while the deca-BDE is composed at 100% of that molecule, penta-BDE is composed 50% molecules with 5 bromine atoms, 45% molecules with 4 bromine atoms and 2-3% molecules with 6 bromine atoms plus traces (0.2-0.3%) of molecules with 3 bromine atoms.

At the beginning of the millennium concerns on the toxicity effect both on the human health and on the environment of these molecules raised, therefore the first ban on their production and use has been performed by the state of California (2006).

Toxicity problems on the use of polyhalogenated molecules

The chemical stability of these molecules is, on one side, the reason of their success as stabilizer and flame retardant and, on the other side, the reason of the concerns about their toxicity. In fact, if during the application their solid structure stabilizes the material, when they are in the human body or in the environment they are hardly degraded, giving problems in bioaccumulation in human body or in aquatic life^[8].

Regarding PCBs, the most evident effect on the human health is the formation of a persistent acne, called “chloracne”; its existence is well known since 1930's, period during which it appeared on the workers in charge of PCBs production. Other problems registered are liver diseases^[9], abnormal concentration in blood and urine.

There are also cases of contamination of food that caused the death by intoxication of many people^[10]. Regarding their bioaccumulation, in particular in human fats, part of the studies is concentrated to the determination of the passage to new generations through the accumulation in breed milk^[11].

Also mental diseases are studied in the sons of women exposed to polyhalogenated molecules^[12] and problems in reproductive activity subjects exposed^[13].

Concerning the cancerogenesis, these compounds are considered suspect cancerogen by all the main organizations that work on human safety. The cancerogenesis is confirmed only for PCB 126 (3,3',4,4',5-pentachlorobiphenyl) and of the mix PCB126/ PCB 153 by an American scientific work^[14].

These two molecules belong to the group with higher toxicity, because the absence of halogenated atom in ortho- position gives to the molecule the possibility to maintain the planar conformation, similar to the one of the chlorodioxine as is possible to see in the Figure 17:

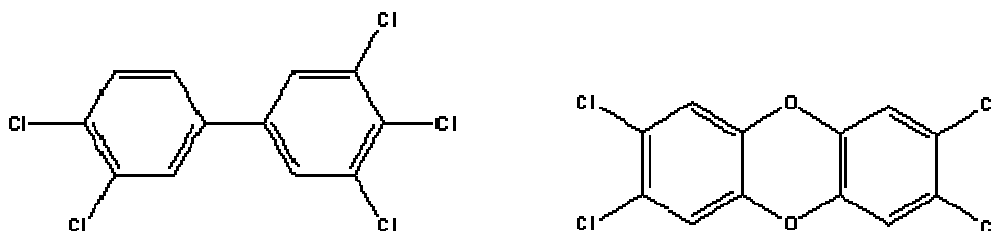


Figure 17: PCB 126 and TCCB formula

Regarding the accumulation in the environment, the chemical stability allows to these molecules to maintain their integrity during time also if solved in water (with a concentration in solution that can vary from 0.1 to 6 mg/L according to the congener considered), therefore during the transport by atmospheric agents.

Because of this, they have been found in all part of the earth in 2002 even if their production has been banned for 20 years.

The best way to eliminate them is the incineration at temperature higher than 1200°C and in excess of oxygen. Unfortunately, the common incinerators work at temperature of 900°C and at this temperature PCBs are transformed in highly toxic chloro-furans.

Regarding PBDEs, toxicity studies are more recent and less articulate (there are less data on the effects on human health) ; however the bioaccumule problem is confirmed, both in the human body and in the environment. Regarding bioaccumulation, studies are focused on liver accumulation and on the interception of the aril hydrocarbon receptor, with effects on sexual, hormonal and neuronal activity^[15].

Legislation on polyhalogenated aromatic molecules in the world

PCBs

Regarding USA, the legislation on the use of PCBs is entrusted to EPA (Environmental Protection Agency) that publishes all the laws regarding PCBs on the TSCA (Toxic Substances Control Act).

The legislation started on 4 November 1976 when the procedures for waste treatment of materials containing PCBs was fixed. All the legislation is contained in chapter 40CFR761, also published on the EPA website^[16] in complete form for public reading of the laws not only on waste treatment but also on production, importation and manufacture. The document is updated the 1^o July of each year if integration are necessities.

Also regarding the EU, the legislation starts with the legislation on waste treatment through the directive 76/403/CEE of 6 April 1976, that rules the disposal of waste containing PCBs or PBDEs.

In Japan, the control of the use of toxic substances is entrusted to the JESCO (Japan Environmental Safety Corporation). Japanese legislation blocked the production of PCBs in 1972 after the Yusho accident in 1968^[17] when the ingestion of rice contaminated with PCBs caused the death of 1680 persons.

In 1974 the "Law Concerning the Examination and Regulation of Manufacture, etc., of Chemical Substances (Class I)" entered in action banning also the importation and the use of PCBs.

PBDEs

Regarding the USA, EPA rules the use of PBDEs on the territory. Great Lakes, the only American producer of PBDEs, has been asked in 2003 to end the production within 31 December 2004. After this date EPA requested that the importation of these compounds in USA to be notified 90 days before^[18].

Regarding national legislation, production and use of PBDEs is forbidden in California and Maine, and forbidding proposal are registered in the state of Washington, Hawaii, Illinois and New York^[19].

In the EU in 2000 waste treatment was regulated and in 2003 production and use of octa- and penta BDEs were forbidden^[20].

CHAPTER 3: (NHFRs)Non Halogenated Flame Retardants

Introduction

Even if the use of some halogenated flame retardants (in example deca-BDE) is still permitted in many countries, problems evidenced in chapter 2 on the toxicity for human health and bioaccumulation in the environment push the research to the development of new flame retardants that can substitute the halogenated ones.

All these compounds are collected under the acronym NHFR (Non Halogenated Flame Retardants) that indicates that their most important feature is their flame retardancy obtained without the presence of halogenated molecules.

However polyhalogenated molecules have great efficiency as flame retardants, good compatibility with the most of polymers and an acceptable commercial cost. Since 1990s NHFR have been considered as a better product thanks to their lower environmental impact, but is not possible to find in this substances the same characteristics of flame retardancy, costs and compatibility with the polymeric matrix.

In particular in this chapter will be treated:

- Metal hydroxides
- Intumescent Flame Retardant
- Phosphor-based flame retardant
- Nanocomposite materials

Metal hydroxides

The most used inorganic flame retardants are aluminum and magnesium hydroxide; at high temperature these materials decompose with water emission, through the following reactions:

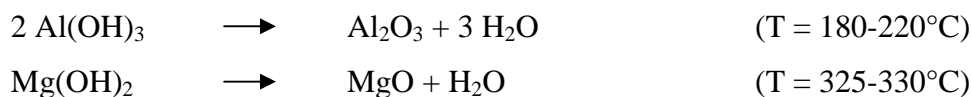


Figure 18: Thermal degradation of metal hydroxides

Aluminum hydroxide is the most used both for the higher amount of water emitted in comparison with the same weight of magnesium hydroxide, and for the lower degradation temperature that permits water emission earlier in case of thermal degradation.

The decomposition reaction of the metal hydroxide gives flame retardant effects both in condensed and in the gas phase:

- in the *condensed phase* the temperature is lowered by the endothermic nature of the decomposition reaction (350 cal/g) and of water evaporation (97 cal/g for Al_2O_3); moreover the thermal stability of the polymeric material increases because of the deposition of metal oxides on the polymer's surface
- in the *gas phase* water vapor emitted slows the combustion's kinetic diluting combustible vapors and can stop the combustion process if lowering combustion vapor's concentration under the flammability point. Moreover the temperature is reduced, lowering the combustion's kinetic.

Metal hydroxides are considered the flame retardants having the lowest environmental impact, because they act only through water emission, lowering the temperature and diluting fumes.

However their efficiency (and in general the efficiency of compounds that act through physical mechanisms, if compared to the ones that act through chemical ones) is very low and it is necessary an insertion of high amounts (50-60% in weight) to reach a good result of flame retardancy.

Intumescent flame retardants

Intumescent flame retardants are a set of chemical substances that act during the combustion process through the formation of a foamed carbon-rich coating that works as a barrier in the condensed phase, blocking the matter and energy exchange with the gas phase.

This kind of flame retardant has been used since 1960s for the protection of metallic and wood-based structures, and at the end of 1970s it has been transferred on the protection of polymeric materials.

The action of intumescent flame retardant is complex because three chemical compounds contribute to the char formation:

- an inorganic acid, inserted itself or formed in situ, that causes the dehydration of carbon-rich compounds (phosphoric, sulfuric or boric acid, or ammonium salts as phosphate, sulfate or amine phosphate).
- a carbon-rich polyhydroxylate compound is the carbon source after the dehydration by the inorganic acid during the thermal degradation.
- a nitrogen-containing organic compound as amine or amides that works as foaming agent (i.e. melamine, polyamides).

The mechanism proposed for this kind of flame retardant is the following one:

1. During thermal degradation, the inorganic acid attacks the polyhydroxilate compound dehydrating it and forming a multistrata carbon-rich coating.
2. The forming agent degrades thermally, emitting an inert gas (i.e. nitrogen) that foams the multistrata char increasing its barrier effect.

The choice of the agents for the intumescent system is bonded to their behavior during the decomposition process: in fact the proper action of the system needs that the inorganic agent dehydrate the poly-hydroxilate compounds earlier than its degradation; moreover the foaming agent must decompose with inert gas emission after the carbon coating formation, when the viscosity of the carbon coating is the right one to have the maximum barrier effect (obtained in the case of 20-50 μm for the bubble diameter and 6-8 μm for the carbon coating).

Intumescent flame retardant having great efficiency are poly-phosphoric acid as dehydrating agent, pentaerythrol as carbon source and urea, melamine and dicyandiamide as foaming agents.

Phosphor-based flame retardant

Phosphor has shown, during the combustion process of a polymeric material, a behavior similar to the one of polyhalogenated molecule: it is able to form poly-phosphoric acid (comparable to the hydrohalic acid formed by polyhalogenated compounds) in the condensed phase, that can dehydrate the polymeric material to form a carbonized coating; moreover it forms PO species that can intercept hydrogen and hydroxide radicals that feed the flame and substitute them with heavier radicals that are slower in feeding the flame through the following reactions:

1. $\text{PO}\cdot + \text{H}\cdot = \text{HPO}$
2. $\text{HPO} + \text{OH}\cdot = \text{PO}\cdot + \text{H}_2\text{O}$
3. $\text{HPO} + \text{H}\cdot = \text{H}_2 + \text{PO}\cdot$

Figure 19: Radical mechanism of phosphor containing molecules

In particular reaction 2 shows that PO species works as catalyst of water formation in gas phase, bringing many advantages in the flame retardancy process. Phosphor can be inserted as red phosphor or as phosphor-containing organic molecule:

- The use of *red phosphor* presents the advantage that all the matter inserted is phosphor and carries the flame retardant property, so it is possible to obtain good result with low amounts of matter inserted. Its use is affected by some problems in phase of manufacture because it is flammable also by simple friction; moreover it is a inorganic compound with low dimension and compatibility problems bonded to its insertion in a polymeric material that has high molecular weight and organic nature, with consequent problems of migration and aggregation.
- The use of *phosphor containing organic compounds* solves problems of flammability and reduces problems of compatibility with the polymeric matrix, but it causes the insertion of an high amount of organic matter without flame retardant property bonded to the phosphor atom. Therefore an higher amount of flame retardant additive is needed to obtain the same result compared with the use of red phosphor.

However, this molecules are considered one of the best alternative to HFR, because of their high efficiency.

Nanocomposite obtained with mineral nanofillers

During the last decades, the effect of the insertion of mineral nanofillers in a polymeric materials has been investigated, focusing on gas permeability, impact resistance and flame retardancy.

The nanometric dimension of the mineral fillers, both lamellar (montmorillonite) and spherical (nanosilica), theoretically allows an homogeneous distribution in the polymeric material with the possibility to maximize the properties through the insertion of a filler with higher surface area than the normal dispersed one^[21].

Regarding flame retardancy properties, mineral filler is inert matter and consequently not interested by the combustion process. Moreover in the case of combustion the polymeric material is consumed, while the inorganic portion is concentrated, giving the formation of an inorganic barrier able to prevent the exchange of matter and energy with the gas phase.

CHAPTER 4: Insertion methods of a flame
retardant in polymeric
material: Compounding
versus Copolymerization

Introduction

Polymeric materials are on the market since the beginning of the 20th century; during the last 100 years, new polymeric matrices have been continuously developed, and new applications have been continuously found for the use of these materials.

Until 1960s there has been an exponential growth of the founding of new polymeric matrices, but now the research of new matrices, both on industrial and academic level, needs the investment of an high amount of time and money, without the certainty of a rapid or sure result. Starting from 1960s a new way to obtain materials with new properties has been found: the physical mixing of the molded polymeric matrix with some particular chemical substances called *compounding*.

The compounding

The compounding process consists in a physical mixing performed in an extruder between the molded polymeric matrix and one or more chemical compound (called “additive”) that confer the new properties.

The compound isn't necessary for all the application: in the production of bottles, films and fibers through extrusion, proper properties for these application are already contained in the pure polymer, and if a minimal changing is needed (for example the insertion of a pigment) it is performed directly at the end of the polymerization phase or at the beginning of the manufacture, without the necessity of a complete step of modification. On the contrary, materials used for mold application need properties that are very different from the ones obtained with the pure polymer.

The compounding process is almost necessary for some polymers (i.e. ABS/PPO) and almost absent for others (see tab 1):

Polymer	Volume (x 1000 ton)	Compound	
		%	(000 ton)
PE	11700	8	950
PP	6600	11	750
PVC	5500	27	1500
PS	2900	12	350
PET	1300	2	30
ABS/SAN	730	89	650
PA	580	72	420
PC	390	46	180
PBT	110	91	100
Acetalics	150	12	18
PPO	60	100	60
PMMA	250	26	65
Others	70	86	60
Total	30340	17	5133

Table 1: Use of compound process on polymeric matrices

It is possible to see that PET, used for the production of bottle through a blow molding process, generally doesn't undergo a compounding process, while in the case of polyamide, the 70% interested by the compounding process is the amount used for the fabrication of molded pieces; the remaining part is used for fiber production.

Principal classes of additives used for the modification of polymeric materials are:

Stabilizers: have the function to inhibit or slow the degradation process of the polymeric material during both the manufacture and the application. Standard stabilizers are antioxidants or anti UV.

Biocides: protect the material from attacks by biological organisms (i.e. silver salts).

Antistatic agents: permit the dissipation of the static charge accumulated on the material (i.e. phtahalats).

Pigments: vary the optical response of the material.

Fillers: improve mechanical properties of the polymer (i.e. minerals, glass fibers).

Plasticizers: improve the flexibility of the material (i.e. phthalats).

Flame retardants: modify the response of the polymer at the combustion process, until the self extinguish of the material.

Impact modifier: functionalized polymer that adsorb the energy coming from an impact.

The compound technique

The compounding process of a polymeric material is performed in an extruder. The classical layout of machine is shown in figure 20:

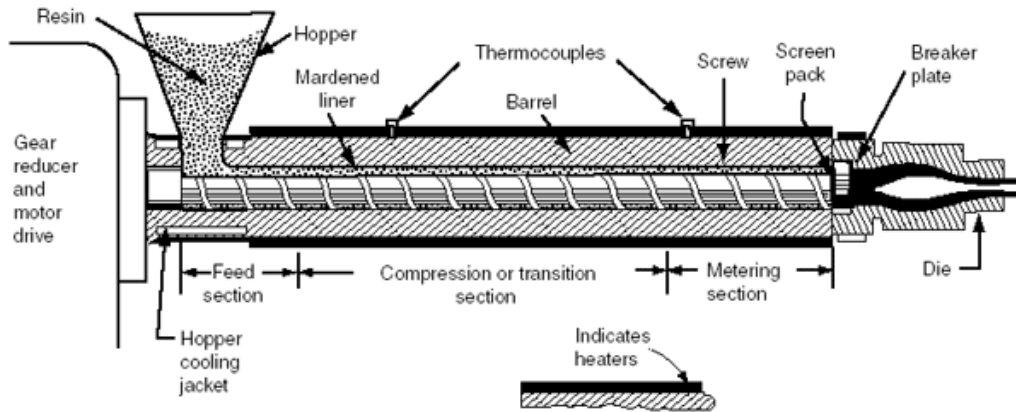


Figure 20: Example of Compounder apparatus

The system is composed of a load point for the polymeric matrix that pass in heated cylinder pushed by one or more no-ending rotating screws. The chamber is heated to temperatures set through a thermocouple, as evidenced in the figure 6.

The path followed by the polymeric matrix is determined by the number, the rotation and the shape of the screws: there are extruders with one or two screws, with a rotation in the same or opposite directions, and with different screw's shape.

The additive can be inserted directly with the insertion of the matrix or later in order to optimize the contact time between the matrix and the additives. Processing temperature must be near to the melting temperature of the polymeric matrix, lower than the degradation temperatures of matrices and additives, and its profile is accurately designed; processing temperature influences also the viscosity of the material, influencing its interaction with the additives.

At the end of the mixing phase the polymer can be colded and granulated.

Concerns on the compounding technique

The compounding technique, as explained, is the most rapid and economic way for the development of materials with new properties.

However its use has advantages and disadvantages that make it attractive for some aspects, and incomplete under others. Advantages and disadvantages of the compounding process are presented in table 2:

<u>Advantages</u>	<u>Disadvantages</u>
Rapid	Compatibility problems
Versatile	Homogeneity problems
Needs low investment	Migration problems
Needs medium scientific knowledge	Unusable for fiber production

Table 2: Advantages and Disadvantages of compounding process

The compounding process permits to obtain rapidly new formulations, obtained through simple mixing of the polymeric matrix with different amounts of one or more additives; it is possible to search in semi-empirical way the right combination of amounts that gives the best result in improving the property of the material.

However compounding must not be considered as simple mixing process without scientific basis. There are a great number of studies, especially on engineering field, that investigate compounding processes. In these studies the knowledge on some important aspects, as screw number, rotation direction and screw shape, are scientifically studied and optimized^[22].

The insertion of a molecule with different origin compared to the polymer rarely carries to an homogenous distribution; one of the most problem is that additives are usually low molecular weight molecules (<1000 g/mol) and that polymer molecules have much bigger dimensions (>10000 g/mol).

This dimensional difference leads to a tendency to migration during time: even if with the compounding process an homogenous distribution is reached, the additives tends to reach the surface of the material.

Matrix and additive have not a chemical bond and the additive in the bulk of the polymeric material is in equilibrium with the one on the surface: the last one can be lost, for example, through evaporation or dissolution in a solvent (i.e. water when raining); in this case the additive in the bulk of the polymeric matrix migrates to the surface impoverishing the material with the consequent loss of the properties.

Moreover, in the case of toxic molecules the loss of the additive in the environment during application or waste treatment can cause problems of environmental impact.

Another problem bonded to the compounding process is, in some cases, the different nature of additive and polymeric matrix: in the case of mineral fillers (for example, metal hydroxides as flame retardants) a physical mixing is performed between a polymeric matrix with organic nature and an additive with inorganic nature, having very different values of surface tension and therefore low interaction; this results in a poor dispersion of the additive in the polymer, with aggregation phenomena that decrease the efficiency of the additive.

Regarding this phenomena there are studies on the optimization of the compatibility between matrix and additive, through grafting treatment. This treatment works covering the surface of the additive with a substance, that has a better interaction with the polymeric matrix, to obtain a better result during the compounding.

Results obtained with some grafting treatments on the interaction between additive and polymeric matrix are appreciable through SEM (Scansion Electronic Microscopy) analysis: in the figure 21 are reported SEM images of polyamide-based composite materials in presence (right) and absence (left) of the grafting agent:

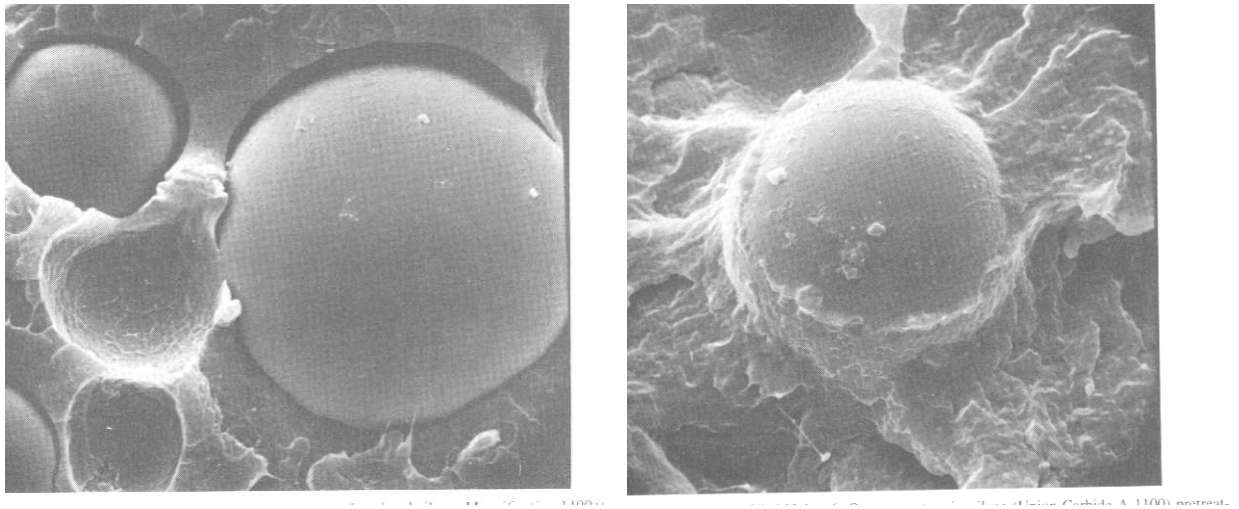


Figure 21: Effect of the graft on the interaction between an inorganic nanofillers and polyamide 6: the result is reported in absence (left figure) and presence (right figure) of graft.

The copolymerization

Copolymerization is a process of macromolecular synthesis that permits to obtain polymeric matrices with chemical-physical characteristics different from the ones of the starting homopolymers, and depends by the comonomers choice, their concentration and their sequence in the macromolecular chain.

The term “copolymerization” indicates the process that forms a macromolecular chains through the reaction of one or more repetitive unit, where this definition interest the complete structure that is repeated in the macromolecular chain (for example, polyamides, obtained by the condensation of diamines and diacids, aren't considered copolymers because the repetitive unit is one).

Copolymer are described defining:

1. The composition: relative comonomers concentration.
2. Repeating units: sequence of enchaining, possible isomeric structures.
3. Incorporation order of comonomers that determines the kind of monomeric sequence obtained.
4. Chain dimension.
5. Presence of branching, cross linking center or cyclization

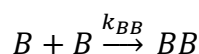
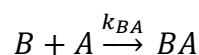
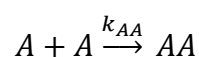
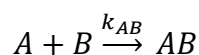
The analysis of the firsts two point carries to the division of the copolymers in 4 groups:

- Statistical copolymers: have a statistical distribution of the monomers following the 1st order Markov law
- Alternates copolymers: are composed by an alternation of the two comonomers in the macromolecular chain.
- Blocks copolymers: there are long sequences of the same comonomer
- Grafted copolymers: chains composed by a comonomer are grafted on a chain composed by the other one.

Theory of the sequence of comonomers in a copolymer:

The sequence of the repeating units in a macromolecular chain obtained through copolymerization is ruled by the kinetic of the reactions involved during the polymer synthesis:

The simplest case considers a copolymer composed by A and B monomers the possible reactions are four, each one ruled by one kinetic constant:



The ratio between different constants causes the sequence obtained:

$$- k_{AB} \sim k_{BA} \sim k_{BB} \sim k_{AA}$$

All the reactions have the same rate and so the sequence is ruled by the statistics.

$$- k_{AB} \sim k_{BA} \gg k_{BB} \sim k_{AA}$$

All comonomers prefer to react with molecules of the other comonomer than themselves.

An alternate copolymer is obtained.

$$- k_{AB} \sim k_{BA} \ll k_{BB} \sim k_{AA}$$

All comonomers prefer to react with themselves than with molecules of the other comonomer. A block-copolymer is obtained.

This is a general and simplified example of the treatment of the kinetic data to discuss on the copolymer composition. In the case of equilibrium reactions (as in the case of polycondensation) also inverse reactions must be considered or the exchange reactions on chains already formed. In some cases, also the “penultimate effect” is present in which the penultimate structural unit inserted in the chain acts on the kinetics of the chain growth; in this case the complexity of the system increases.

In the following table some advantages and disadvantages of copolymerization are reported:

<u>Advantages</u>	<u>Disadvantages</u>
Homogenous Distribution	Economical investment
Inherent and stable property	Starting scientific investment
High efficiency	Possibility to modify the plant
Usable for fiber production	
Intellectual property	

Table 3: Advantages and Disadvantages of the copolymerization process

The insertion of a property through copolymerization has the advantage that the property becomes inherent of the material and the distribution of the comonomer in the macromolecular chain permits an homogenous distribution of the property on all the material.

This good distribution can also allows for a better efficiency of the molecule used, with the possibility to obtain good properties with low amount of the comonomer; considering that this molecule has a prize higher than the polymeric matrix, the use of a lower amount of it gives a material with lower cost and more stability. Moreover the molecule is chemically bonded to the polymeric matrix, so there are not concerns of migration or agglomeration phenomena as in the case of compounding.

Last but not least for these materials is not needed the compounding process. This causes a lower cost of the final material, while the absence of a thermal treatment makes the material more stable.

However, even if this process carries to materials with good chemical and physical properties, it is not usually considered the preferable way in comparison with the compounding process for the initial difficulties both in economical and scientific investment.

A potential comonomer must have the following characteristics:

- *Reactivity*: it must possess reactive groups that permits the insertion in the macromolecular chain without disturbing the polymerization process.
- *Stability*: it must be stable in polymerization and application conditions. Moreover it must form stable bonds with the monomers of the matrix to avoid being a weak point in the macromolecular chain.
- *Toxicity*: the molecule must not represent a danger for human or environment safety, and must be synthesized by a environmentally sustainable process

Moreover, by an economical point of view, the study of a new polymeric materials obtained through copolymerization must deal with investment higher than in the case of the compounding.

- *Scientific study*: is more important than in the case of the compounding
- *Modification or building up of a production plant*: there is the possibility that the copolymer cannot be synthesized in the same production plant of the homopolymer. In this case the last one must be modified or a new plant must be built-up.
- *Compatibility with in continuous plant*: polymeric matrices are now considered commodities, where a good part of the economic advantage is the high amount of material produced in a continuous plant. This kind of plant are not very compatible with the production of new materials, because not versatile.

Conclusions:

In conclusion the two presented techniques permit to modify of one or more properties of a polymeric matrix, adapting it to the desired application, passing through two very different ways.

In the field of the industrial research the tendency is to obtain new properties for the existing matrices passing through the compounding process, because of its versatility, rapidity in obtaining results and low economical investments.

Unfortunately, the ease to obtain data on the materials performed through compounding pushes also the academic research to chose it in spite of the improving of the knowledge on new polymeric matrices or copolymers.

On the other hand the research of new materials through copolymerization is the technique that has the possibility to repay starting investments in money, time and scientific knowledge, because it produces materials with properties of stability and homogeneity that are not obtainable by compounding.

The research of a new material through copolymerization is the way to reach innovation that can be crucial in the field of the development of new materials, with better mechanical properties, low cost and lower environmental impact.

CHAPTER 5: Flame retardant's market and our choice of materials

To identify the target market, and to give the possibility to evaluate the innovation contained in this work, this chapter is focused on the description of the flame retardants market, with particular attention on production volumes and typologies.

At the end of the chapter, a section will discuss about the choice of the material for this research project.

Flame retardants market

The global market of FR^[23] in 2007 involves a market evaluated in 4.2 billion of dollars; the production of the HFR is higher than NHFR's one, and evaluated in 2,6 billions of dollar, but it is important to point out that the trend is the substitution of HFR with NHFR, that increases during the time.

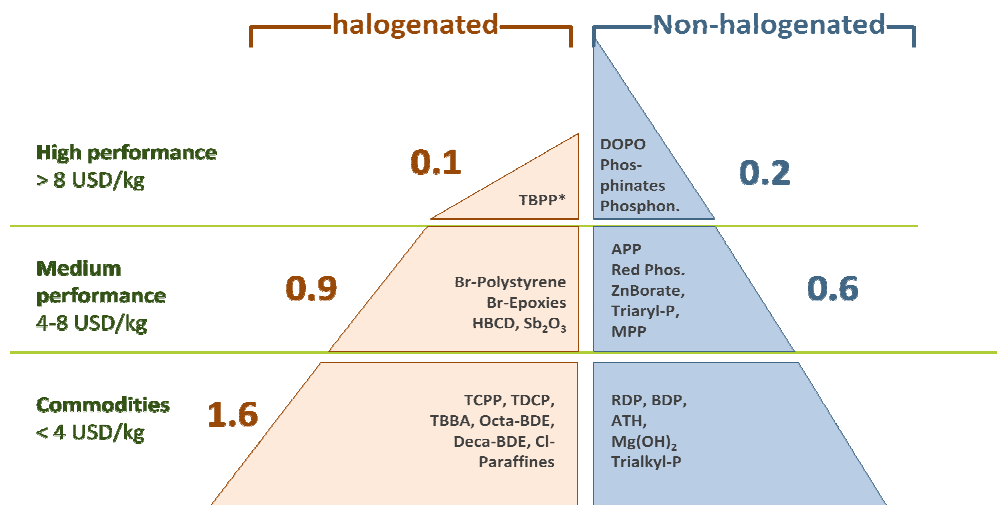


Figure 22: World production of HFR and NHFR

In the previous figure, the areas represent the economic volume of the flame retardants produced, divided according to their cost. It is possible to note that in the case of HFR the low cost fraction is the highest, while in the case of NHFR it represents the 50% of the total production.

Scientific and industrial research about NHFR is more recent; usually a higher efficiency of the FR is searched even in spite of higher production costs, to allow for a lower amounts of FR in the material.

The low cost fraction of NHFR is composed by aluminum and magnesium hydroxides and organo-phosphor compounds with low content of P and low efficiency (i.e Resorcinol bis-diphenylphosphate RDP).

The average cost group is composed by red phosphor and other compounds with medium efficiency, while in the high cost group there are organo-phosphor compound with high P content and high efficiency, that can be used as comonomers, as 2 carboxyethyl-phenil-phosphinic acid (CEPP) used in copolymerization with PET to obtain the only example of inherent FR fiber, TREVIRA CS[®].

An example of market: Electronic & Electric Equipment (EEE)

One of the most important market for the use of FR plastics is the Electronic & Electric Equipment one. In this field, in fact, the polymeric material is used in condition of direct contact with metallic materials in presence of electric current, with the possibility of sparks formation, and energy accumulation that can be dispersed as heat causing the increasing of temperature and the development of accidental fires.

This is one of the most important fields of development and use of NHFR as evidenced in the following figure, reporting the main application fields of NHFR:

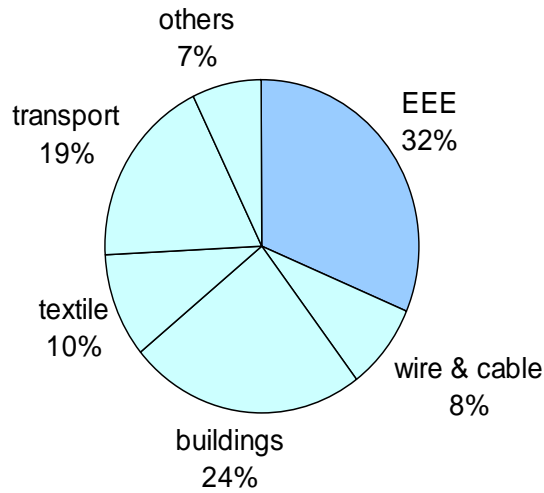


Figure 23: Field of Use of NHFR

A more detailed analysis of the amounts of the main classes of FR produced in Europe in the field of EEE is presented in the following figure: NHFR fractions are indicated with different tones of blue, while HFR are indicated with different colors.

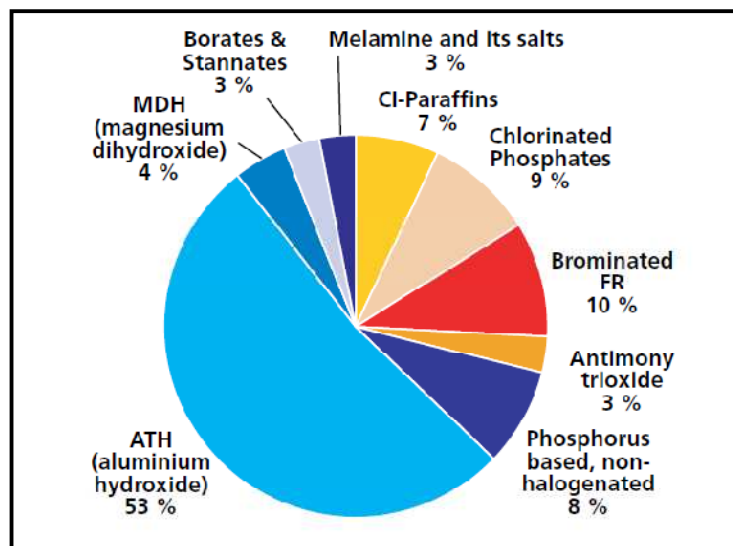


Figure 24: Distribution of FR used in EEE field

The main product is aluminum trioxide (53%), preferred to magnesium hydroxide (4%), because it develops an higher amount of water (1 mol for 52 g versus 1 mol for 58 g of the second) and because it has lower degradation temperature (220°C versus 350°C of magnesium hydroxide) allowing to obtain the flame retardant effect at lower temperature.

Usually in order to obtained a standard value of flame retardancy, HFR are added in amounts of 10-20% w/w on the final material, a phosphor-containing compound in the order of 5-10% w/w of phosphor and metal hydroxides in amount of 30-50% of the material.

Our material's choice

The passage from the use of HFR to the NHFR creates a series of problem to plastics producers and manufacturers: the lower efficiency of NHFRs, and in some cases, their lower compatibility with the polymeric matrix, are some examples of the unsolved problem in the use of these new kind of FR.

Moreover the legislations on the toxicity and on the flammability of plastic materials pushes the market to materials with higher flame retardancy standards.

These two tendencies (on one side the necessity to substitute the most efficient group of FR, the halogenated ones, and on the other to have higher flame retardancy and low toxicity) pushes the research to the development of new products, but it is almost impossible to get a response for all applications.

One of the most important gaps in the present market is the absence of a polyamide textile fiber with flame retardant properties. As shown in chapter 4, flame retardancy in a fiber cannot be obtained through the compounding process, because the presence of a extraneous material to the polymeric matrix is not usually compatible with the spinning process.

Moreover the fraction of polyamide used for the fabric of molding pieces (70% on the total) interests a series of application that need a high level of flame retardancy (usually pieces are used in electric and electronic fields, or in automotive).

In the family of polyamides, Nylon 6 has been chosen as matrix for this project, because it is a commodity and it is obtained through the polymerization of an α - ω amino acid, moreover it is a polymer easily analyzable in the case of the insertion of one or more chain regulator.

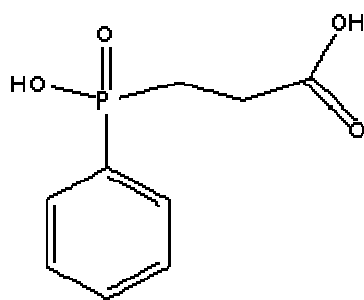


Figure 25: CEPP molecule

As chain regulator, 2 carboxyethyl-phenyl-phosphinic acid has been chosen. The molecule is presented in the Figure and is already used on an industrial scale in copolymerization with PET in an amount of 5% in weight to obtain the material sold with the trade name of TREVIRA CS[®], one of the most important trade in the textile field and the only example of synthetic flame retardant fiber. The copolymerization of CEPP with nylon 6,6 has been claimed (WO98/52991 and US5952406) but this synthesis doesn't lead to a material with the desired properties; the evidence is the non-existence on the market of commercial products obtained following these kind of synthesis.

A second part of the thesis deals with the evaluation of the possibility to obtain flame retardant nanocomposite materials through in situ polymerization, since many papers explore the use of mineral nanofillers as potential flame retardant^[24].

Two minerals, very different from each other, have been used with several differences have been chosen:

- The first one is montmorillonite: this mineral has lamellar shape and in the commercial product used in this work Cloisite 15A[®], produced by the Southern Clay, lamellae are intercalated by ammonium ions containing long aliphatic chains. Data on the chemical and physical parameters of this product are presented in the chapter 9.
- The second one is nanosilica: is a material composed of Si-O bonds and organized in spherical particles. The product has been chosen for the low value of the average diameter of the particles (20 nm) and the high surface area (600 m²/g).

CHAPTER 6: SEC (Size Exclusion Chromatography) Calibration

Size exclusion chromatography is an analytical technique that distinguishes the molecules, basing on their hydrodynamic volume, measuring their retention time in the apparatus; the molecular weight is measured basing on a calibration of the system obtained with a series of standard through the equation:

$$\log(Mn) = a (t)^3 + b (t)^2 + c t + d$$

The hydrodynamic volume of a macromolecule is the volume taken up in solution and is determined by chain length, molecular architecture and polymer-solvent interaction. During SEC analysis, the polymer is solved in an proper solvent (that represents the mobile phase of the chromatography) and is pushed under pressure in a series of columns that contain a polymeric gel having pores with variable dimensions (stationary phase).

Retention time is determined by the dimensional interaction between the solved sample and the pores of the chromatographic columns: molecules with low hydrodynamic volume permeate pores and take a longer way, exiting after longer time of retention, while macromolecules with higher molecular weight are excluded and passes through the interstitial spaces exiting quickly from the apparatus.

Calibration is generally performed through the analysis of monodisperses standard polymers with known molecular weight (usually polystyrene and polymethylmetacrilate but is possible to obtain also monodisperse polyamides through anionic polymerization); considering that they are monodisperse, they have a well defined time of retention, that is related to the molecular weight to obtain the calibration curve using the equation already presented. n

However the calibration obtained through the analysis of monodisperse polymers gives punctual values of molecular weights, without indications on the polydispersity of the macromolecule.

During this work a new calibration has been obtained, using standard polyamides 6 with controlled molecular weight, obtained varying the ratio caprolactam/aminohexanoic acid in a closed system, to change the amount of water present and moving the equilibrium of the polycondensation reaction. 5 polymers have been prepared with the goal to cover all the molecular weights generally analyzed during our work, from high polymer to the oligomers.

In the table are reported molecular weight data for prepared polymers:

Sample	Desired M_n	Measured M_n
1	32000	18282
3	10000	8546
4	6000	6526
5	2500	4311

Table 4: Samples prepared for SEC calibration

Since they are polymers synthesized through step polymerization (equilibrium polycondensation), the molecular weight distribution equals 2 and the distribution curve is evaluated through a mathematical model (Flory's model).

The molecular weight (M_n) of the model polymer synthesized is easily measurable through potentiometric titration ("measured M_n " reported in the table).

In this way is possible to obtain the real value of M_n , while values of M_w , M_p and d are evaluated according to the model:

$$M_w = 2 M_n$$

$$M_p = M_w$$

$$d = 2$$

It is possible to build up the theoretical SEC curve of the polymer comparing it point by point to the experimental one and obtaining a value of molecular weight and retention time for all the points of the curve as presented in the following figures:

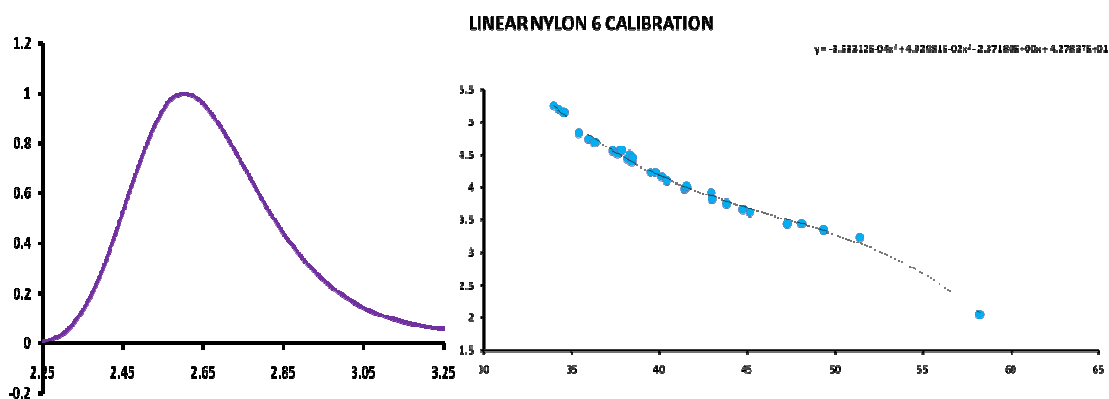


Figure 26: Data Elaboration for the Nylon 6 linear Calibration

This calibration allows to evaluate the molecular weight of the polymer considering also its polydispersity, that now is a parameter inherent of the calibration system.

However, in the analyses of species with modified molecular architecture (i.e. star, branched etc.), the relation between the molecular weight and the hydrodynamic volume varies, causing an error if the molecular weight is calculated through a calibration obtained with linear polymers.

The use of a linear nylon causes an error much lower if compared to the one resulting from polystyrene

In the case of the synthesis of a polymer in presence of a multifunctional agent, the variety of species obtained makes not possible to obtain the conditions to evaluate the molecular weight through a calibration.

For example, in the case of the synthesis of a nylon 6 in presence of a multifunctional agent with $f=6$, the polymer will have different kinds of macromolecules obtained following main variables:

- *Presence of the multifunctional agent*: only a fraction of the macromolecules contain the multifunctional agent, the residual fraction is composed by linear macromolecules.
- *Number of the branches*: star shaped molecules can have 3,4,5,6 branches
- *Length of the branches*: statistically, not all branches have the same length

In presence of these variables, that influence the hydrodynamic volume, is not possible to define with accuracy the molecular weight correspondent to a value of retention time.

CHAPTER 7: Star shaped polyamides

Calculation on the distribution of the molecular weights in star shaped polyamides

Flory's Model

Flory, Nobel prize in 1974 in the chemistry, was the first studying polycondensation reaction of caprolactam with multifunctional agents having 2 or more reactive groups with the same reactivity (carboxylic acids or amine groups). During its study he hypothesized that all reactive groups of the multifunctional agent had reacted and that the polymer contained only molecules with a determined number of branches with similar length. The presence of terminal groups not present in the multifunctional agent (i.e. amino groups in a nylon 6 obtained in presence of a molecule with several carboxylic groups) reveals the presence and the number of linear macromolecules in the final product. Basing on these evidences, Flory developed a mathematical model^[25], that allows the prevision of the number-average and weight average molecular weight and of the fraction of linear macromolecules when an AB monomer reacts with a multifunctional agent defined RA_b

The number-average molecular weight is defined as:

$$\overline{M}_n = \frac{Qm_b + m}{Q/b + L}$$

Where Q indicates the equivalents of the RAb multifunctional agent in a mole of AB monomer, b the number of the functionalities of RAb, L the number of terminal groups in lower quantity, and consequently the number of linear chains, m is the molecular weight of the AB monomer after insertion in the macromolecular chain, an M_b the molecular weight of the multifunctional agent divided by the number of b functionalities.

The weight fraction of the linear species is defined as:

$$w_L = \frac{L}{\left\{ L + Q \left[1 + \left(\frac{m_b}{m} - 1 \right) \left(\frac{Q+L}{Q+1} \right) \right] \right\}}$$

While the weigh-average molecular weight is:

$$\overline{M}_w = w_L \overline{M}_{n,L} \left(\frac{\overline{x}_w}{\overline{x}_n} \right)_1 + (1 - w_L) \overline{M}_{n,Q} \left(\frac{\overline{x}_w}{\overline{x}_n} \right)_b$$

Where:

$$\overline{M}_{n,L} = m \left(\frac{Q+1}{Q+L} \right) \quad \overline{M}_{n,Q} = b \left(m \frac{1-L}{Q+L} + m_b \right)$$

$$\left(\frac{\overline{x}_w}{\overline{x}_n} \right)_1 = 1 + \frac{(1-L)(1+Q)}{[(1-L) + (Q+L)]^2} \quad \left(\frac{\overline{x}_w}{\overline{x}_n} \right)_b = 1 + \frac{b(1-L)(1+Q)}{[b(1-L) + (Q+L)]^2}$$

This model is valid for reactions with an high conversion's degree and low concentration of multifunctional agent, because only in these conditions the hypothesis of complete conversion of the terminal groups of the multifunctional agent is valid. This means that under this hypothesis the polymer contains complete star shaped molecules.

Considering the last formula presented, that furnishes the molecular weights distribution for a complete star shaped polymer, considering low concentration of the multifunctional agent and high conversion, Q and L can be neglected, and the equation coincides with the one calculated by Schulz in 1939:

$$\left(\frac{\overline{x}_w}{\overline{x}_n} \right)_b = 1 + \frac{1}{b}$$

Later Prof. Farina worked on the same principles of Flory's model, developing new equation for the description of the behavior of star shaped polycondensates. In a recent study, Dr. Yuan developed a new complete mathematical model, reconsidering all the kinetic model developed by Flory.

Prof. Farina's Model^[26]

Prof Farina, working on the modification of the distribution of the molecular weight of polyamides, with the goal of studying the impact on technological properties, studied the problem of the equations regarding the distribution of molecular weights of polycondensates products obtained in the presence of a multifunctional agent (RAf) Polymers obtained are considered, with an high approximation, as an homogeneous mixing of non regulated chains (linear species) and star shaped ones with a number of branches equal to the number of reactive groups of the multifunctional agent. Also in this case, as in Flory's model, the presence of regulated species with number of branches lower than the reactive groups of the multifunctional agent is not considered. Following these principles, Farina, basing on Flory's work about the properties of the polymeric mixture, elaborated the following equation:

$$D = 2 - \frac{(f-1)^2}{f} x_{w2}^2 + \frac{(f-1)(f-2)}{f} x_{w2}$$

Where X_{w2} indicates the weight fraction of the polymer that contains the multifunctional agent. The proposed equation, in spite of its simplicity, permits to obtain a value of polydispersity with an approximation of 1% respect the real one, very lower in comparison with the experimental error obtained through the use of the analytical techniques used for the measurement of the molecular weight (i.e. SEC analysis)

In the figure 27 the behavior of the polydispersity index versus of X_w with a different value of the terminal groups of the multifunctional agent is reported:

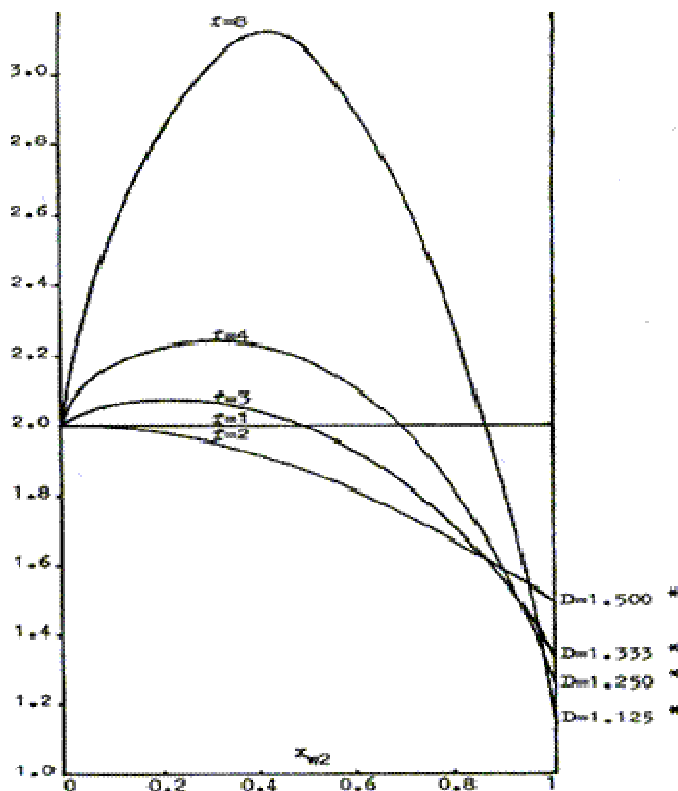


Figure 27: Variation of D in varying f and conversion of the reaction

In the case of $f=2$ in all the composition range the well known effect of the decreasing of the polydispersity can be observed, while in the case of an higher value of f , D can be higher than 2 also for a long range of compositions of the feeding.

It is demonstrated that the insertion of a multifunctional agent in an AB polymer can induce opposite effects on the distribution of the molecular weights.

The equation can be elaborated indicating X_{w2} with different parameters, as the concentration of the multifunctional agent (C_0) and the concentration of the terminal groups not contained in the multifunctional agent (in this case $[NH_2]$). In this case the equation obtained is:

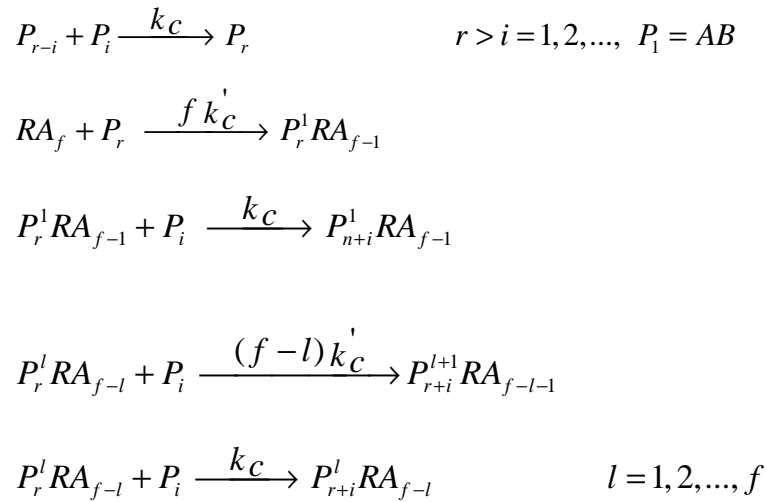
$$D = 2 - f(f-1)^2 \left(\frac{C_0}{fC_0 + [NH_2]} \right)^2 + (f-1)(f-2) \frac{C_0}{fC_0 + [NH_2]}$$

Recently Dr. Yuan has elaborated a model more complex and complete of Farina's one.

Yuan model

In Yuan model^[27], the expressions of the number-average molecular weight(DP_n) and weight-average (DP_w) one, and the polydispersity index (D) of several polymeric species are obtained as functions of the terminal groups conversion of the multifunctional agent (RAf).

Considering that the reacting system after the start of the polymerization reaction is always composed by a mixture of linear and regulated chains, having the maximum f branches, the reaction scheme proposed by Dr Yuan is the following:



In the scheme P_r represents the pure linear chain, that hasn't reacted with the multifunctional agent and is composed by r repetitive units, $P_r^l RA_{f-l}$ indicates species composed by r repetitive units and reacted with the multifunctional agent where only l branches have been formed, and that can be named "star with l branches" (in the case of $l=1$ or $l=2$ the macromolecule is linear).

Differently from Flory's theory, there are three kinds of linear macromolecules: the ones formed by the only AB monomer (primarily linear) and the ones deriving by the reaction of one or two of the functionalities of the multifunctional agent (star deriving linear). The ones that are formed by the reaction of more than 2 functionality of the multifunctional agent are star macromolecules.

A kinetic model with the complexity of the one proposed by Dr. Yuan, needs some approximation to be quantitatively solved in all the taken into account species. The hypothesis introduced regarding the equal reactivity of all the reactive groups in the growing chain, the equal reactivity of all the groups of the multifunctional agent not considering the time of the reaction (i.e. is not considered the effect on the growing chain and the increase of viscosity in the polymer), and the absence of secondary reactions (not involved in the model scheme).

Using these approximations all the reactive acts are considered ruled by the same kinetic, and Yuan obtains these equations:

$$\sum_{r=1}^{\infty} P_r = N_0(1-x) - f[RA_f]_0 x$$

$$[RA_f] = [RA_f]_0 (1-x)^f$$

Where N_0 is the starting concentration of the AB monomer and gives the conversion of the reactive groups of the multifunctional agent RAf. Is possible to observe that when $\sum P_r = 0$, meaning that there aren't linear species, the reaction is quantitatively complete, if all the species are regulated, only A groups are present. In this theoretical case all B groups have reacted, therefore the maximum conversion of A groups can be calculated by the following equation:

$$x_{\max} = \frac{N_0}{N_0 + f[RA_f]_0} < 1$$

The maximum value of conversion is a theoretical value that cannot be reached with a real polymerization but it represents a referring point, in the case that in the elaboration of the real data a conversion's value higher than the one obtained by the equation is found.

The reaction scheme can be quantitatively solved for the single species P_r e P_r^l with the following relations, obtained during the developing of the model proposed by Yuan.

$$P_r = \{N_0(1-x) - fC_0x\}(1-x)x^{r-1}$$

$$P_r^l = C_0 \binom{f}{l} \binom{r-1}{l-1} (1-x)^f x^r$$

Where P_r e P_r^i represent the molar amount of the correspondent species in the reaction mixture for a defined feed and degree of conversion.

In the following table, some important parameters are reported for the reaction scheme proposed by Yuan:

	Primary Polymer P_r	i-branched Polymer P_r^i	Linear Polymer $L_r = P_r + P_r^1 + P_r^2$	Star Polymer $S_r = \sum_{i=3}^f P_r^i$
Number Concentration	$N_p = \sum_{r=1}^{\infty} P_r$	$N_{pi} = \sum_{r=1}^{\infty} P_r^i$	$N_L = N_p + \sum_{r=1}^{\infty} P_r^1 + \sum_{r=2}^{\infty} P_r^2$	$N_s = \sum_{r=3}^{\infty} S_r$
Weight Concentration	$W_p = \sum_{r=1}^{\infty} r P_r$	$W_{pi} = \sum_{r=1}^{\infty} r P_r^i$	$W_L = W_p + \sum_{r=1}^{\infty} r P_r^1 + \sum_{r=2}^{\infty} r P_r^2$	$W_s = \sum_{r=3}^{\infty} r S_r$
Number fractional molecular weight distribution	$n_p(r) = \frac{P_r}{N_p}$	$n_{pi}(r) = \frac{P_r^i}{N_{pi}}$	$n_L(r) = \frac{L_r}{N_L}$	$n_s(r) = \frac{S_r}{N_s}$
Weight fractional molecular weight distribution	$w_p(r) = \frac{r P_r}{W_p}$	$w_{pi}(r) = \frac{r P_r^i}{W_{pi}}$	$w_L(r) = \frac{r L_r}{W_L}$	$w_s(r) = \frac{r S_r}{W_s}$
Number-average degree of polymerization	$\overline{DP_n(P)} = \sum_{r=1}^{\infty} r n_p(r)$	$\overline{DP_n(P^i)} = \sum_{r=1}^{\infty} r n_{pi}(r)$	$\overline{DP_n(L)} = \sum_{r=1}^{\infty} r n_L(r)$	$\overline{DP_n(S)} = \sum_{r=3}^{\infty} r n_s(r)$
Weight-average degree of polymerization	$\overline{DP_w(P)} = \sum_{r=1}^{\infty} r w_p(r)$	$\overline{DP_w(P^i)} = \sum_{r=1}^{\infty} r w_{pi}(r)$	$\overline{DP_w(L)} = \sum_{r=1}^{\infty} r w_L(r)$	$\overline{DP_w(S)} = \sum_{r=3}^{\infty} r w_s(r)$
Dispersion index	$D_p = \frac{\overline{DP_w(P)}}{\overline{DP_n(P)}}$	$D_{pi} = \frac{\overline{DP_w(P^i)}}{\overline{DP_n(P^i)}}$	$D_L = \frac{\overline{DP_w(L)}}{\overline{DP_n(L)}}$	$D_s = \frac{\overline{DP_w(S)}}{\overline{DP_n(S)}}$
Mole Fraction	$f_p = \frac{N_p}{N_p + \sum_{i=1}^f N_{pi}}$	$f_{pi} = \frac{N_{pi}}{N_p + \sum_{i=1}^f N_{pi}}$	$f_L = \frac{N_L}{N_p + \sum_{i=1}^f N_{pi}}$	$f_s = \frac{N_s}{N_p + \sum_{i=1}^f N_{pi}}$
Weight Fraction	$F_p = \frac{W_p}{W_p + \sum_{i=1}^f W_{pi}}$	$F_{pi} = \frac{W_{pi}}{W_p + \sum_{i=1}^f W_{pi}}$	$F_L = \frac{W_L}{W_p + \sum_{i=1}^f W_{pi}}$	$F_s = \frac{W_s}{W_p + \sum_{i=1}^f W_{pi}}$

Table 5: Main parameters in Yuan's model

Considering as the only unknown parameter the conversion degree of the reactive groups of the multifunctional agent RAf, it is possible to express the statistical moments μ_0 , μ_1 and μ_2 , both for linear species and for the star shaped ones:

$$\mu_0(L) = N_L = N_0(1-x) - fC_0x(1-(1-x)^{f-1}) + \frac{C_0}{2} f(f-1)(1-x)^{f-2} x^2$$

$$\mu_1(L) = \sum_{r=1}^{\infty} rL_r = N_0 - \frac{fC_0x}{1-x} (1 - (1-x)^{f-2} (1+x(f-2)))$$

$$\mu_2(L) = \sum_{r=1}^{\infty} r^2 L_r = N_0 \frac{1+x}{1-x} - \frac{fC_0x}{1-x} + fC_0x(1-x)^{f-4} (1-x^2 + x(f-1)(2+x))$$

$$\mu_0(S) = N_S = C_0(1-x) - fC_0x(1-(1-x)^{f-1}) + \frac{C_0}{2} f(f-1)(1-x)^{f-2} x^2$$

$$\mu_1(S) = \sum_{r=1}^{\infty} rS_r = \frac{fC_0x}{1-x} (1 - (1-x)^{f-2} (1+x(f-2)))$$

$$\mu_2(S) = \sum_{r=1}^{\infty} r^2 S_r = \frac{fC_0x}{1-x} \left(1 + (f-1) \frac{x}{1-x} - (1-x)^{f-3} (1-x^2 + x(f-1)(2+x)) \right)$$

$$\mu_0 = N_0(1-x) - fC_0x + C_0(1-(1-x)^f)$$

$$\mu_1 = N_0$$

$$\mu_2 = N_0 \frac{1+x}{1-x} + C_0 f(f-1) \left(\frac{x}{1-x} \right)^2$$

The molar fraction of star shaped polymer (f_s) and of the linear one (f_l) are obtained by the following reactions:

$$f_s = \frac{\mu_0(S)}{\mu_0}$$

$$f_l = \frac{\mu_0(L)}{\mu_0}$$

The number and weight average degree of polymerization, and the polydispersity for the total of the molecular weights can be calculated by the equations:

$$\overline{DP}_n = \frac{\mu_1}{\mu_0} = \frac{N_0}{N_0(1-x) - fC_0x + C_0(1-(1-x)^f)}$$

$$\overline{DP}_w = \frac{\mu_2}{\mu_1}$$

$$D = \frac{\mu_2\mu_0}{(\mu_1)^2}$$

Similarly, it is possible to calculate number and weigh molecular weight of the fractions related to linear molecules and to star shaped ones.

$$\overline{DP}_n(L) = \frac{\mu_1(L)}{\mu_0(L)}$$

$$\overline{DP}_w(L) = \frac{\mu_2(L)}{\mu_1(L)}$$

$$\overline{DP}_n(S) = \frac{\mu_1(S)}{\mu_0(S)}$$

$$\overline{DP}_w(S) = \frac{\mu_2(S)}{\mu_1(S)}$$

Substituting the equation of the complete conversion in the equation presented at the beginning of the page 86 it is possible to evaluate the distribution of molecular weights in the limit case of complete conversion:

$$\overline{DP}_n(\text{lim}) = \frac{1}{a \left(1 - \left(\frac{fa}{1+fa} \right)^f \right)}$$

$$\overline{DP}_w(\text{lim}) = 1 + \frac{1}{a} \left(1 + \frac{1}{f} \right)$$

$$D(\text{lim}) = \left(a + 1 + \frac{1}{f} \right) \left(1 - \left(\frac{fa}{1+fa} \right)^f \right)$$

Where a indicates the initial ratio C_0/N_0 . Through these last equations it is possible to define some important conclusions:

- the molecular weight of polymer depends by the C_0/N_0 ratio. The higher is the amount of multifunctional agent, the lower the molecular weight obtained at the end of the reaction.
- The higher is the number of terminal groups of the multifunctional agent, the lower the distribution.
- Polydispersity index doesn't depend only on the value of f , as described in Farina model, but also on the starting molar ratio between monomer and multifunctional agent.
- When $f \geq 2$ and $a \leq 0,01$, limit values for number average degree of polymerization and polydispersity index are respectively equal to $(1/a)$ e $(a+1+1/f)$.

Moreover is interesting to observe that during the initial phase of the polymerization the higher part of the chains are linear and only later, at high conversion x , the percentage of star shaped molecules is relevant.

The figure shows the percentage of the linear chains and the star shaped ones, in function of the conversion of the hexafunctional comonomer.

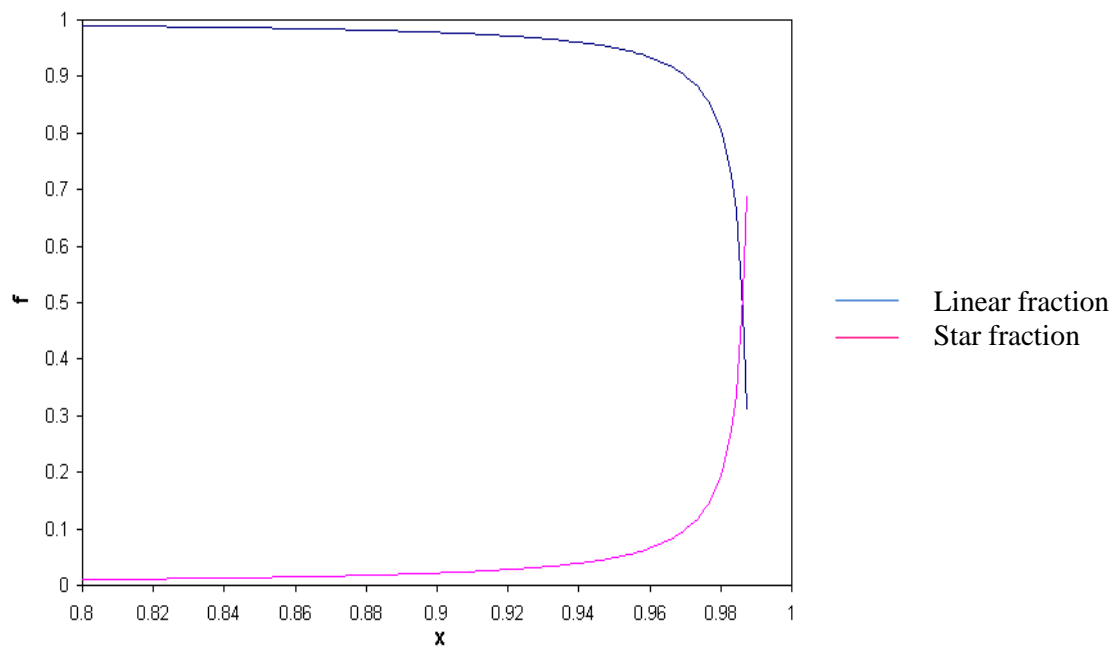


Figure 28: Variation of linear and star shaped macromolecules in varying the conversion

In conclusion it is possible to state that the use of star shaped polymers in the manufacture of complex pieces is subordinated to the optimization of the production process, considering that linear fraction is responsible for the mechanical properties of the material while the star fraction rules the decreasing of the viscosity.

CHAPTER 8: Study on the crystallization
of co-polyamides

Introduction

Chapter focuses the improvement of the knowledge on the crystalline phase of polyamides. The biphasic model of semi-crystalline polymers, based on the presence of an amorphous phase and a crystalline one is well known.

Despite, starting from 1990 several studies, in particular on the dielectric properties of different polyamides, study the relaxation phenomena at temperature higher than T_g , resulting in a description of the state of the polymer that exceeds the biphasic model.

The BDS (Broadband Dielectric Spectroscopy) analysis studies the relaxation of a polymer in increasing the temperature and varying the applied electric field, analyzing the dielectric constant of the polymer, and is one of the instruments that permits an improved study on polymeric materials.

In the BDS analysis of a polyamide it is possible to detect 4 different relaxation phases: they are called, in following the order of appearance at increasing temperature, γ , β , α , and α' , graphically presented in the figure 29:

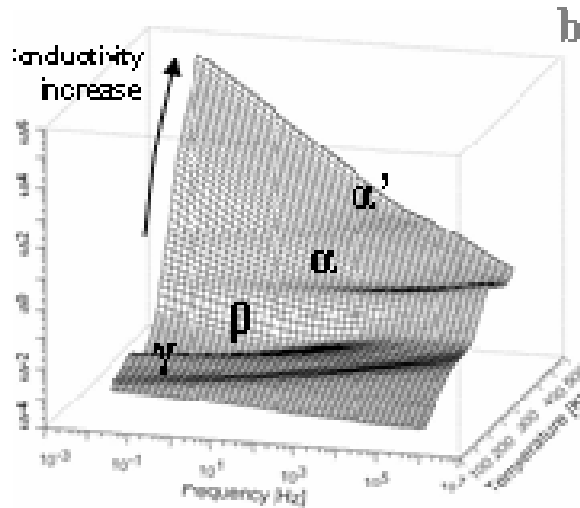


Figure 29: BDS analysis of PA 6

- γ relaxation: is a relaxation that corresponds to the movement of the aliphatic chain comprised between two amide groups (it occurs at the same temperature than in polyethylene).
- β relaxation: is a relaxation that involves the amide groups Of the amorphous phase It's not easy to detect.
- α relaxation: is due to the macromolecule's movement, and bonded to the T_g
- α' relaxation: has the same nature of the α one, but occurs at higher temperature; this means that more energy is required for the relaxation of these fraction of the amorphous phase

In figure 6 is possible to see the 4 relaxation in a PA 6 during the analysis of the dielectric properties of the polymer. Similar studies have been conducted on PA 4,6^[28] and PA 6,6^[29].

The existence of two different amorphous phases is the explication for the existence of two different α relaxation.

The crystalline phase of a polyamide is organized, in a first stage, in lamellae that aggregate and form, in a second stage, complex structures named spherulites (stacking phenomenon). The amorphous phase contained in a spherulite, and the one comprised between two different spherulites have two different degrees of liberty.

In the first figure it is represented the lamellar structure, while in the second one is represented one stack:

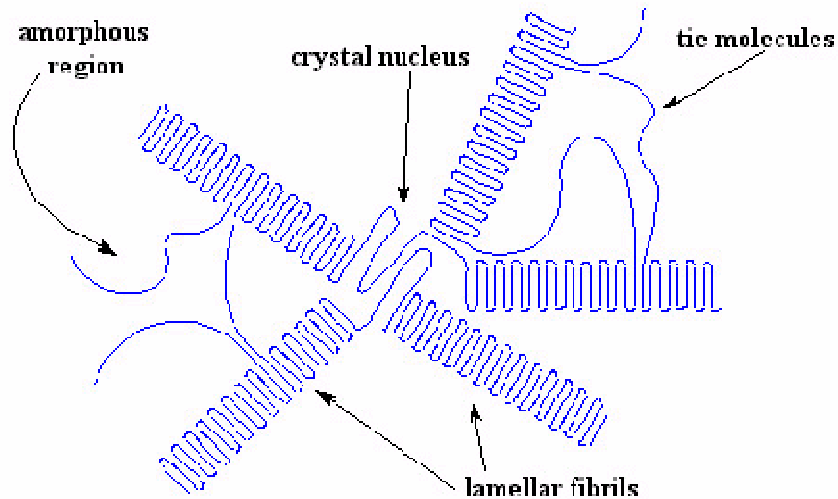


Figure 30: lamellar organization of crystalline phase in polyamide

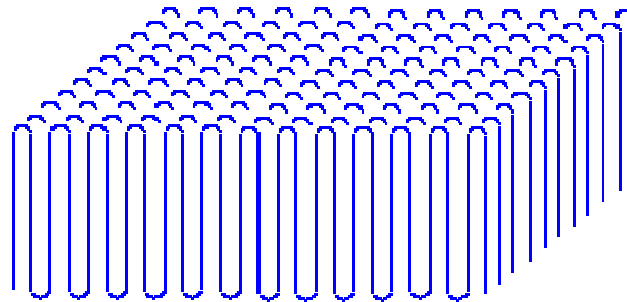


Figure 31: Stack organization in polyamide

The two different amorphous phases are called MAP (Mobile Amorphous Phase) and RAP (Rigid Amorphous Phase).

MAP: is the classical amorphous phase, composed by a fraction of polymer without any crystalline form

RAP: is the amorphous phase that is strictly connected with the crystalline phase. For this reason it is highly oriented and a surplus of energy is necessary to obtain its relaxation.

Our work on the amorphous phase of polyamide

Starting from the description of the new semicrystalline model proposed for polyamides, our goal is the preparation of several model polymers with different crystallinity percentages, different lattices in the crystalline phase and different rates of crystallization.

In the model polymers synthesized, we have worked trying to maintain the same amount of the same amide groups density of PA 6 (ratio amide group, carbon atoms 1/6).

2 way have been done:

- Synthesis of a polyamide with a dimethyled diamine, with the goal to prevent the hydrogen bond formation
- Synthesis of copolyamides with different comonomers to change the tendency to the crystallization of the final material

The measure of the tempering effect on polyamides and copolyamides permits to evaluate the effect of the cooling rate on the crystallization process.

All the reactions have been conducted first with a glass reactor or and then in a pilot reactor (300 ml); at the beginning all the reactions have been conducted in the glass reactor; even if this methods doesn't allow for the best conditions for the polymerization, it presents some advantages, as the possibility to work on small amounts of material to take samples and so on.

In a second time some synthesis have been performed in the pilot reactor.

Synthesis of polyamides in presence of a dimethylated diamine with the goal to prevent the formation of hydrogen bonds

After the polycondensation reaction, secondary amides formed with the use of these monomers, cannot give hydrogen bonds; the difference between this polymer and the standard polyamide 6,6 is presented in the following figures:

The case of standard PA 6,6:

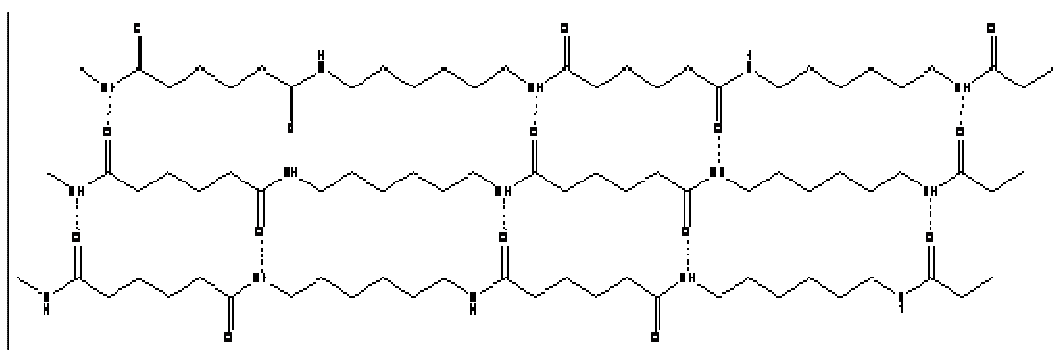


Figure 32: Formation of hydrogen bond in polyamide 6,6

The case of PA 6M,6

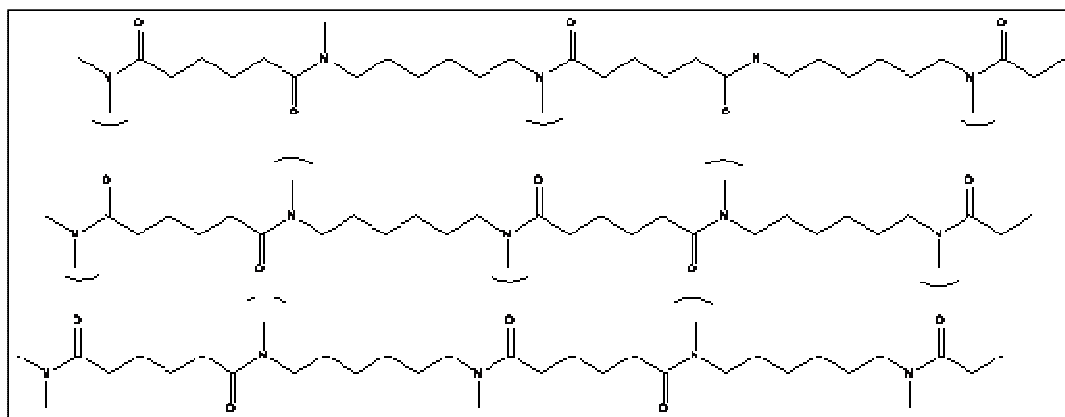


Figure 33: Non formation of hydrogen bond in polyamide 6M,6

Synthesis of PA 6M,6

This synthesis is performed in the glass reactor to study the behavior of a secondary diamine in the polycondensation's conditions and to limit the cost of the N,N' dimethyl-hexamethyldiamine.

The monomers are:

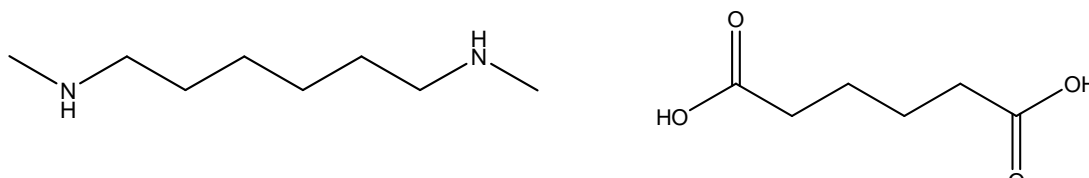


Figure 34: General formula of monomers in PA 6M,6

The product obtained is an highly unbalanced oligomer because the loss of a lot of amine during the synthesis. Its appearance is honey like and the terminal groups are:

- Carboxylic Terminal Groups (CTG): 658 meq/kg
- Amino Terminal Groups (ATG): 46 meq/kg

And they give a value of molecular weight of 2840 g/mole:

$$\frac{1000000}{(658 + 46)/2} = 2840$$

The lost diamine has been found in the distilled solution collected during the reaction, and titrated with HCl 1 M. This loss is caused by the lower reactivity of the secondary diamine in comparison to the primary one. An H^1 NMR spectra of the distilled solution shows that the amine is distilled without decomposition or secondary reactions.

The DSC analysis of the polymer shows that the product is completely amorphous: it presents a T_g transition at -12°C and after that no crystallization or melting phenomena have been observed:

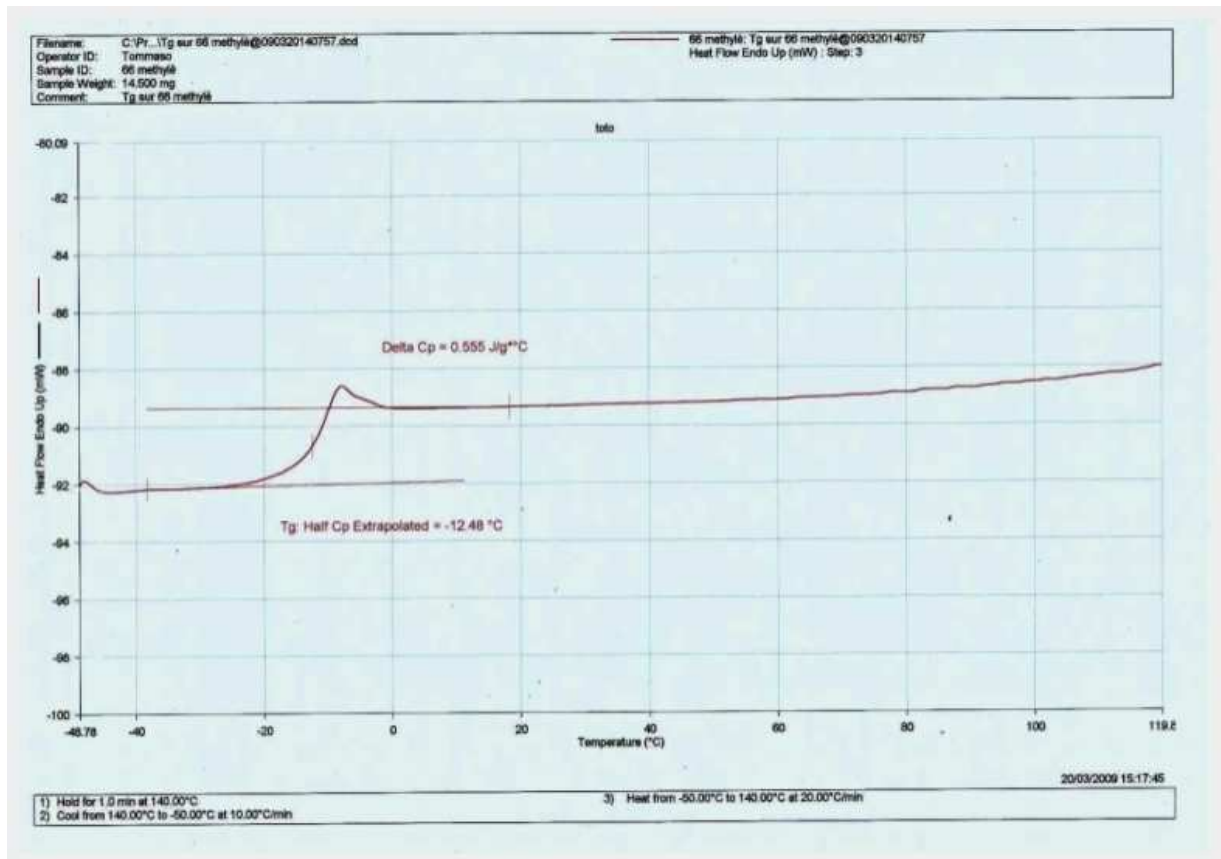


Figure 35: DSC analysis of polyamide 6M,6

Synthesis of copolyamide 6,6/ 6M,6 (50:50)

At the beginning the synthesis have been performed on the glass reactor starting from a feeding composed by 50% in weight of N-salt (obtained from hexamethyldiamine with adipic acid), and 50% of adipic acid/N,N' dimethyl-hexamethyldiamine.

The resulting product has these values of terminal groups:

- CTG: 259 meq/kg
- ATG: 45 meq/kg

That gives to an average number molecular weight of 6600 g/mol.

This product is solid and crystalline, as confirmed also by DSC analysis:

Polymer	T_g (°C)	T_c (°C)	T_m(°C)	ΔH_m (J/g)	T_m-T_c
PA 6,6/6M,6	19	137	187	32	50
PA 6,6 Std.	65	220	262	68	42

Table 6: DSC data of polyamide 6M,6/6,6 (50:50) in glass reactor

It is possible in this case, to compare the value of the enthalpy of fusion of this polymer with the one of PA 6,6. In fact the 6M,6 fraction cannot crystallize, and the fraction of crystalline polymer in this copolyamide is completely formed by lattices of 6,6 chains.

An H¹ NMR spectrum of the polymer has been performed to obtain the exact ratio between the 6,6 and the 6M,6 portion. In fact through the NMR it is possible to identify and to quantitate clearly the signal related to the CH₂ group in α position to the tertiary amine group and the CH₂ group in α position to the secondary amine group. The copolyamide is composed by the 57% of PA 6,6 and the 43% of PA 6M,6.

One PA 6,6 with 100% of crystallinity has a ΔH_m of 188 J/g^[30], while a standard PA 6,6 has a ΔH_m of 70 J/g that corresponds to a crystalline percentage of 37%. In our case the polymer contains the 57% of PA 6,6 and the value of ΔH_m measured is 32 J/g.

In conclusion we can consider that the crystallinity of the copolymer is about 30% and that lattices are formed by the 6,6 fraction. We obtain a polymer with a lower crystallinity in comparison with standard PA 6,6 meaning that the copolyamide is made of alternate copolymer and blocks of PA 6,6.

In a second stage we performed the synthesis in the steel reactor; we synthesized the polymer with an excess of the secondary diamine in the feeding to compensate its loss, observed during the synthesis in the glass reactor (200 meq/kg).

The polymer is synthesized using the standard conditions used for the PA 66 synthesis and the results obtained are:

- CTG: 431 meq/kg
- ATG: 111 meq/kg

That give a value of M_n of 3700 g/mol, while DSC results are:

Polymer	T_g (°C)	T_c (°C)	T_m(°C)	ΔH_m (J/g)	T_m-T_c
PA 6,6/6M,6	10	120	173	32	53
PA 6,6 Std.	65	220	262	68	42

Table 7: DSC data of polyamide 6M,6/6,6 (50:50) in steel reactor

Thermal properties of the polymer obtained in the steel reactor have little difference in comparison to the ones obtained in glass reactor (T_g is 10°C lower while T_c and T_m are 15°C lower). The H^1 NMR analysis gives the same results for the fraction of 6,6 and also the value of the ΔH_m is comparable.

The unbalancing of terminal groups is higher in the steel reactor than in the glass one (320 meq/kg versus 214) and the value of ATG is higher in the steel reactor (111 meq/kg versus 45 meq/kg) meaning an higher degree of polymerization in the glass reactor.

In the following figures are presented the temperature profiles in each of the two synthesis:

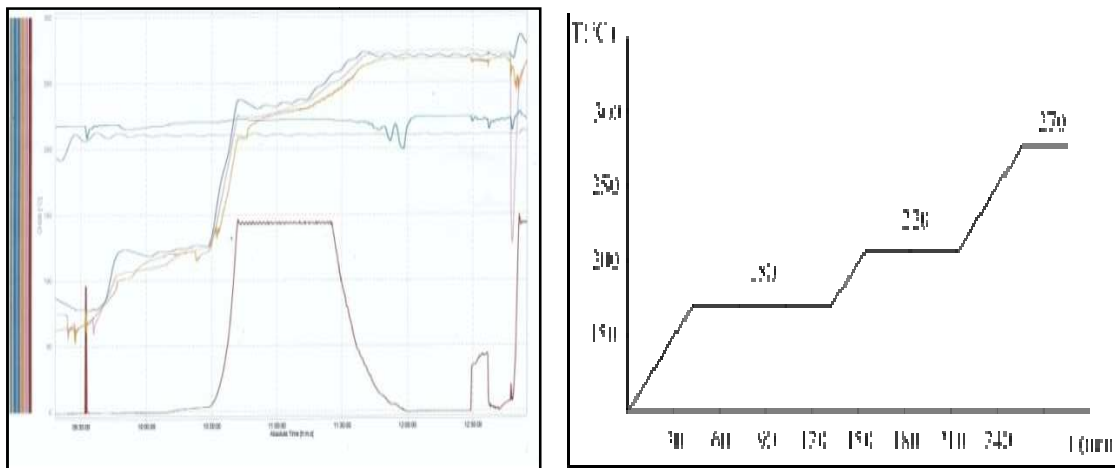


Figure 36: Temperature profile for polyamide 6M,6/6,6 (50:50) in steel (l) and glass (r) reactor

Figure on the left presents the thermal profile in the steel reactor, on the right the thermal profile in the glass reactor is shown.

In the glass reactor the reaction is longer and a lower temperature is maintained for a longer time.

The faster increase of temperature in the steel reactor limits the oligomerisation and causes an higher loss of diamine during the synthesis (also if the reaction is conducted under pressure in the steel reactor).

To obtained a good value of molecular weight with an acceptable value of loss of secondary diamine, it is necessary to perform a slower increase of the temperature and a longer time of reaction in steel reactor.

Synthesis of copolyamides with different comonomers to make crystallization more difficult and slower.

Synthesis of the copolyamide 6,6/4,8 (50:50)

It has been tested the coPA 6,6/4,8 where the density of the amide groups of the PA 6,6 are conserved; at the beginning the synthesis has been performed in the glass reactor, and later in a steel reactor using the same conditions used for the synthesis of the PA 6,6.

In this case the diamine used is more volatile than the one used in the PA 6,6 (b.p. 160°C versus 205°C of the HMDA) and in literature is reported its tendency to the cyclisation^[31].

Analysis on polymers obtained give the following results:

- CTG: 136 meq/kg
- ATG: 23 meq/kg

That means a molecular weight of 12700 g/mol

DSC:

Polymer	Tg (°C)	Tc (°C)	Tm(°C)	ΔHm (J/g)	Tm-Tc
PA 6,6 /4,8	45	137	187	41	50
PA 6,6 Std. (°C)	65	220	262	68	42

Table 8: DSC data of polyamide 6,6/4,8 (50:50)

In this case it is not possible evaluate from the enthalpy of fusion crystallinity fraction because its value is owed to the melting of lattices of 6,6, 4,8, 6,8, or 4,6 lattices.

In this case the H¹ NMR spectrum doesn't give evaluable data because all signals are overlapped.

The loss of diamine during the synthesis is not referable to the loss of hexamethylenediamine or putrescine, but is quantifiable in 8 mmol of diamine on the 285 mmol introduced, meaning a loss of the 2.8% versus a value of 1.3 for the standard PA 6,6.

Synthesis of PA 6,7

Through this synthesis (and the following one of 6,6/6,7) is investigated what happen when a couple even/uneven of comonomers is used. In this product the crystallinity is not ruled by the chain size but by the orientation of the amide groups.

In the case of an diacid with uneven number of carbon, the two carbonyl groups are placed on the same side of the molecule with a possible perturbation of the chain regularity that can cause a perturbation on the formation of hydrogen bonds and therefore on the polymer crystallinity:

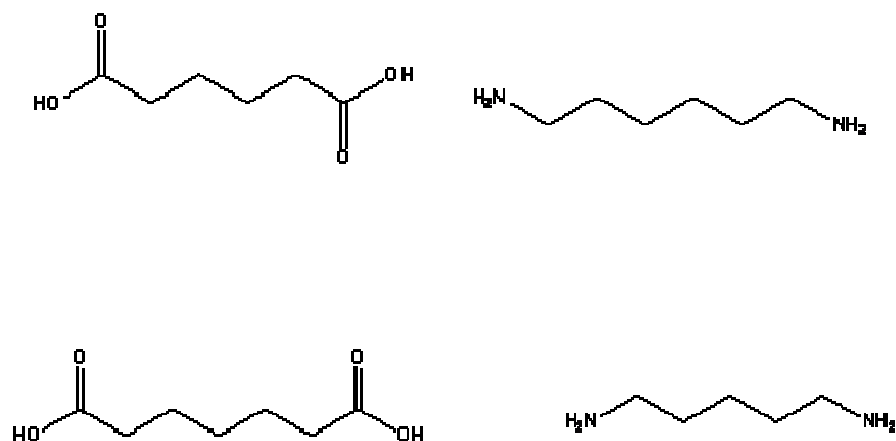


Figure 37: Monomers for PA 6,7 and 6,6/6,7

The synthesis of the PA 6,7 gives the following results for the terminal groups:

- CTG: 54 meq/kg
- ATG: 43 meq/kg

And the following ones through DSC analysis:

Polymer	Tg (°C)	Tc (°C)	Tm(°C)	ΔHm (J/g)	Tm-Tc
PA 6,7	57	189	229	60	40
PA 6,6 Std. (°C)	65	220	262	68	42

Table 9: DSC data of polyamide 6,7

In this case the value of CTG is higher than ATG: pimelic acid decomposes at higher temperature than adipic acid. Is not possible to calculate the molecular weight because not all terminal groups are measured by titration.

However the high mechanical properties of the product leads to a classification as an high polymer.

Synthesis of coPA 6,6/6,7 (50:50)

In this case the effect of the alternation of two acids with even and uneven number of carbon is studied.

The goal is to obtain a perturbation of the crystallinity of the material.

The synthesis have been conducted in the glass reactor and the results obtained are the following:

Terminal groups titration:

- CTG: 64 meq/kg
- ATG: 46 meq/kg

DSC:

Polymer	Tg (°C)	Tc (°C)	Tm (°C)	ΔHm (J/g)	Tm-Tc
PA 6,6/6,7	53	167	213	48	45
PA 6,6 Std. (°C)	65	220	262	68	42

Table 10: DSC data of polyamide 6,6/6,7 (50:50)

Also in this case a polymer with good mechanical properties is obtained; in the solution distilled during the synthesis a loss of the 2.05% of HMD has been found, compatible with a glass reactor's synthesis.

Synthesis of the coPA 6,6-11

In this case an AA BB/ AB copolymer with a great difference in the comonomers length has been tested.

The reaction is easy to conduct without side reactions at 250°C. The reaction is stopped at the stage of oligomers to avoid the crash of the glass reactor in the phase of extraction of the final product.

The result obtained by titration is:

- CTG: 423.1 meq/kg
- ATG: 229.5 meq/kg

That give a value of M_n of 1532 g/mol, while DSC results are:

Polymer	Tg (°C)	Tc (°C)	Tm (°C)	ΔHm (J/g)	Tm-Tc
PA 6,6/11	36	151	181	32	30
PA 6,6 Std. (°C)	65	220	262	68	42

Table 11: DSC data of polyamide 6,6/11

Is possible expect a synthesis on the steel reactor to evaluate the properties on a polymer with high molecular weight.

In this case the loss of diamine during the synthesis is quantified in 3.8 mmol; a better results in a polymerization conducted under pressure in the steel reactor is expect.

Quenching process on the synthesized polymers

The goal of this experiment is to evaluate the kinetic of the crystallization process, studying the effect of a rapid quenching that can block fractions of polymers in the amorphous phase. The slower the crystallization process, the higher the amount of polymer that crystallize during the heating scan. The amorphous state forced by the rapid cooling process is conserved only if the temperature is maintained lower than T_g , because at a temperature higher than T_g macromolecular chains have the possibility to change their position and crystallize.

PA 6,6 has a high rate of crystallization and the quenching process hasn't effect on the crystallization process: it isn't possible to obtain, through this methods a polyamide with higher amorphous fraction than its equilibrium state, and during DSC analysis there is no presence of a peak of from cold crystallization, but only a very small exothermic peak, just before the melting phenomenon, as evidenced in the following figure:

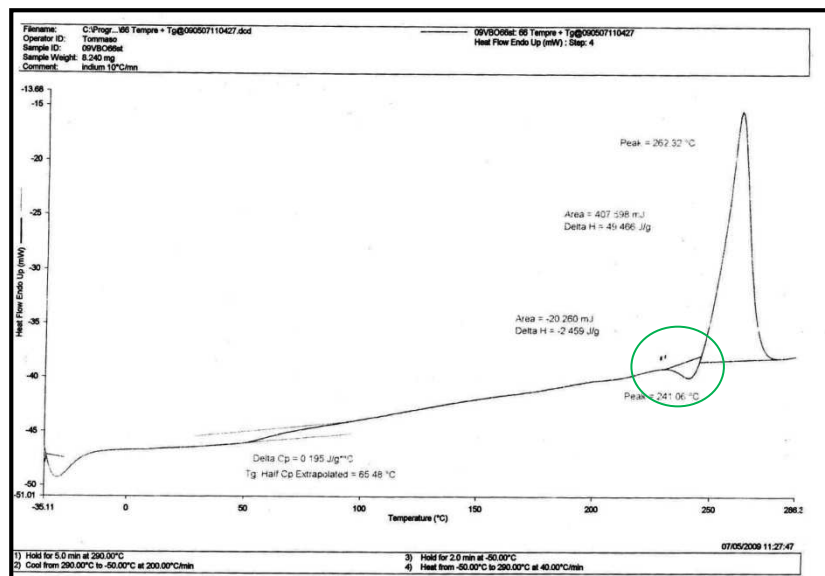


Figure 38: Tempering effect on PA 6,6 (sub-Tm peak evidenced)

This peak, called sub melting temperature exothermic peak, is well known in the processing of the polymeric materials, and represents the relaxation of the thermal and physical stresses accumulated by the material. To eliminate this effect it is possible to lead the sample to a temperature higher than the melting temperature, maintain it for a some time and then cool it slowly.

In this work the quenching effect is studied through a rapid cooling of the polymer (-200 °C/min) in the DSC apparatus.

The thermal program used is the following one:

- Isotherm at 280°C for 5 minutes. (Temperature higher than the melting point of all the polymers)
- Cooling from 280°C to -50°C at -200°C/min (Quenching phase)
- Isotherm at -50° for 2 minutes
- Heating from -50°C to 280°C at 40°C/min

Results obtained on the polymers and copolymers tested are very different. The key parameter is the from cool crystallization phenomenon after the T_g in the last phase of the DSC program.

If the quenching process produce the desired effect, the polymer hasn't the possibility to crystallize with the consequence of the formation of an amorphous phase that isn't thermodynamically stable.

If in a second time, during the heating phase, temperature becomes higher than T_g , macromolecular chains have the possibility to crystallize; the effect of the quenching process is related to the observed peak in from cold crystallization.

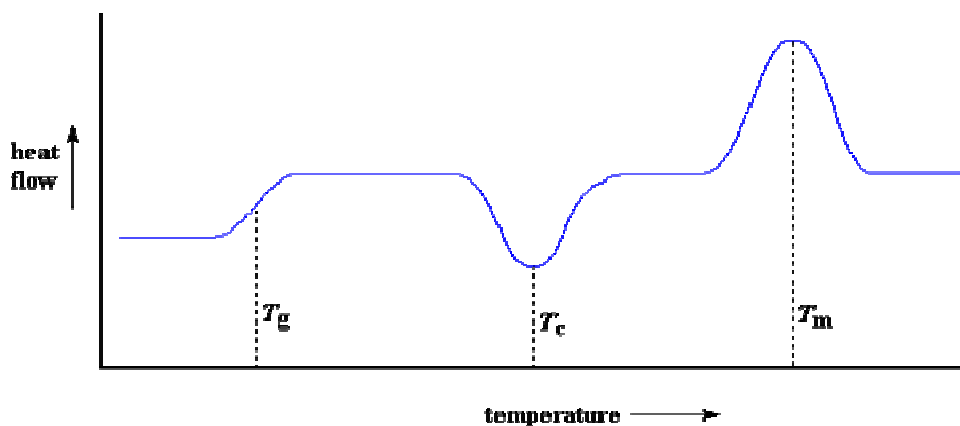


Figure 39: Temperature profile of a DSC scanning

If it is considered that:

1. All the fraction crystallized after the Tg is the amount constricted in amorphous phase by the quenching process.
2. The non-crystallized fraction is related to the rate of crystallization
3. The rate of crystallization is a parameter directly dependent from the easiness of crystallization.

the higher the peak obtained for the from cold crystallization, the higher the difficulty for the polymer to crystallize

Results:

Products	Tg (°C)	ΔCp (J/g°C)	Tc (°C)	ΔHc (Joule/g)	ΔHm (Joule/g)	% ΔHc/ ΔHm
PA 66 Std.	60	0.19			68	
6,6/6,6M	19	0.47	70	-21	32	66
6,6/4,8	45	0.26	78	-13	41	31
6,7	57	0.161			56	
6,6/6,7	53	0.25	87	-1	43	2
6,6/11	35	0.28	85	-13	36	36

Table 12: DSC data after tempering process

The crystallization phenomenon considered in the table is the crystallization from cold; the values presented in the last column indicate the percentage of crystalline fraction blocked by the quenching process.

Polyamide 6,7

The 6,7 polyamide is the doesn't present a crystallization peak, but only the sub-T_m exothermic peak already observed in the case of polyamide 6,6.

This result shows that the use of a comonomer with a carbons number different from the one of the adipic acid hasn't effect on the rate of crystallization if the number is near to the one of the reference molecule..

Copolyamide 6,6/6,7

In this case a small result of the quenching process is registered: a little peak of from cold crystallization appears in the analysis:

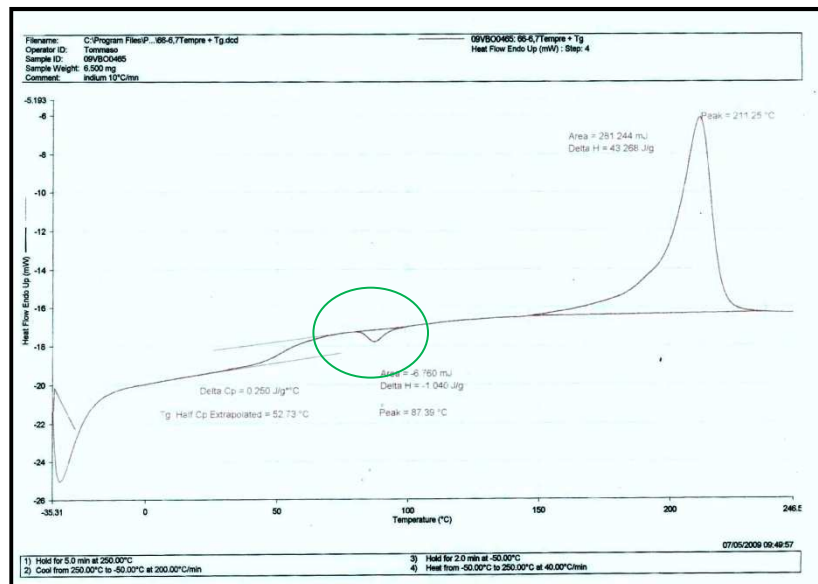


Figure 40: Tempering effect on PA 6,6/6,7

Copolyamide 6,6/4,8

In this case an higher effect is registered, regarding the crystallization from cold, obtained through the use of comonomers with an higher difference of the molecule's length, than in previous case

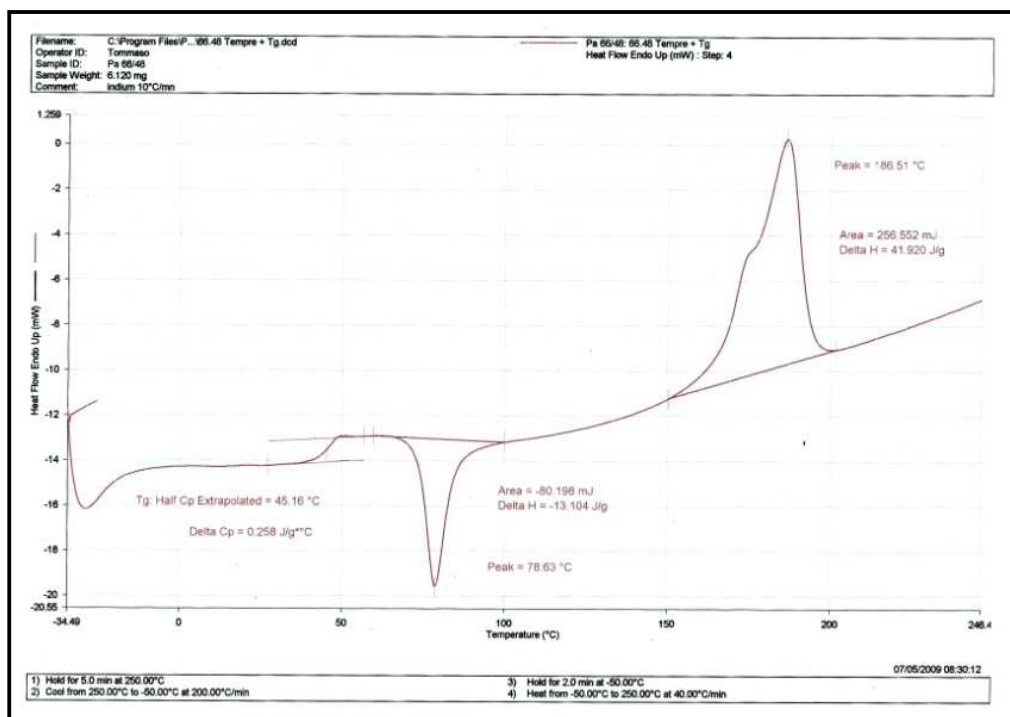


Figure 41: Tempering effect on PA 6,6/4,8

In this case the quenching process blocks the 31% of the crystalline phase in a constricted amorphous state.

Copolyamide 6,6/11

In this model polymer are contained both the alternance of AA BB and AB monomers and a difference between the length of the comonomers. Moreover in this case an oligomer is analyzed, with higher mobility of the molecular chains, giving more relevance to its difficulties in the crystallization.

In fact difficulties in crystallization for an oligomer is more relevant because its relative easiness to crystallize caused by the lower viscosity of the melt material.

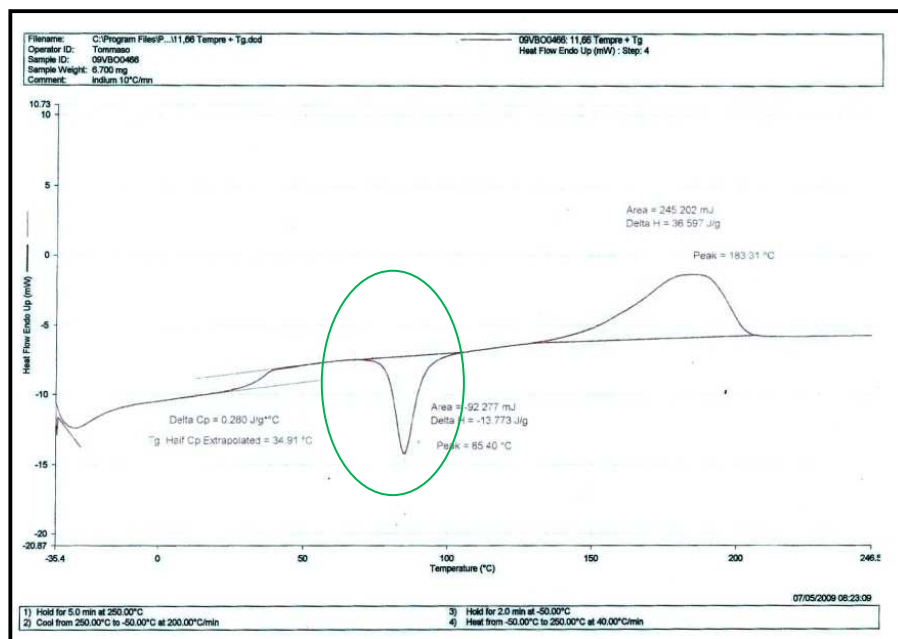


Figure 42: Tempering effect on PA 6,6/11

Copolyamide 6,6/6M,6

In this model polymer, is not the length of the comonomer that rules the crystallization rate, but the presence of hydrogen bonds that don't permit the formation of hydrogen bonds.

The result is most relevant in terms of from cold crystallization:



Figure 43: Tempering effect on PA 6,6/6M,6

In this case the percentage of polymer crystallized from cold is the 66% of the total melted when increasing the temperature.

The crystallization degree of the polymer obtained is calculable considering the amount of fraction crystallized after the quenching process (obtained by the difference between the fraction totally melted and the from cold crystallized) in comparison to the one of a standard 100% crystalline PA 6,6:

$$(32 \text{ J/g} - 21 \text{ J/g}) / 188 \text{ J/g} \times 100 \% = 5,85 \%$$

Conclusions:

A series of model polymers have been synthesized with the goal to obtain differences in the ratio amorphous/crystalline phase, maintaining similar characteristics to PA 6,6.

The absence of the data on the 100% of crystallinity for the copolyamides analyzed, prevents the possibility to evaluate the amount of crystalline fraction in relation to the PA 6,6, excepting for copolyamide 6,6/6M,6.

Considering the impossibility to evaluate the crystallinity percentage, through the quenching process it is possible to analyze the attitude to crystallization.

As expected, the polymerization product obtained starting from adipic acid e N,N' dimethyldiamine is completely amorphous.

CHAPTER 9: Synthesis of star shaped
polyamides with phosphor-
containing comonomers

Introduction

As previously explained, 2 carboxy-ethyl-phenyl phosphinic acid reacts as a monofunctional chain ender in copolymerization with polyamide based matrices, because the phosphinic acid is not able to create a stable bond with an amino terminal group in the synthesis condition of PA6 (bulk polymerization).

The only active group during the copolymerization reaction is the carboxylic group; the presence of a monofunctional chain controller causes a decrease in the molecular weight of the polymer that is directly proportional to the molar amount inserted.

The following table presents theoretical data on the molecular weight obtained after the insertion of a different amounts of a chain ender in comparison with the molecular weight obtained when the same amount of terminal groups is obtained through the insertion of a multifunctional agent with $f = 6$.

Amount of end groups	Mw obtained with f=1 comonomer	Mw obtained with f=6 comonomer
460 meq/Kg	2073	10321
255 meq/Kg	3886	16603
160 meq/Kg	6264	22656

Table 13: Molecular weight calculated to obtain the same amount of terminal groups using mono- and hexa-functional agent

The calculation has been performed through the Yuan's Model^[26]. Through the values reported in the table it is evident that using a multifunctional agent with high value of f it is possible to obtain an high value of terminal groups maintaining an high value of molecular weight.

The synthesis of star molecule is the way that has been chosen in this work to insert high quantities of CEPP in the polyamide matrix maintaining an high value of molecular weight, to get a material with good flame retardant property that maintains also mechanical and physical characteristics comparable with the one of standard nylon 6.

Multifunctional agents used

The star shaped architecture is obtained in a macromolecule through the insertion, during the synthesis process, of a multifunctional molecule with a number of equal reactive functions equal or higher than 3.

As multifunctional agents, two molecules have been tested: hexafunctional bis-hexamethylentriamine (HBHT) and Polyhedral Olygmeric Silsesquioxane (POSS). In the following paragraphs, the characteristics of each molecule will be explained.

HBHT

This molecule derives from hexamethylenediamine (HMDA) synthesis, this molecule is one of the two monomers of nylon 6,6, industrially obtained through the reduction of adiponitrile (from which is also obtained, through oxidation, also the other monomer of nylon 6,6, the adipic acid):

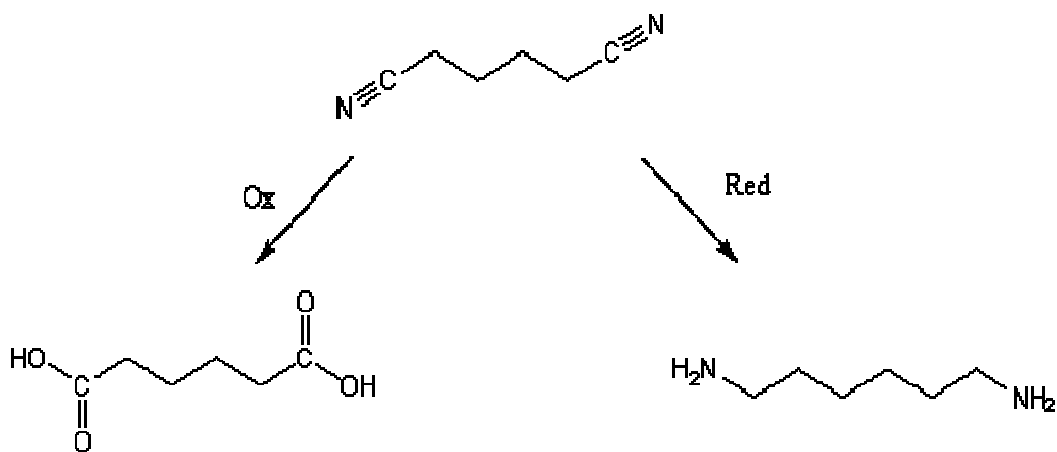


Figure 44: Synthesis of adipic acid and hexamethylenediamine

After the synthesis, HMDA is purified through distillation; the main tail product of this distillation is the BHT (Bis Hexamethylene Triamine) that is formed through an ammonolise reaction between two molecules of HMDA:

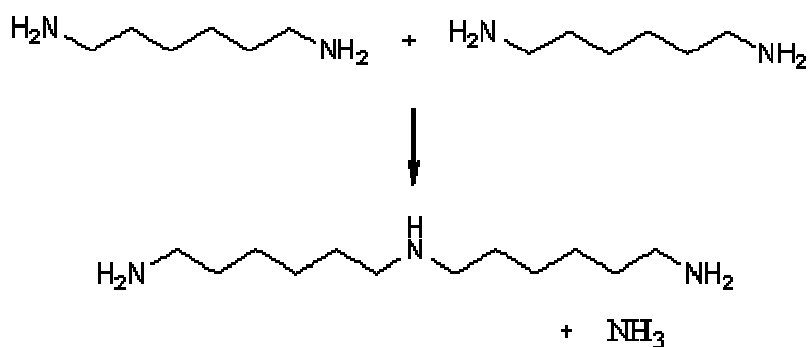


Figure 45: Synthesis of bis-hexamethylenetriamine

This product is used as fluidificant in the synthesis of polyamides. Its presence in the macromolecular chain causes the formation of three branches star molecule that lowers the viscosity of the material making it more adapt for the manufacture of complex molded pieces.

The ammonolise reaction that brings to BHT formation can continue in the distillation tail to give molecules with higher molecular weight and higher value of f. In our case we obtained, through a collaboration with an industrial partner a product with higher molecular weight that has been identified as the following molecule:



Figure 46: Molecule of HBHT

Property	Value
Chemical formula	$C_{30}H_{68}N_6$
Molecular Weight	512.9
Equivalent Weight	85.5

Table 14: Chemical properties of HBHT

This molecule can be obtained through the ammonolise reaction between an HMDA molecule with two BHT molecules: since its functionality is equal to 6 has been called hexafunctional BHT (HBHT).

This molecule is stable in polymerization conditions, and is perfect as star shaping molecule for PA 6 copolymerization.

POSS

In this work, with the acronym POSS (Polyhedral Olygmeric Silsesquioxane) is identified the self-condensation product of the 3 amino-propyl-(triethoxy) silane; the self condensation of silane molecules to obtained defined polyhedral structures composed by a Si-O skeleton and organic pendants with several functionalities is a well known process in scientific literature^[32].

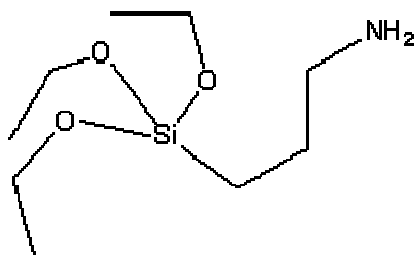


Figure 47: Molecule of 3 amino-propyl-(triethoxy) silane

In our case, the self condensation of the 3 amino-propyl-(triethoxy) silane is self catalyzed by the amino group at the end of the organic chain; and the reaction proceeds spontaneously in water solution with ethanol loss and forming Si-O-Si bonds.

The value of conversion can be calculated by the analysis of the equivalent weight in the obtained structure, measured through potentiometric titration of the amino end groups; the equivalent weigh obtained can be considerate the average molecular weight of the repetitive unit composing the final structure, indicating the degree of the self condensation reaction:

The obtained value is comprised in a range of the equivalent weight of the complete condensed silane and the weight of the unreacted silane: in the following table are reported the molecular weights of silane's molecule in the case of the reaction of 0,1,2,3 ethoxyl groups (EtO-) in the self condensation process (since there is one oxygen atom in the Si-O cage for each couple of Si atoms, when calculating the weight of the repetitive unit, its half oxygen atom is considered for each reacted group).

Number of reacted bonds	Equivalent molecular Weight (g/eq)
0	221
1	184
2	147
3	110

Table 15: Silane weight based on the condensation degree

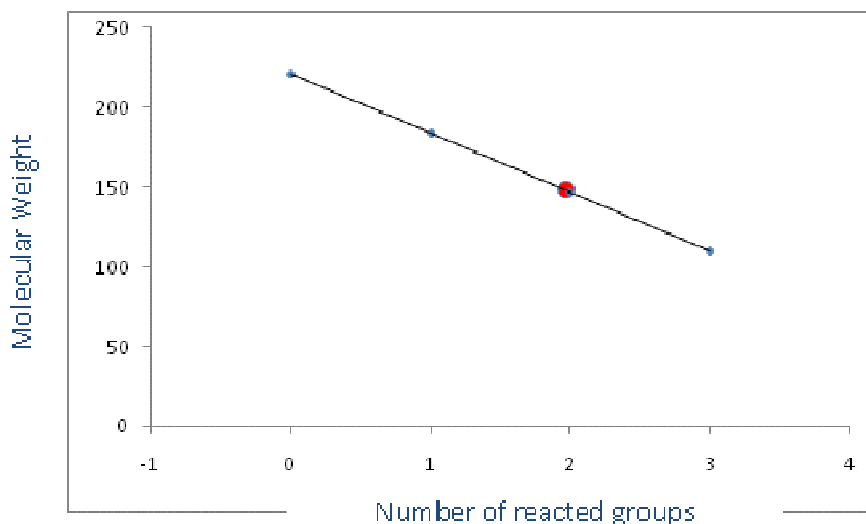


Figure 48: Loss of weight of the repetitive unit caused by condensation of the silane

The result obtained show that the product has a condensation degree that is near to the reaction of 2 groups on 3; therefore the silane is only partially reacted, and the unreacted part can have an important role on the polymers obtained using it as multifunctional agent. The nature of mixture of species of the self condensed silane, doesn't permit to attribute to this multifunctional agent a determined value of f , preventing the possibility to use a mathematical model to predict the polymerization result.

Polymers Synthesized

Star shaped polymers

Sample	meq NH ₂ /kg from POSS	meq NH ₂ /kg from HBHT
460 S	460	
255 S	255	
160 S	160	
460 B		460
255 B		255
160 B		160

Star shaped polymers ended with benzoic acid

Sample	meq NH ₂ /kg from POSS	meq NH ₂ /kg from HBHT	meq COOH/kg from benzoic acid
460 SB	460		460
255 SB	255		255
160 SB	160		160
460 BB		460	460
255 BB		255	255
160 BB		160	160

Star shaped polymers ended with CEPP

Sample	meq NH ₂ /kg from POSS	meq NH ₂ /kg from HBHT	meq POOH/kg from CEPP
460 SC	460		460
255 SC	255		255
160 SC	160		160
460 BC		460	460
255 BC		255	255
160 BC		160	160

Blends between Nylon 6 Standard and Our polymers

Sample	80% in weight	20% in weight
Blend-460 SC	Nylon 6 std	460 SC
Blend-255 SC	Nylon 6 std	255 SC
Blend-160 SC	Nylon 6 std	160 SC
Blend-460 BC	Nylon 6 std	460 BC
Blend-255 BC	Nylon 6 std	255 BC
Blend-160 BC	Nylon 6 std	160 BC

Table 16: Polymers synthesized with complex molecular architecture

Star Shaped Polymers

Using the two presented molecules, two series of polymers with star shaped molecular architecture have been prepared; considering that in this work the value that determines the amount of flame retardant agent (CEPP) bonded to the polymeric material is the amount of amino terminal groups, this value is taken as referring point.

Polymers have been synthesized with the goal to obtain 460, 255 and 160 meq NH₂/kg as terminal groups, both using POSS and HBHT.

Results obtained using POSS as multifunctional agent

The results of molecular weight and terminal group titration of polymeric materials obtained through silane insertion are presented in table 17:

Sample	M_n	d	-NH₂ meq/Kg	-COOH meq/Kg
460 S	15307	1.45	460	X
255 S	15908	1.85	255	X
160 S	25493	1.94	160	X

Table 17: SEC and titration data on polymers containing POSS

Data analysis evidences the star shape of these materials: the high number of the amino terminal groups (in relation to the no-detection of the carboxylic ones) and the D value lower than 2, are typical of materials with this molecular architecture.

Regarding the molecular weight of these materials it is possible to observe a decreasing of the molecular weight when increasing the molar amount of multifunctional agent, as predicted polymerization theory of an AB monomer in presence of a multifunctional agent (see chapter 7): in this kind of polymerization only a molecule of multifunctional agent is present for each macromolecule; the amount of multifunctional agent rules in this way the number of macromolecules that is possible to form. The higher the number of macromolecules, the lower the number of monomers that can react for a single macromolecule, lowering the average molecular weight.

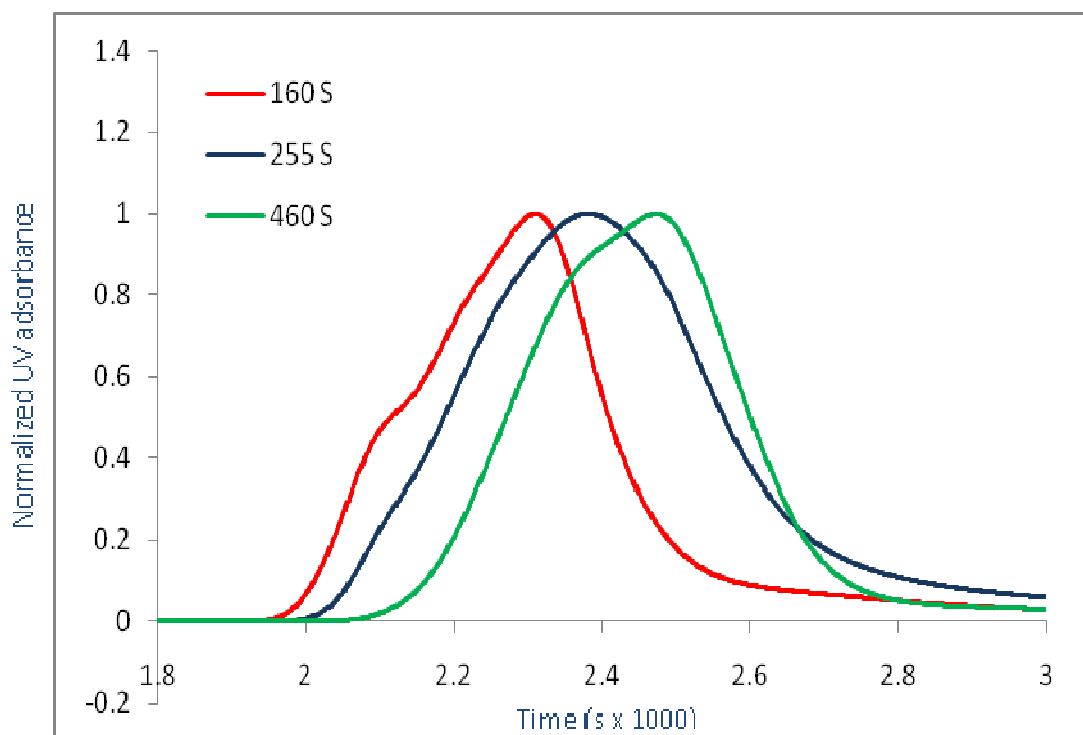


Figure 49: SEC curves of polymers containing POSS

Rheological data of synthesized polymers confirm the star shaped architecture of the macromolecule, with a viscosity lower than the one of the linear nylon 6 for all the polymers: this effect of higher fluidity for a star shaped macromolecule is due to the average length of its branches that is lower than the chain length of the linear one. With the same molecular weight, in fact, the viscosity of the melt polymer is determined by the flow of a macromolecule on another; this flow is easier when the length of the macromolecular chains decreases because the longer are the chains, the higher the probability to form nodes (entanglements) that increase the viscosity.

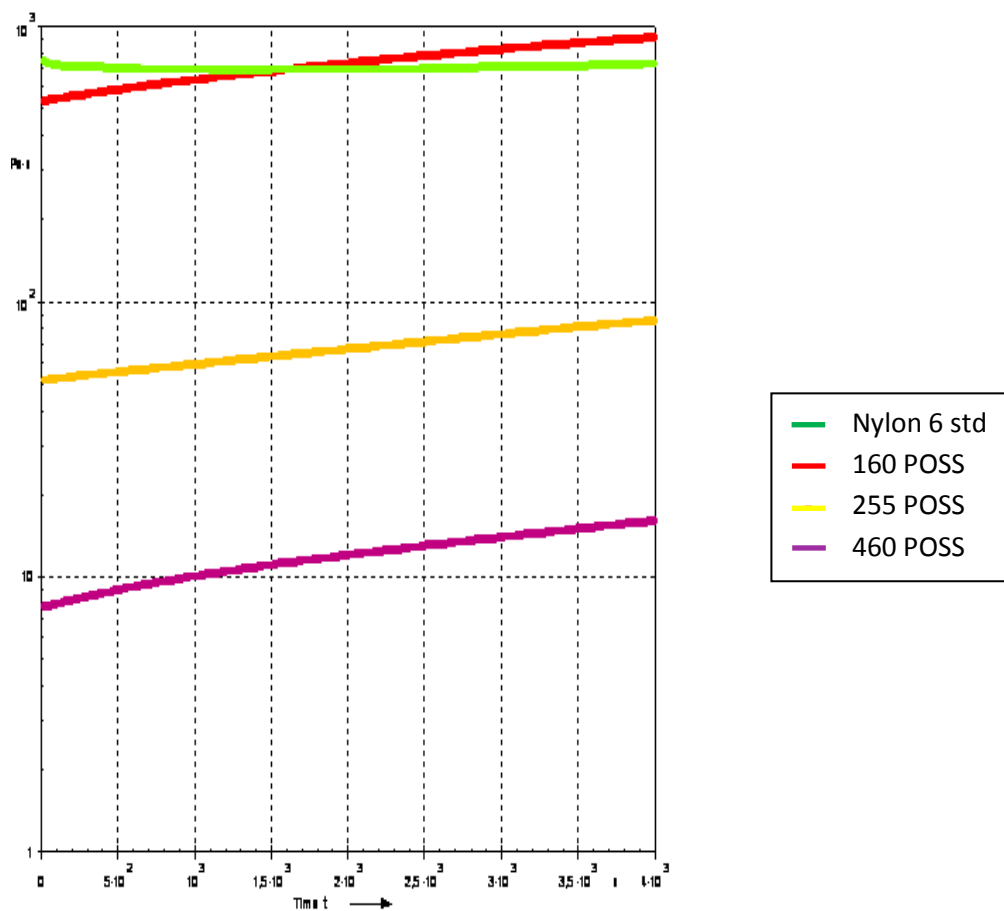


Figure 50: Rheological curves of polymers containing POSS

Another data is the decrease of the viscosity when increasing the amount of multifunctional agent in the feeding. This decrease is caused by the lowering of the molecular weight already discussed in the analysis of SEC data.

Regarding the thermal properties of the materials, DSC analysis have been performed with the following results:

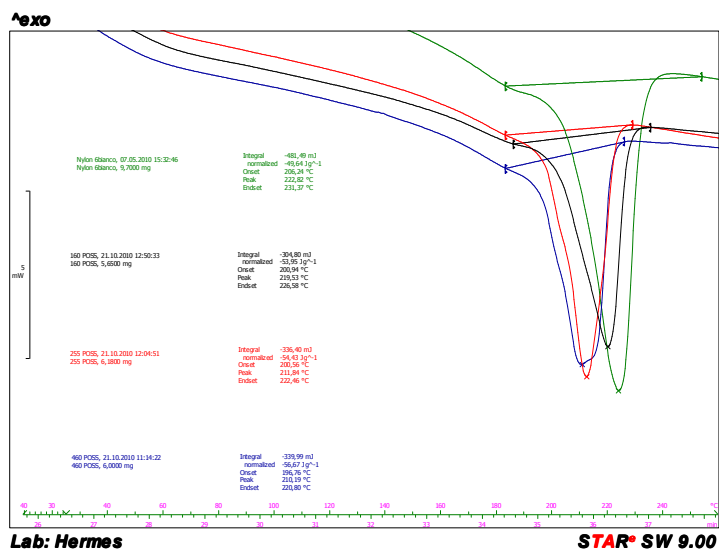


Figure 51: DSC curves of polymers containing POSS

Polymer	T _m (°C)	Normalized ΔH _m (J/g)
Nylon 6 std	222.7	-42.21
460 S	219.53	-53.95
255 S	211.54	-54.43
160 S	210.19	-56.67

Table 18: DSC data on polymers containing POSS

Data confirm the increase of crystalline fraction in the polymer, caused by the presence of the star architecture, while the decrease of the melting temperature is caused by the formation of disordered lattices.

Results obtained using HBHT as multifunctional agent

Polymeric materials synthesized using HBHT as multifunctional agent give the results of molecular weight and terminal groups titration presented in the following table:

Sample	M_n	d	-NH ₂ meq/Kg	-COOH meq/Kg
460 B	4177	1.53	514	54
255 B	5350	1.83	313	48
160 B	8832	1.68	191	31

Table 19: SEC and titration data on polymers containing HBHT

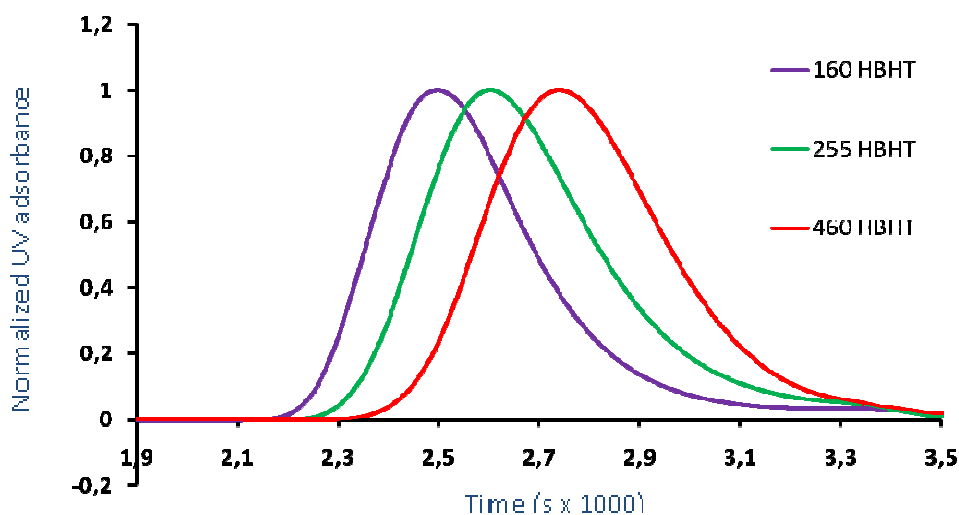


Figure 52: SEC curves of polymers containing HBHT

Also in this case the star shaped molecular architecture is confirmed by the high amount of amino terminal groups in comparison with the carboxylic ones by the low value of polydispersity.

The molecular weight of these polymers decreases by increasing the amount of multifunctional agent; moreover all these materials have a molecular weight lower than in the case of POSS-containing materials.

Rheological analysis evidences that the viscosity decreases in decreasing the molecular weight of the material and, consequently, in increasing the amount of amino terminal groups.

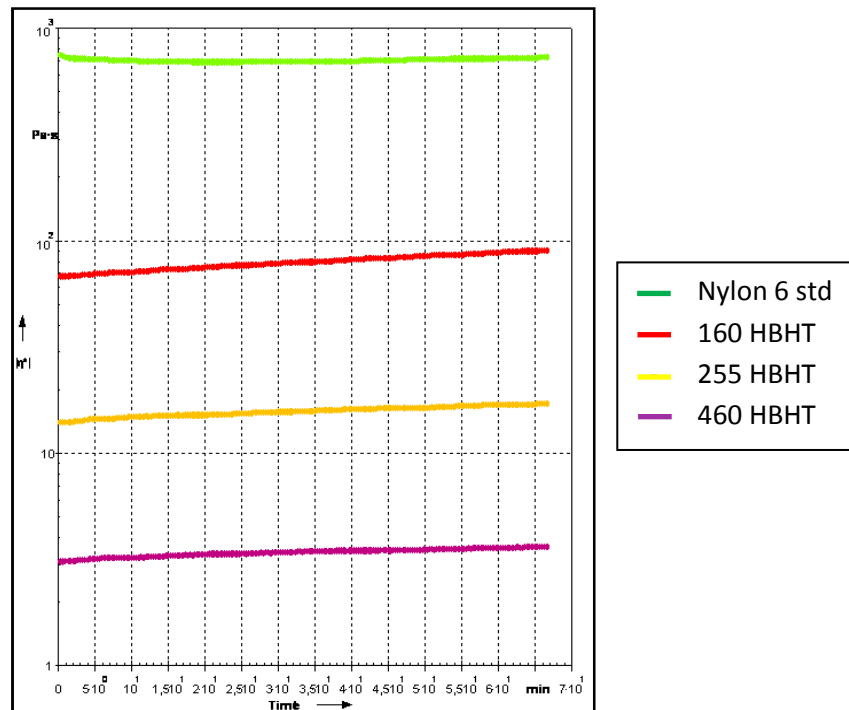


Figure 53: Rheological curves of polymers containing HBHT

Moreover all the values of viscosity measured for these materials are lower than standard polyamide 6, corresponding to their molecular architecture.

This characteristics, inherent of our materials, leads to the necessity to find an equilibrium that can be considered acceptable at the industrial level, between the necessity to obtain polymers with high amount of amino terminal groups (to bond an high amount of flame retardant) and the fluidity caused both by the star architecture and the low molecular weight.

Regarding the thermal behavior of these materials, by the Differential Scansion Calorimetry (DSC) data on crystallinity and melt behavior have been collected:

Nylon 6 std	222.7	-42.21
460 B	215.9	-62.02
255 B	218.9	-60.21
160 B	220.1	-58.44

Table 20: DSC data on polymers containing HBHT

Data in the table show the lowering of the melting temperature when increasing the amount of multifunctional agent inserted, and the increase of the enthalpy of fusion for star shaped molecules, higher than in standard PA 6 for all our materials and that increases when increasing the amount of multifunctional agent inserted.

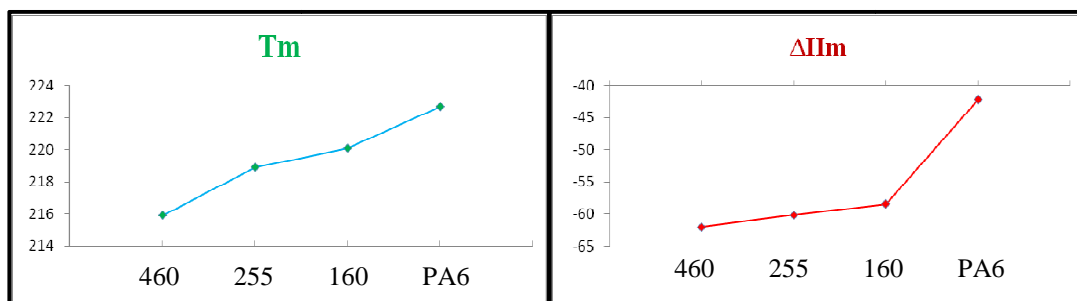


Figure 54: Melting temperature and enthalpy of fusion in polymers containing HBHT

The enthalpy of fusion indicates the amount of energy adsorbed by the melting of the crystalline fraction; if lattices are composed by the same repetitive units, as in our case, its value is proportional to the amount of crystalline fraction of the polymer.

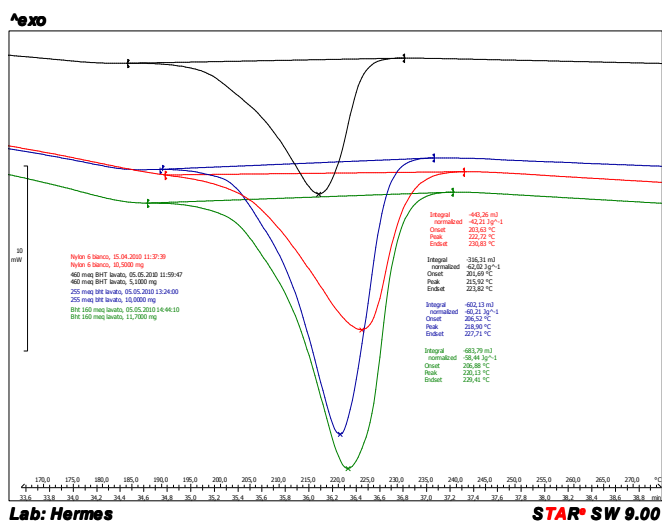


Figure 55: Melting peaks in polymers containing HBHT

In conclusion we can state that these polymers are more crystalline than standard PA 6; this property is due to two factors:

- The multifunctional agent acts as nucleant agent that promotes the crystallization process
- Star architecture causes a lower dimension of the macromolecular chains and, consequently a lower viscosity (as evidenced in the treatment of rheological data), that means more simplicity in the movement of the chains and in the formation of the lattices

On the other side, the presence of an high amount of nucleant agent creates an irregular crystalline phase and this is the explication for the lowering of the melting temperature. In fact a lower temperature is enough to melt lattices smaller and irregular in comparison with the ones formed in the linear macromolecule.

Comparison POSS – HBHT

Even if the values of molecular weight obtained by the SEC analysis cannot be considered valuable for the value of M_n obtained in the case of the evaluation of star shaped molecules, they can be considered indicatives in the case of internal comparison between two polymers with the same architecture.

Retention times measured for the materials containing POSS indicate that they have higher molecular weight than the ones obtained with HBHT. As example in the following figure are reported SEC curves for materials with 460 meq NH_2/kg , obtained with HBHT and POSS.

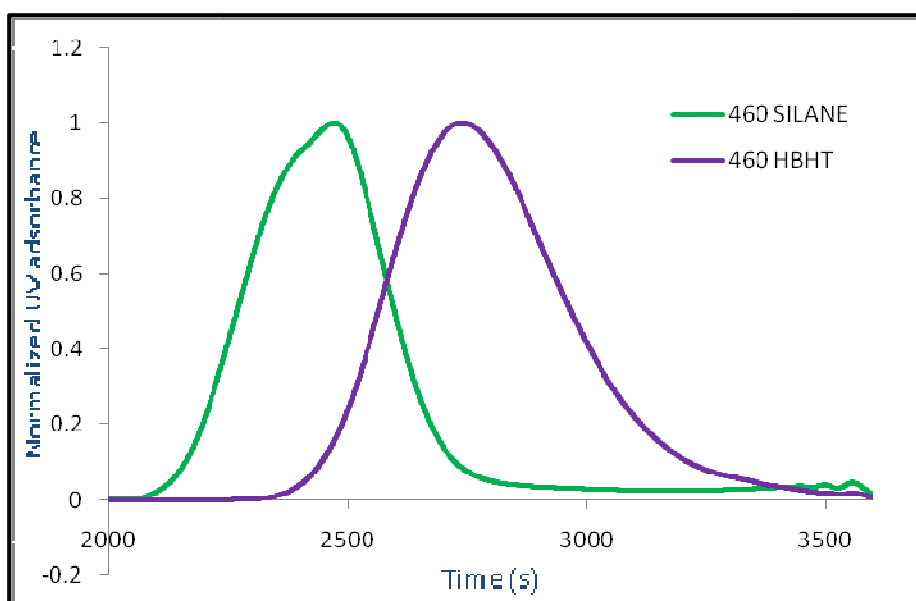


Figure 56: SEC curves of polymers obtained in presence of HBHT and POSS

Also in this case the difference in the molecular weight is related to the number of multifunctional agents present that causes the variation in the molecular weight. However in this case the analysis gives another important information: if obtaining the same amount of terminal groups of the material higher molecular weight is obtained, it means that an higher number of branches is present on the multifunctional agent.

The result indicates that POSS is a molecule with an average functionality higher than 6, that permits to obtain an higher number of NH₂ with the same molecular weight (or an higher value of molecular weight with the same amount of NH₂ terminal groups).

Is not possible to define precisely the value of f in the case of the POSS because:

- The condensation process leads to a mixture of complex structures where the formation is controlled by the statistic and the number of the variables are too high to define the final composition.
- Program used to develop mathematical models is able to predict the behavior of a step polymerization in the case of the insertion of a multifunctional agent with $f \leq 6$. The increase of the value of f creates an increase of the difficulty of the polymerization that need an improvement of the model.

Polymers obtained in presence of benzoic acid

As previously explained, the insertion of CEPP in the polymerization process of a polyamide correspond to the insertion of a molecule that works as a monofunctional chain ender, because the second acid group (the phosphinic one) isn't able to give stable bonds in polymerization conditions. To evaluate the behavior of CEPP molecule during the polymerization it has been decided to study to the general copolymerization system using our multifunctional agents in presence of a monofunctional acid molecule, that works as chain ender. Benzoic acid has been chosen since it is monofunctional, stable in polymerization conditions, and for the presence of the benzoic groups, as the CEPP molecule.

Polymers containing benzoic acid have been obtained adding the same amount of multifunctional agent than in the previous series, and an amount of benzoic acid covering the unbalancement of the amino terminal groups.

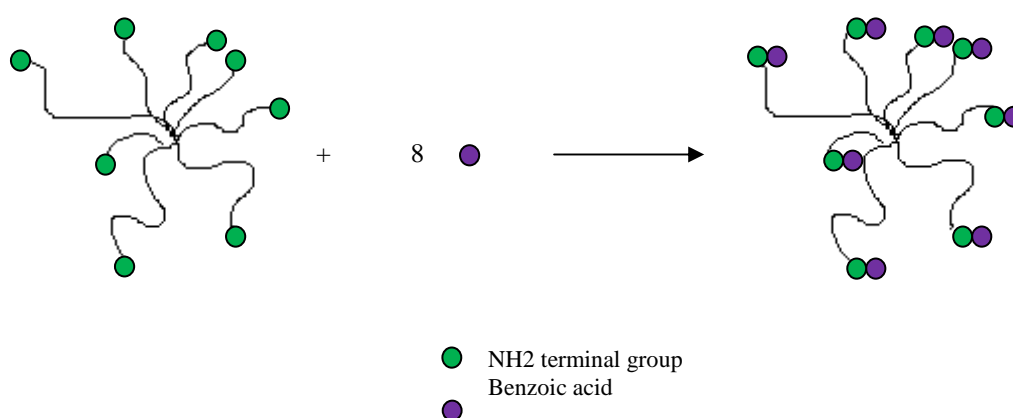


Figure 57: Use of benzoic acid as chain ender

The goal is to obtain macromolecules with the structure represented in the figure; obviously the result of the copolymerization is a mixture of structures that go from the linear macromolecule to the star shaping one with the maximum number of branches, passing through all the intermediates.

This kind of copolymerization have an high number of variable and its prediction through the use of mathematical model is not possible.

Polymers obtained with POSS and benzoic acid

In the following table are reported the data on the SEC and titration analysis for this series of polymer:

Sample	M_n	d	Terminal NH ₂	Terminal COOH
460 SB	5154	2.28	100	70
255 SB	13133	2.23	32	45
160 SB	12030	2.10	32	47

Table 21: SEC and titration data on polymers containing HBHT

The tendency of the molecular weight of these polymers is similar to the one obtained in absence of the benzoic acid: increasing the amount of chain regulator (in this case both mono- and multi-functional) the molecular weight decreases. However in this series the presence of the chain ender promotes the formation of species with low molecular weight, that lead to an increase of the polymer polydispersity.

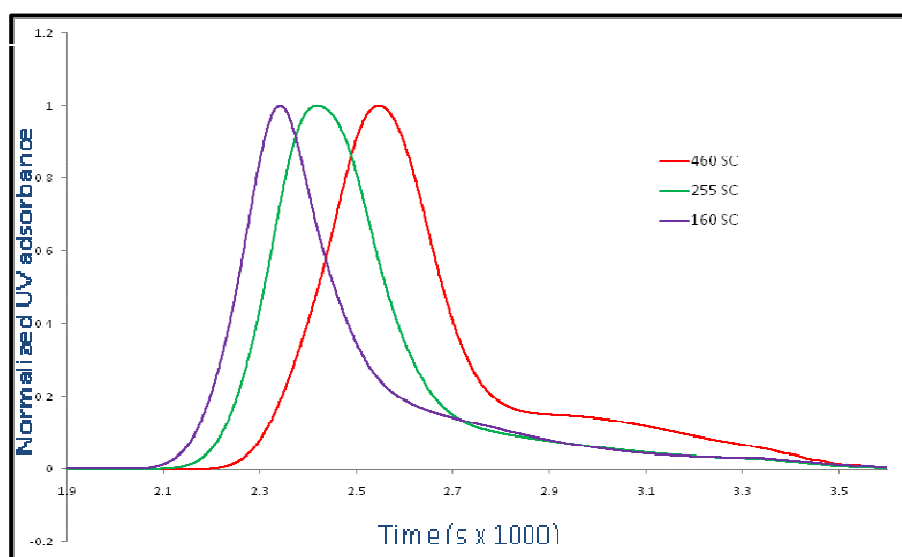


Figure 58: SEC curves of polymers containing POSS and Benzoic Acid

Moreover the formation of species with low molecular weight is proportional to the amount of chain regulator inserted, and the value of polydispersity increases following the same tendency.

Rheological analysis of these materials shows viscosity values slightly lower than the ones of materials obtained in absence of chain ender; this confirms that these materials maintain the star shaped architecture and that the presence of the chain ender causes a decrease in the molecular weight, that leads to low values of viscosity.

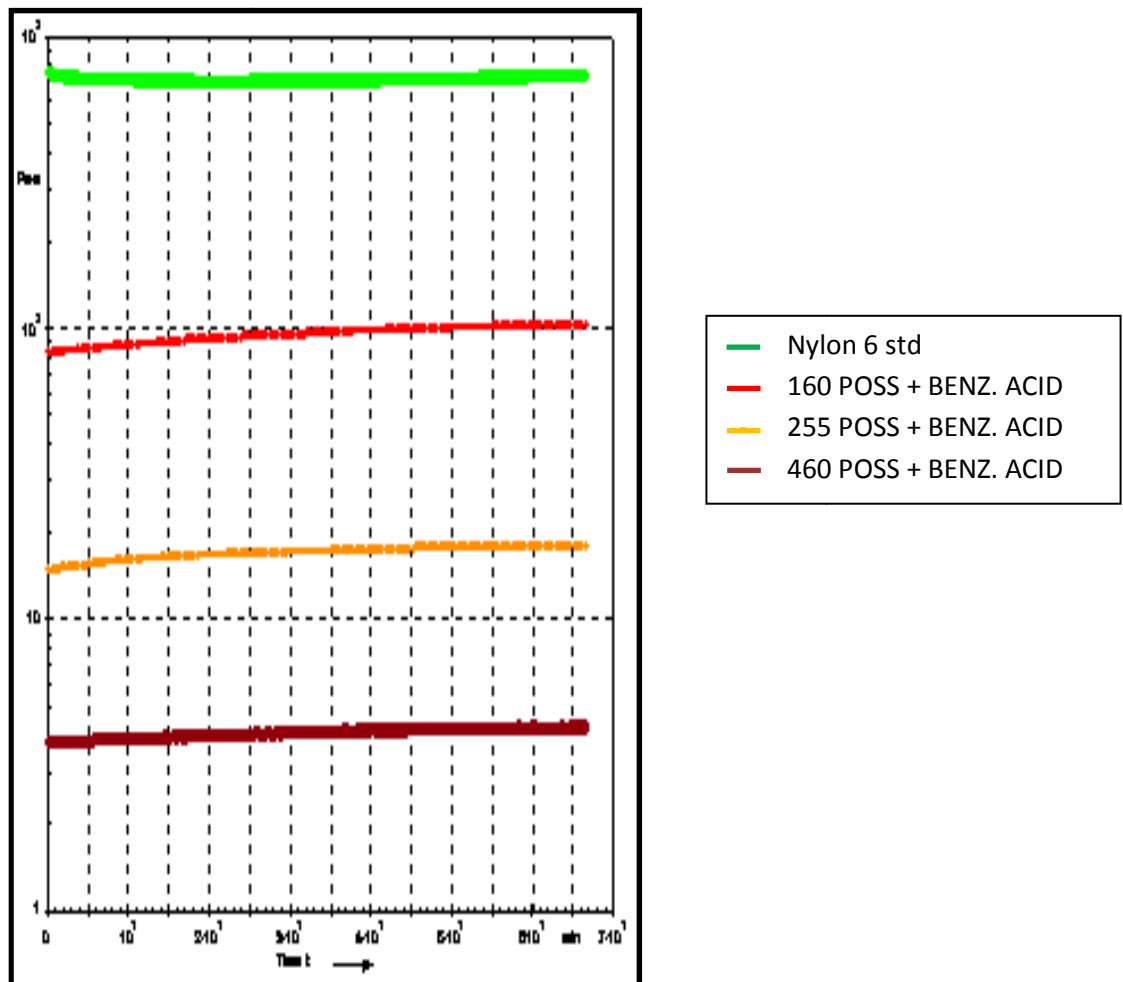


Figure 59: Rheological data of polymers containing POSS and Benzoic Acid

In the following table data on thermal properties, investigated through DSC analysis are reported:

Sample	T _m (°C)	ΔH _m norm (J/g)
Nylon 6 std	222.7	-42.21
460 SB	212.8	-48.54
255 SB	216.5	-46.26
160 SB	218.0	-45.16

Table 22: DSC data on polymers containing POSS and Benzoic Acid

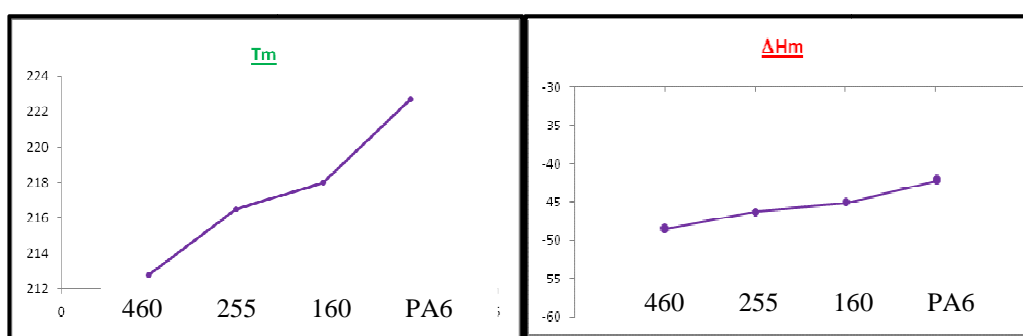


Figure 60: Melting temperature and enthalpy of fusion in polymers containing POSS and Benzoic acid

In this series, the presence of the benzoic acid disturbs the crystallization process of the polymeric material since the elimination of the gap in the crystallization degree between the standard 6 polyamide and our star shaped polymers.

However these polymers result slightly more crystalline than the standard polyamide 6 and their crystallinity increases by increasing the amount of chain regulator.

At the same time increasing the amount of chain regulator, a decrease of the melting temperature is registered, caused by the insertion of an higher amount of molecules that disturb the chain regularity.

Polymers obtained with HBHT and benzoic acid

In the following table data on molecular weight and titration of terminal groups are reported:

Sample	M_n	d	Terminal NH ₂	Terminal COOH
460 BB	3457	1.53	60	44
255 BB	4803	1.62	49	43
160 BB	6812	1.76	45	35

Table 23: SEC and Titration data on polymers containing HBHT and Benzoic Acid

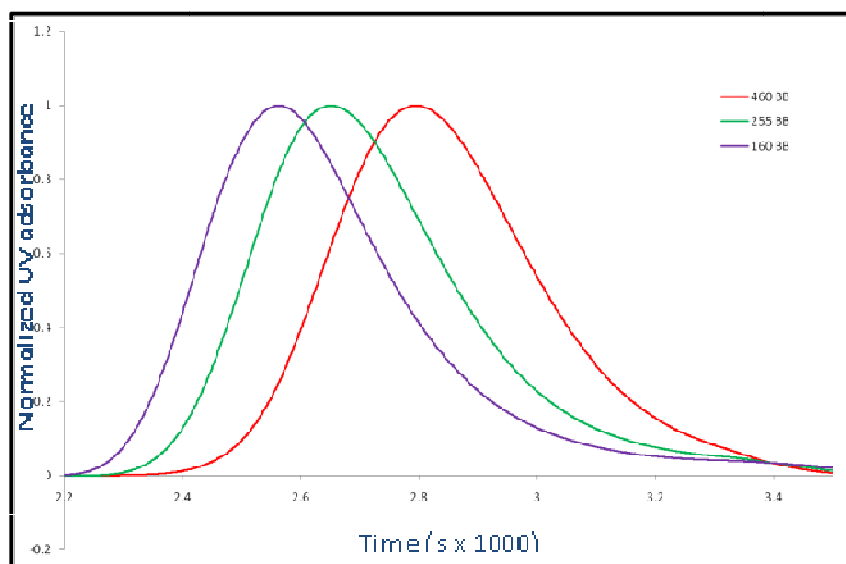


Figure 61: SEC curves of polymers containing HBHT and Benzoic acid

Also in this case the increase of the amount of chain regulator present in the polymer, causes the diminution of its molecular weight. However in this case there isn't the increase of polydispersity registered for the polymers with POSS and benzoic acid.

Rheological analysis show a tendency already observed in the other series, with a decrease of the viscosity in increasing the amount of multifunctional agent inserted and a value of viscosity lower than the corresponding material obtained without chain ender.

In the following table data registered by DSC analysis are reported:

Sample	T _m (°C)	ΔH _m norm (J/g)
Nylon 6 std	222.7	-42.21
460 BB	212.2	-53.47
255 BB	216.4	-52.93
160 BB	218.8	-51.63

Table 24: DSC data on polymers containing HBHT and Benzoic Acid

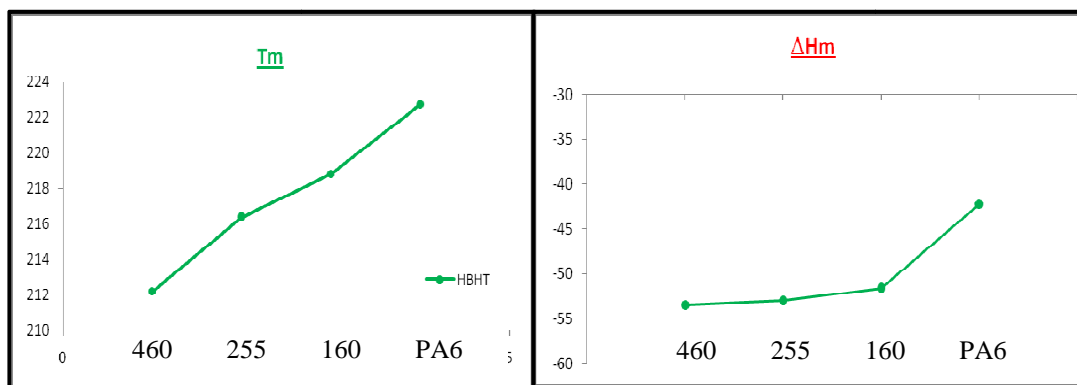


Figure 62: Melting temperature and enthalpy of fusion in polymers containing HBHT and Benzoic acid

As evidenced in the Figures that reports the behavior of melting temperature and enthalpy, polymers obtained with HBHT and benzoic acid have a higher crystallinity than nylon 6 and polymers obtained with POSS and benzoic acid; this means that the use of a multifunctional agent with a structure near to the one of the nylon 6 gives a higher regularity and a high degree of crystallinity.

The melting temperatures decrease in increasing the amount of chain regulator as in all other series.

Treatment of the results obtained in the polymers containing benzoic acid

As in the polymers obtained using only the multifunctional agent, also using benzoic acid as chain ender the polymers containing POSS have higher molecular weight than the ones containing HBHT (M_n value for the two series are reported in the following table):

Polymer	M_n without benzoic acid	M_n with benzoic acid
460 S	15307	5154
255 S	15908	13133
160 S	25493	12030
460 B	4177	3457
255 B	5350	4803
160 B	8832	6812

Table 25: M_n data on polymers containing and not-containing Benzoic Acid

The presence of benzoic acid causes a loss of weight that is registered for each star shaped polymer. In the following figure is reported the diminution of the molecular weight in the polymer 255 BB in comparison with 255 B:

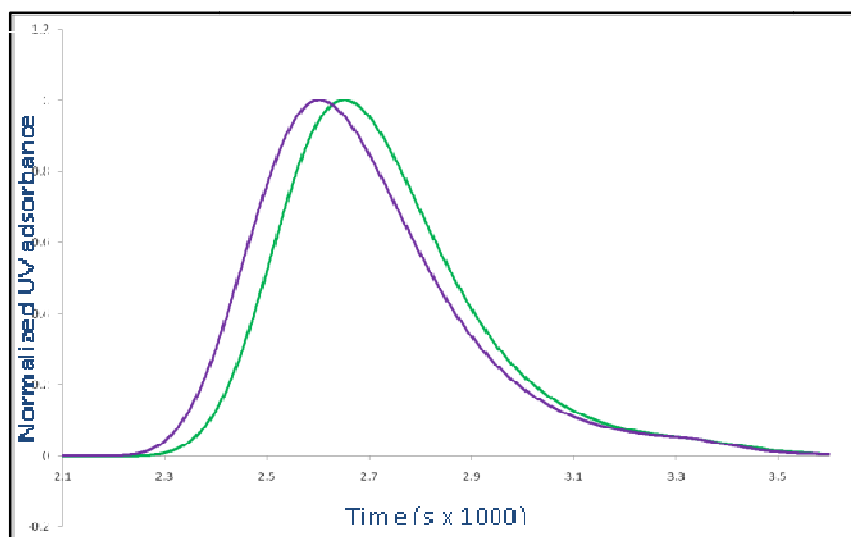


Figure 63: SEC curve of polymers with 255 meq NH_2/kg by HBHT containing or not Benzoic acid

Polymers containing benzoic acid show also lower viscosity in rheological analysis, while a lower crystalline fraction is evidenced by the DSC.

Polymers obtained in presence of CEPP

In the third phase of this work, CEPP has been used as chain ender in copolymerization with star shaped nylon 6 with characteristics illustrated in previous paragraphs.

In this case the polymeric materials are obtained with the same amounts of the 2 multifunctional agents presented, and the amount of amino terminal groups obtained has been balanced with CEPP.

Polymers obtained using POSS and CEPP

Data of molecular weight and terminal groups are collected in the following table:

Sample	M_n	d	Terminal NH₂	Terminal COOH	Terminal POOH
460 SC	3916	2,82	180	185	316
255 SC	5140	2,87	120	115	185
160 SC	5869	2,87	95	92	127

Table 26: SEC and Titration data on polymers containing POSS and CEPP

In this series, molecular weight is for all materials lower than the corresponding ones synthesized in presence of benzoic acid; the decrease of the molecular weight means that not only CEPP works as a monofunctional chain ender but also that its presence disturbs the polymerization process.

Moreover, in the considered series, a peculiar interaction between the multifunctional agent and the chain ender is evidenced through the SEC analysis of these polymers (see figure)

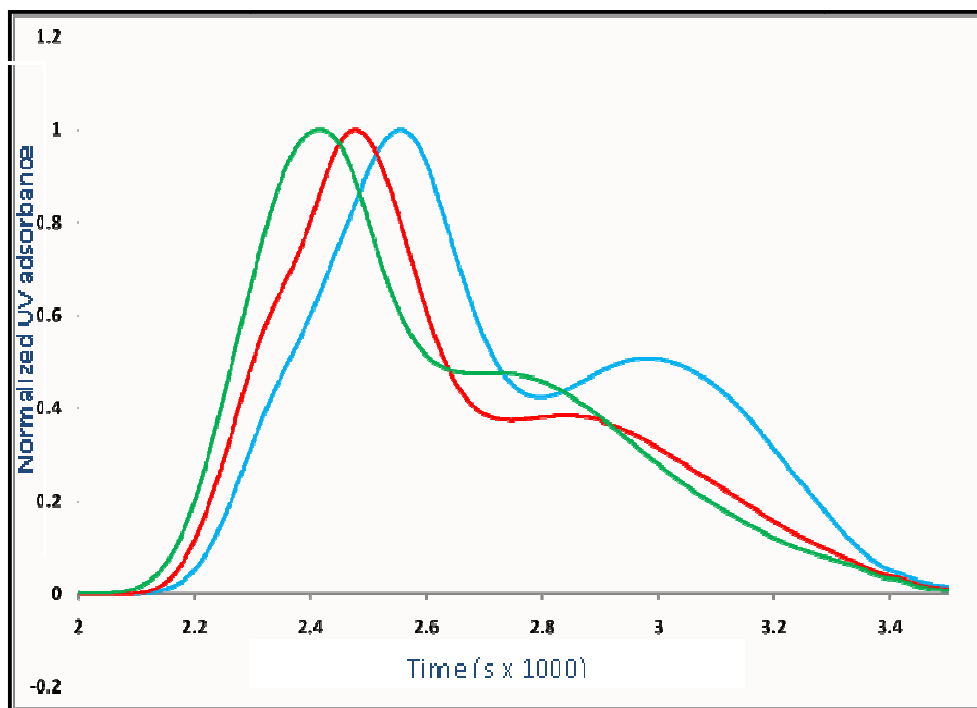


Figure 64: SEC curves of polymers containing POSS and CEPP

Analyzing the figure it is possible to see that low molecular weight species form a second peak that decreases in molecular weight (shift to the right side of the graph) and increases in the amount (increasing in the weight of the peak) in increasing the amount of chain regulator present. Regarding the main peak a shift to lower molecular weight is obtained in increasing the amount of chain regulator present, as in all other series.

Regarding rheological analysis, in this case (and only in this one, considering all materials tested) an increase of the viscosity of the material during the analysis is registered, caused by a reaction of the terminal groups of the polymeric material. This reactivity leads to a crosslinking phenomenon; the polymer extracted after rheological analysis is not soluble, but is foamed.

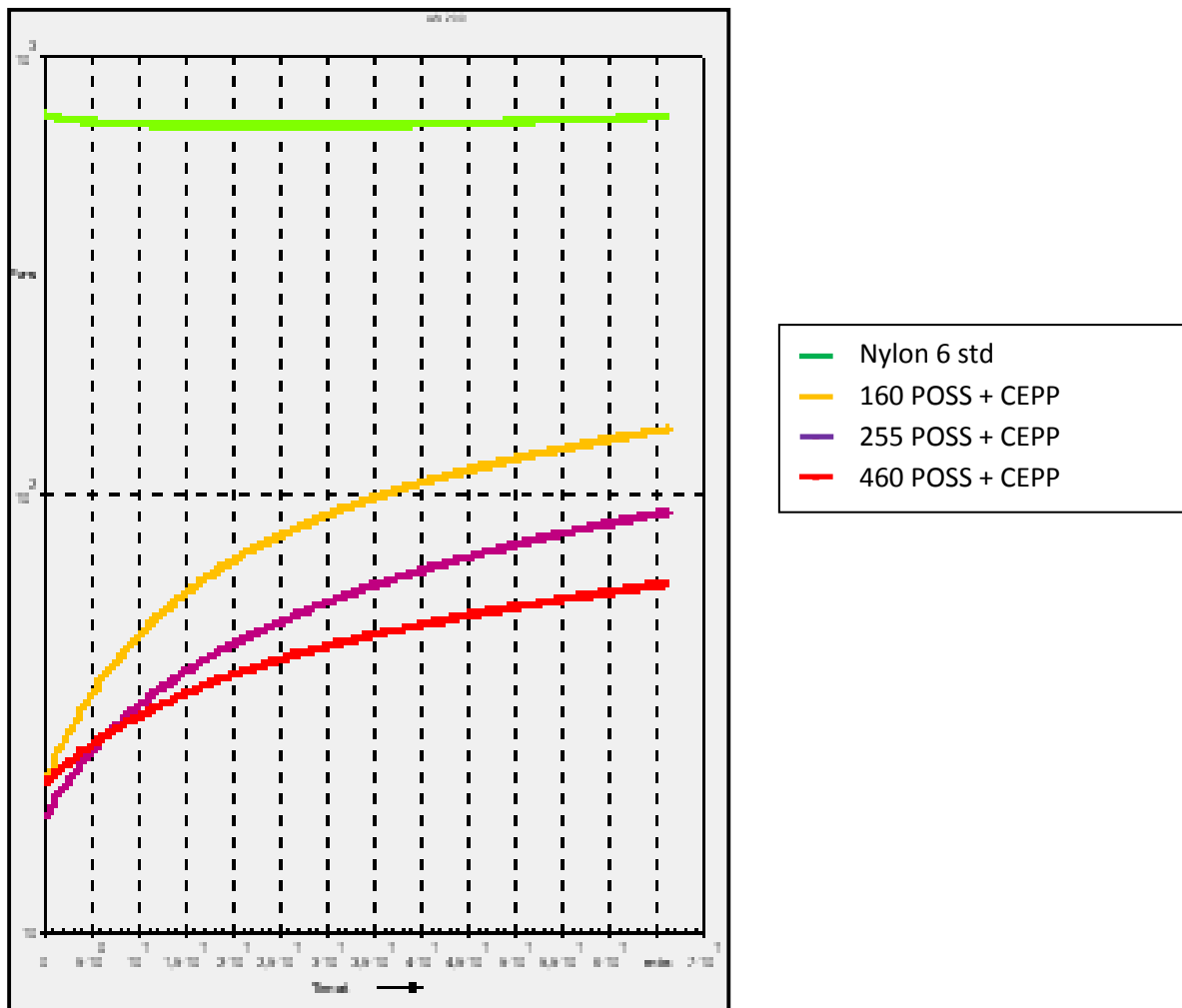


Figure 65: Rheological data of polymers containing POSS and CEPP

This phenomenon is attributed to the reaction of phosphinic terminal groups of the CEPP, with the unreacted groups of the POSS.

As explained at the beginning of the chapter, the POSS is a product obtained by partial self condensation of 3 amino propyl triethoxy silane, that contains ethoxyl or hydroxyl groups. Even if the CEPP can be considered as a monofunctional chain ender regarding the formation of an amidic bond, in the case of formation of ester bonds the CEPP works as difunctional chain extender.

This crosslinking reaction doesn't occur during the polymerization because reactive groups are diluted in an high amount of unreacted caprolactam and cyclic oligomers, but during rheological analysis, the polymer has been washed (therefore has not caprolactam left) and the remaining part has the possibility to react.

In the following table data obtained through DSC analysis are reported:

Polymer	T _m (°C)	ΔH _m (J/g)
Nylon 6 std	222,7	-42,2
460 SC	211,4	-46,1
255 SC	214,0	-42,0
160 SC	216,5	-47,4

Table 27: DSC data on polymers containing POSS and CEPP

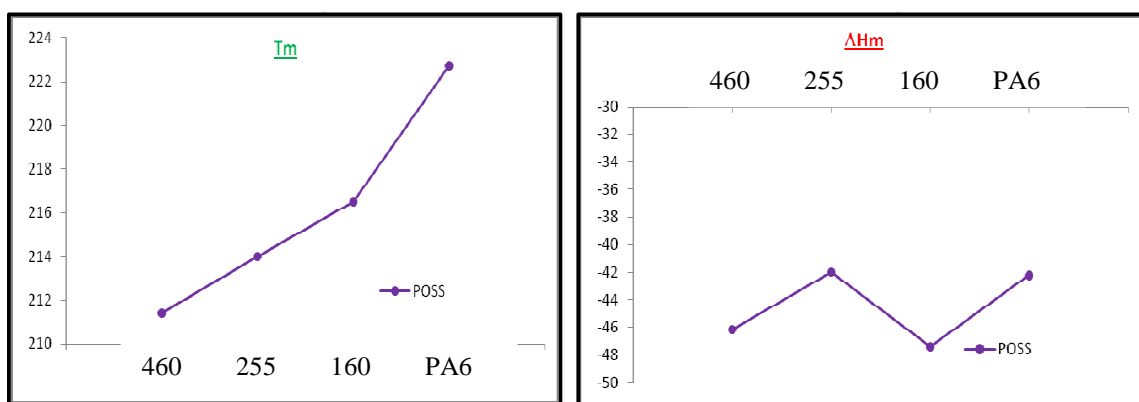


Figure 66: DSC data of polymers containing POSS and CEPP

In this case the highest level in the crystallization disturb is registered; the enthalpy of fusion values are comparable with the one of the linear polymer, showing that the insertion of the CEEP in the presence of a non-ordered multifunctional agent cancels the increase of crystallinity typical of the star shaped macromolecules.

In this series are also registered the lower melting temperatures of all materials synthesized; T_m decreases by increasing the amount of chain regulator in the material.

Polymers obtained using HBHT and CEPP

Data obtained through SEC analysis and potentiometric titration are reported:

Sample	M _n	d	Terminal NH ₂	Terminal COOH	Terminal POOH
460 BC	2610	1,65	138	132	315
260 BC	3501	1,76	93	91	176
160 BC	4185	1,89	72	66	133

Table 28: SEC and Titration data on polymers containing HBHT and CEPP

Also in this case a decrease of the molecular weight when increasing the amount of chain regulator is registered and, in general, the molecular weight obtained is lower than the one measured in presence of a classical chain ender as benzoic acid:

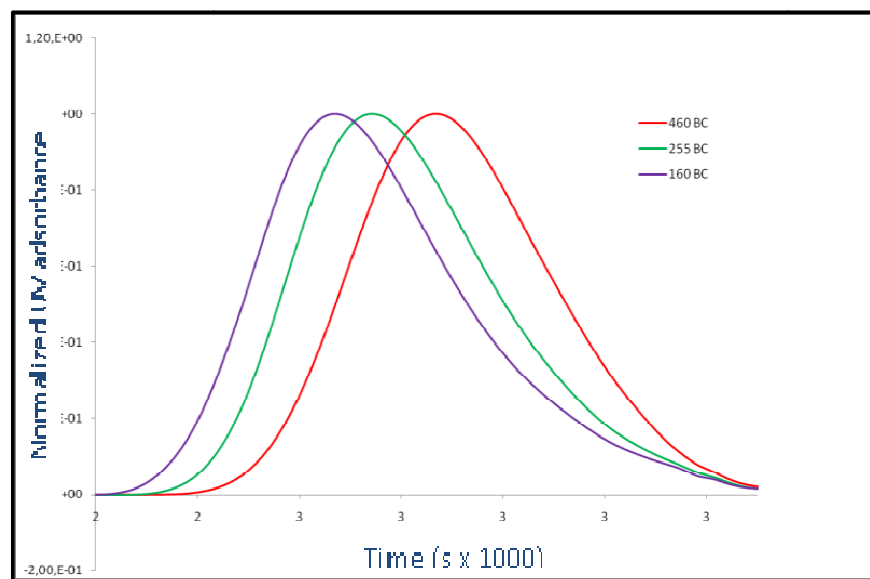


Figure 67: SEC curves of polymers containing HBHT and CEPP

However properties registered for this series are higher regular than the ones obtained using POSS as multifunctional agent. In this case there is no formation of a second peak during the SEC analysis, and the polydispersity value is lower than 2, as the theory express for star shaped molecule.

Regarding rheological analysis, in these samples results follow the tendency registered in all other series (except for the series containing POSS and CEPP), with a decrease of the viscosity when increasing the amount of chain regulator and lower than corresponding material obtained using benzoic acid as chain ender.

In the following table data obtained by DSC analysis are reported:

Polymer	T _m (°C)	ΔH _m (J/g)
Nylon 6 std	222,7	-42,2
460 BC	208,7	-52,0
255 BC	215,2	-58,1
160 BC	215,0	-56,6

Table 29: DSC data on polymers containing HBHT and CEPP

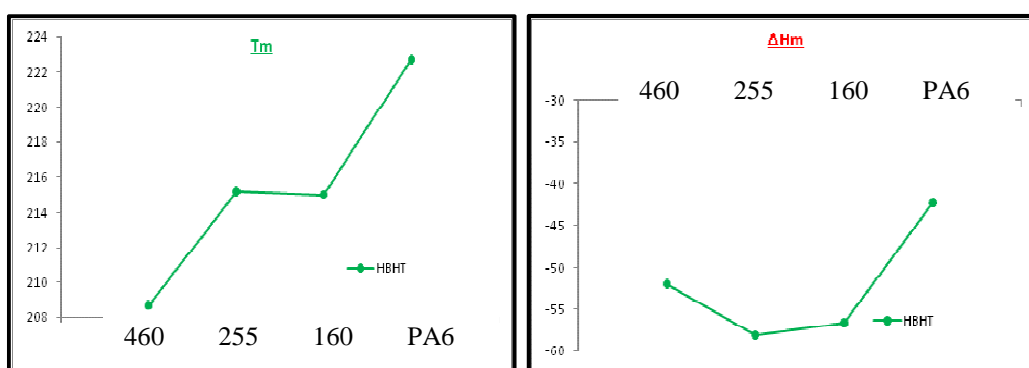


Figure 68: DSC data on polymers containing HBHT and CEPP

Also in this case a disturb in the crystallization of the polymer is registered, obtained by the insertion of a bulky comonomer. In this case the crystallinity percentage is higher than in the PA 6, because the amount of CEPP inserted is not high enough to cancel the crystallinity effect of star shape architecture if the multifunctional agent is regular molecule as HBHT (in contraposition with data obtained in the use of POSS); however it is not possible to find a regular correlation between thermal properties and amount of chain ender inserted.

Titration of terminal groups of CEPP- containing materials

A peculiar feature of materials containing CEPP is the impossibility, during the titration analysis, to measure all the phosphinic groups. The amount of CEPP contained in the material is obtained through the titration of phosphinic terminal groups, that because their higher acidity, have a peculiar peak of titration, different from the one of the carboxylic ones.

However the amount of CEPP measured, calculated basing on the titration of phosphinic groups, is really lower than the one inserted and also than the one detected by H^1 NMR spectrometry.

After different tests the problem has been identified as the salification of phosphinic groups with the terminal ones of the material; this salification is maintained in titration conditions and makes the POOH group inaccessible by the NaOH used as titrant. On the other side it is possible to detect the amount of amino terminal groups using HCl.

The result is that the amount of real POOH groups contained is obtainable by the sum of amino and POOH terminal groups measured. Following this procedure correspondence between titration data and NMR analysis has been found.

Through the titration important data have been obtained, regarding the amount of monofunctional chain ender effectively bonded to the material. This data is important both on the academic side of the work and on the practice of the material obtained: it results in fact that in the materials obtained by copolymerization in presence of HBHT or POSS the same amount of CEPP is found.

The two series of materials are very different regarding molecular weight, its distribution, appearance, thermal properties, but the amount of CEPP contained is the same.

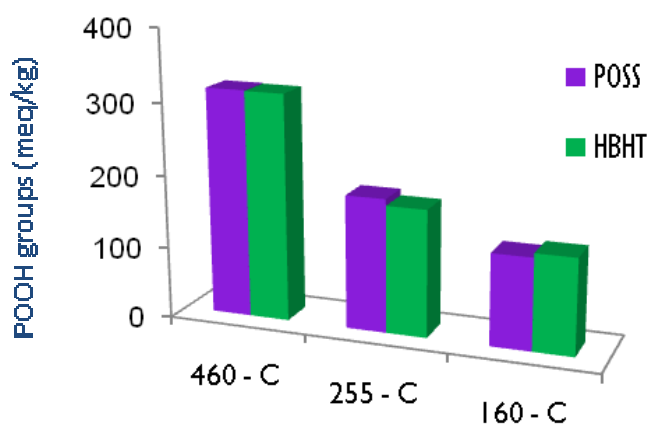


Figure 69: Titration data on polymers containing CEPP

This is one of the most important results obtained in this work, since the level of insertion of the molecule that leads the flame retardant property, is linked only to the amount of amino and acid terminal groups inserted during the feeding phase, a value easily controlled by the producer.

Conclusions

In conclusion from the data obtained in all synthesized materials, it is possible to affirm that:

- POSS is a multifunctional agent that leads to higher molecular weight than HBHT, and in the point of view to obtain the best compromise between the insertion of an high amount of CEPP and the maintaining an high molecular weight, the use of this kind of multifunctional agent is very important.
- POSS is an only partially reacted material, that can react during the polymerization and the manufacture phases giving a behavior that must be defined according to the time and temperature of the processes.
- HBHT is a multifunctional agent that leads to lower molecular weights but with higher reliability, maintaining the expected behavior in all polymers synthesized.
- HBHT leads to materials with higher crystallinity even if used in presence on comonomers having a benzene ring.
- Even if cristallinity increases by increasing the amount of multifunctional agent inserted, this behavior is accompanied to a decrease of the melting temperature in DSC analysis, meaning that the crystallinity is higher but lattices are less regular in comparison with standard nylon 6.
- CEPP behavior as monofunctional chain ender has been demonstrated and also its disturb in the polymerization process, because using it lower molecular weight than using benzoic acid has been reached.

CHAPTER 10: Synthesis of
nanocomposites materials
through in situ
polymerization of nanofillers
with polyamide 6

In the last decades, the research in polymer field have persecuted the research of nanocomposites to obtain materials with new properties.

In chapter 3, where the main classes of NHFR have been presented, is underlined that the insertion of nanodispersed mineral fillers is a promising way to get flame retardant properties in several research studies.

The basing idea on the use of a nanofiller in a polymeric matrix is that the low dimension and the high surface area of the particle permits a better distribution in the material; the result is a huge increment of desired properties (the most researched ones, using mineral nanofillers, are impact resistance and flame retardancy), in comparison with the insertion of the same amount of a classical filler, because the nanodisperse one leads to more homogenous and lighter materials with high properties.

In this work we have studied the insertion through in situ polymerization of two kind of nanofillers with very different shape e characteristics, focusing on the modification of the surface area with the goal to increase the compatibility between the polymeric matrix (organic matter), and mineral nanofiller (inorganic matter).

Nanosilica

Nanosilica is an inorganic material composed by a network of Si-O bonds, that is organized in spherulites, with variable dimensions. It is a very porous material, and controlling the synthesis phase, dimension and surface area of the particles can be controlled.

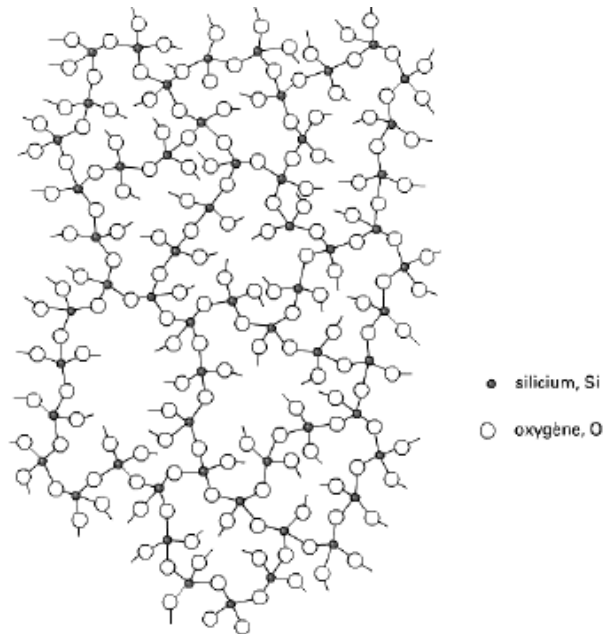


Figure 70: Structure of nanosilica

The chosen material is a commercial product with an average diameter of 20 nm and a value of surface area of 600 m²/g. The high value of surface area is the parameter that determined our choice.

Montmorillonite

Montmorillonite is a clay material composed by lamellar shaped particles; the chosen product is a commercial material produced by Southern Clay, with the trade name of Cloisite 15A[®]. Is a mineral nanofiller composed by lamellae with 100 nm of width and 1 nm- thick. These lamellae are alternate with an ammonium ion bonded to two methyl groups and two aliphatic chains, according to the formula:

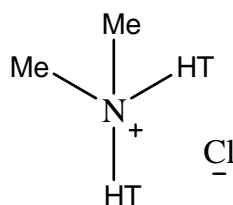
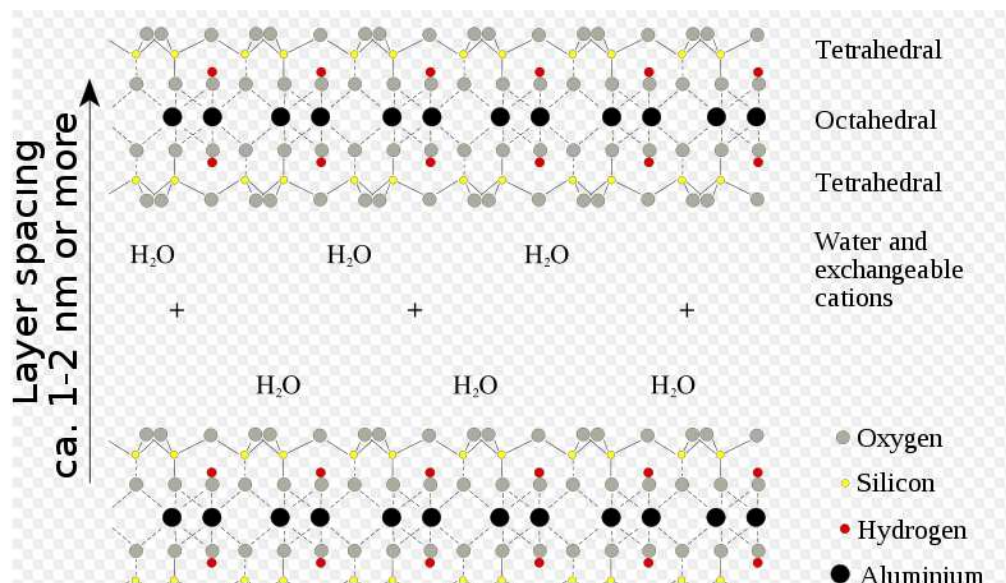


Figure 71: Ammonium ion in Cloisite 15 A[®]

In this scheme “HT” is the acronym for “Hydrogenated Tail” and indicates a mix of hydrogenated aliphatic chains composed 65% C₁₈, 30% C₁₆, 5% C₁₄.

The presence of the ammonium ion favors the separation of the lamellae and increases the surface area that is measured in 750 m²/g, while in the case of pure nanofiller lamellae are strongly packed in aggregates and only a little part of their surface is exposed.

The ammonium ion is a very important component of the final material in the commercial product and represents the 43% in weight of it.

Differences in thermal degradation of two nanofillers

The two presented nanofillers are very different in chemical composition, shape, external surface; considering that these materials are inserted in the polymeric matrix to increase the flame retardant properties, their behavior at thermal degradation has been investigated through TGA analysis.

Curves of loss of weight during temperature scan from 50 to 700°C at the rate of 20°C/min and in nitrogen atmosphere are presented for the two materials in the following figure:

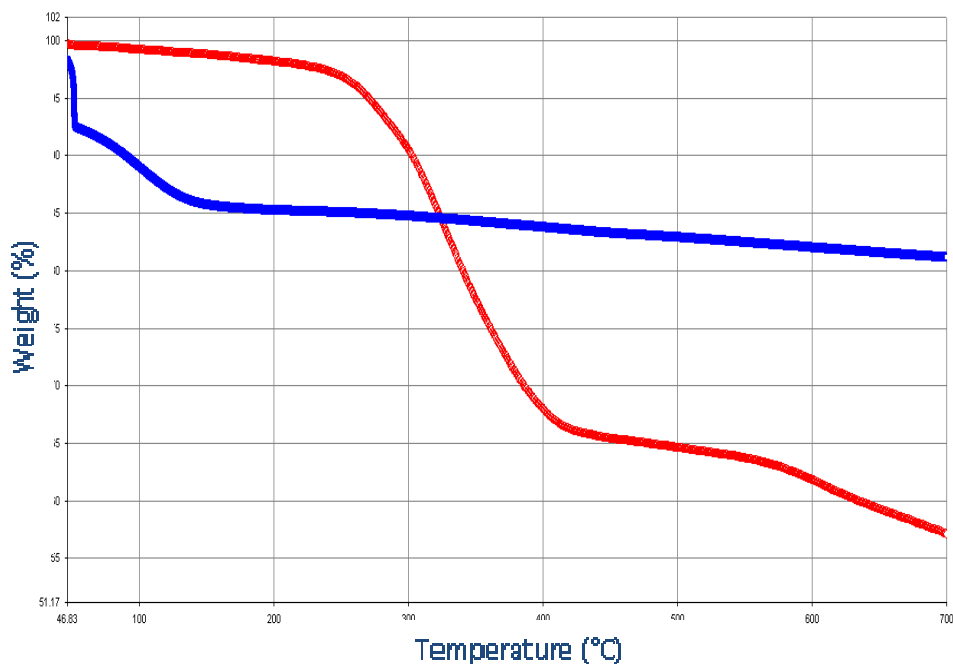


Figure 72: Thermal degradation of cloisite 15 A[™] (red curve) and nanosilica (blue curve)

As evidenced, nanosilica (blue curve) given its tendency to adsorb water, has as loss of weight (the loss of water adsorbed) registered at temperatures between 50 and 200°C and quantified in 12% of the total weight.

Regarding Montmorillonite (red curve), it presents a lower weight owed to water adsorption (1,8% of the total weight of the material) while the higher loss of weight is registered around 400°C and is quantified in 40% of total weight. This phenomenon is due to the loss of ammonium ion inserted in the material.

Surface modification of nanofillers

The insertion of a mineral filler (inorganic matter) in a polymeric matrix (organic matter) leads problem of compatibility that can cause effects of aggregation of the filler: the filler, that has poor interaction with the matrix, is not well dispersed, and the advantage to use a material with nanometric dimension is cancelled.

A possible solution for a better interaction between the matrix and the filler is the use of an hybrid (organic/inorganic) molecule (in our case a silane) able to give a better compatibility both with the filler and the matrix.

The effect of a combatibilization process obtained using a silane is appreciable in the following figure:

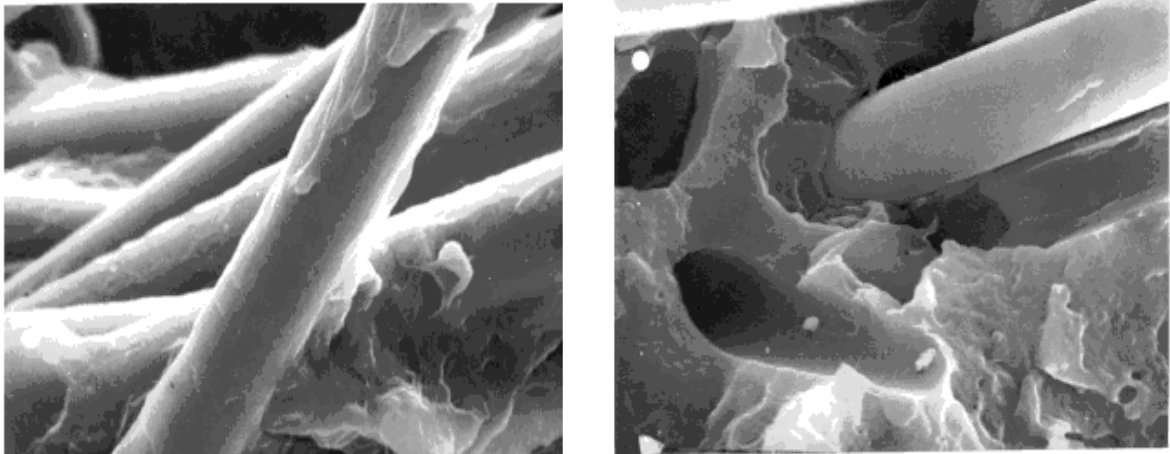


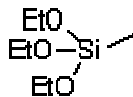
Figure 73: Effect of the graft on glass fiber in PA6

On the left is possible to see the incompatibility with a glass filler and a polyamidic matrix, while in the right figure the effect of the use of a silane on glass fiber is presented.

Three silanes have been chosen, to evaluate the effect of a graft that interacts with the polymeric matrix following three different path:



3- amino-propyl -(triethoxy) silane (it will be indicate as NH₂ silane) . The organic portion of this molecule can react with the polymeric matrix during the in situ polymerization.



Methyl-(triethoxy) silane (it will be indicate as Me silane). The use of this silane causes a covering of the filler with a low amount of organic matter for molecule, a low idrofobicity of the graft and no possibility of chemical reaction with the polymeric matrix.



Hexadecyl (trimetoxy) silane (in it will be indicate as silane C₁₆). The use of this silane causes a covering with an high amount of organic matter, no possibility of reaction with the polymeric matrix and higher hydrophobicity.

The grafting process is performed through a condensation reaction of the silane with the OH terminal groups of the filler, following the reaction:

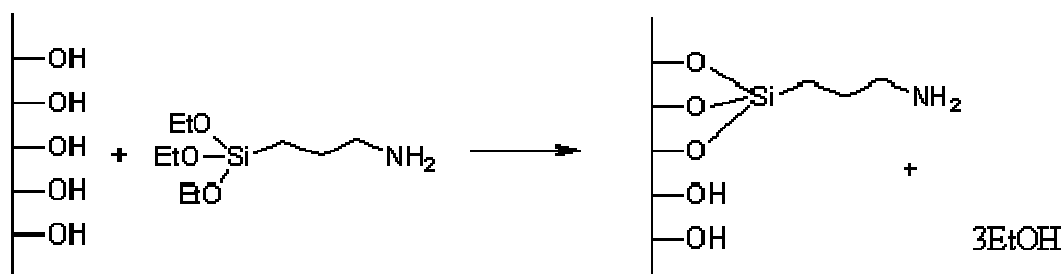


Figure 74: Grafting reaction

The reaction is conducted adding the silane drop by drop to a suspension of the nanofiller in organic solvent. When the addition is terminated, the mixture is maintained under stirring at room temperature for 4 hours. After this time silane and solvent are distilled, first under atmospheric pressure, then under high vacuum. During the last phase also the unreacted silane is taken away, and no other purification phases are required.

Samples of modified nanofillers are presented in the table:

Clay Name	Silane used	% in weight (*)
Nanosilice		
Cloisite 15 A		
Nanosilice 2% NH ₂	NH ₂	2
Nanosilice 7.5% NH ₂	NH ₂	7.5
Nanosilice 15% NH ₂	NH ₂	15
Nanosilice 35% NH ₂	NH ₂	35
Nanosilice 100% NH ₂	NH ₂	100
Cloisite 2% NH ₂	NH ₂	2
Cloisite 7.5% NH ₂	NH ₂	7.5
Cloisite 15% NH ₂	NH ₂	15
Cloisite 35% NH ₂	NH ₂	35
Cloisite 20% Me	Me	20
Cloisite 40% Me	Me	40
Cloisite 10% C ₁₆	C ₁₆	10
Cloisite 20% C ₁₆	C ₁₆	20

Table 30: Nanofillers prepared through surface modification

The weight percentage presented in the table is measured as reacted, and bonded to the filler, silane; this value is very different from the one of unreacted silane inserted in the feeding phase and the difference increases in decreasing the weight of the silane, as shown in the following table:

Silane	Molecular Weight unreacted	Molecular Weight reacted	Loss of weight (%)
Me	178.1	43.1	75.8
-NH ₂	221.1	86.1	61,0
C ₁₆	402.4	303.4	24.6

Table 31: Loss of weight of silane molecules after grafting reaction

Moreover the surface interested by the graft is related to the density of OH groups that reacts with silane at the surface of the filler, therefore data on the grafting process need to be based on the molar amount of graft inserted.

The need to work with data functional for an internal comparison (so expressed in molar amount) and comparable with published in literature (expressed in weight of silane/weight of final material) lead to the decision to present all data as weight of amino silane reacted.

Regarding the grafting process with amino silane, the amount effectively bond to the filler can be measured through titration of the amino terminal groups. The analysis gives a value of meq NH₂ that, through multiplication for the value of molecular weight of the reacted silane, can lead to the amount of bonded silane.

Both nanosilice and Montmorillonite have been grafted with 4 different amounts of amino silane. Results in titration of these nanofillers is reported in the following table:

Sample	% silane NH ₂	meq NH ₂ /kg theo.	meq NH ₂ /kg meas.	% Silane meas.
Nanosilice 2%NH ₂	1.96	236	148	1.22
Cloisite 2%NH ₂	1.96	236	241	2.00
Nanosilice 7.5%NH ₂	6.98	840	671	5.56
Cloisite 7.5%NH ₂	6.98	840	485	4.02
Nanosilice 15%NH ₂	13.04	1571	1287	10.68
Cloisite 15%NH ₂	13.04	1571	942	7.81
Nanosilice 35%NH ₂	25.93	3124	2447	20.31
Cloisite 35% NH ₂	25.93	3124	3053	25.33

Table 32: Nanofillers prepared through surface modification

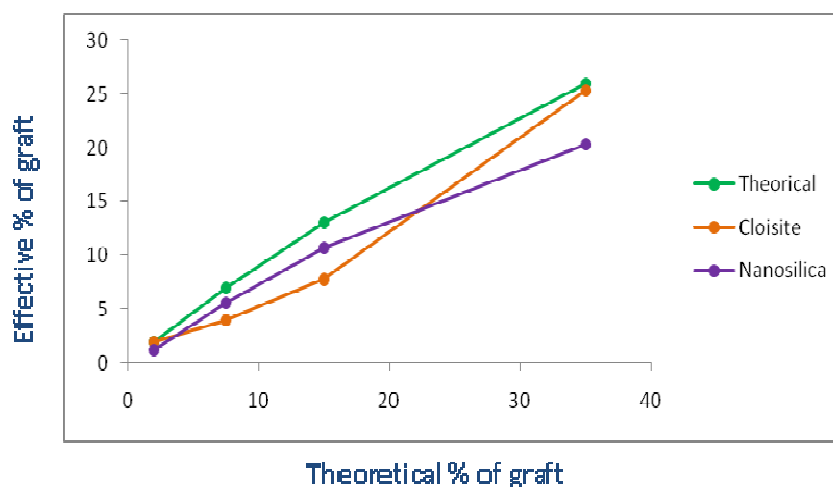


Figure 75: Amount of silane grafted measured by titration

The results show a better regularity in the results obtained for the graft of nanosilica: in this case, in fact, the percentage of measured graft on the theoretical value decrease in increasing the amount inserted. Is not possible to find a tendency in the case of the graft with Montmorillonite, because the highest values are registered in the case of the maximum and the minimum amount of silane inserted.

The effect of the graft on the thermal degradation of the filler

As already shown, Montmorillonite and nanosilica have two different behaviors during the analysis of thermal degradation. In this paragraph differences in this behavior associated to the presence of the graft on the surface area of the filler are investigated.

The effect of the graft with amino silane on the loss of weight of the nanosilica is presented in the following graph: the red one is the curve of the loss of weight of the pure nanosilica; the other ones are relative to grafted nanosilica.

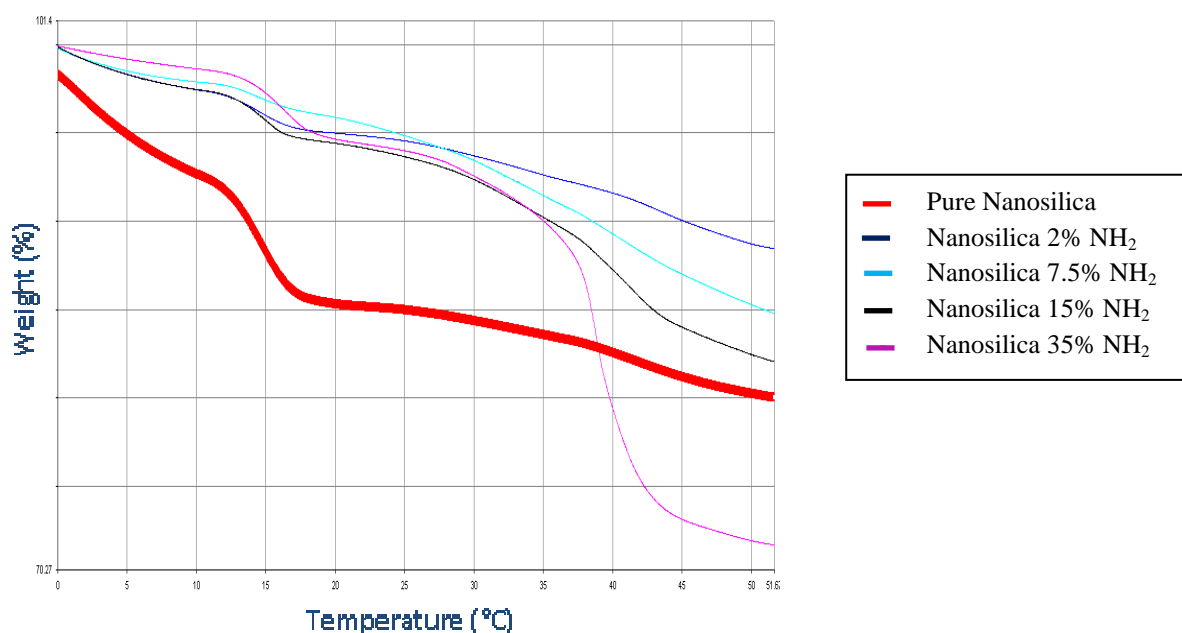


Figure 76: Effect on the graft of the loss of weigh curve of the nanosilica

Differences in the behavior of the grafted nanosilica are placed in 2 region of the graph:

- The first difference in the grafted silane is the decrease of water adsorption that leads to a lower loss of weight in the left part of the graph. Therefore the presence of a graft even if having polar terminal group prevents the water adsorption typical of this filler.
- The second difference is registered at high temperatures, where there is an higher loss of weigh for grafted nanosilica than the pure one. This loss of weight corresponds to the degradation of the graft and increases when increasing the amount of grafted silane.

Regarding the loss of weight registered for grafted montmorillonite, results are rationalized considering two transitions: the one registered under 200°C, related to the loss of the adsorbed water, and the one registered at 400°C that interests the thermal degradation of the ammonium ion.

The following table contains the values registered during the analysis of pure montmorillonite and of the grafted ones:

Cloisite Prepared	% Water Adsorbed	% loss of weight at 400°C
Pure Cloisite 15 A	1.8	32
Cloisite 2% NH ₂	1.3	26.3
Cloisite 7,5% NH ₂	1.4	25
Cloisite 15% NH ₂	3	21.9
Cloisite 35% NH ₂	5.6	20.1
Cloisite 20 % Me	1.5	29.8
Cloisite 40% Me	1.3	25.1
Cloisite 10 % C ₁₆	1.0	20.0
Cloisite 20 % C ₁₆	0.7	15.1

Table 32: Results in TGA analysis of modified montmorillonites

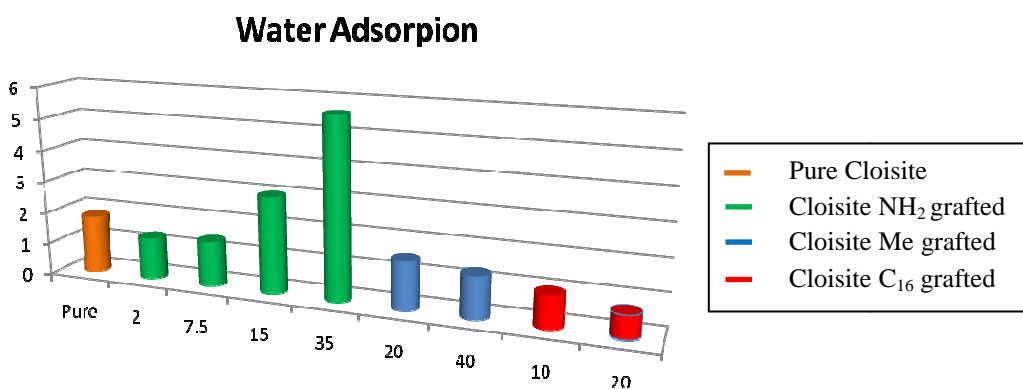


Figure 77: Effect on the graft on the water adsorption of monmorillonites

Regarding water adsorption, two different tendencies are registered: in the case of the graft with amino silane, the value of water adsorbed decreases for low amounts of silane inserted and increases in the case of high amount (indicatively after the 10% by weight of reacted amino silane).

Regarding the graft with methyl silane and C₁₆ silane, the presence of the graft causes a decrease of the water adsorption that is higher, higher the amount and the dimension of silane grafted.

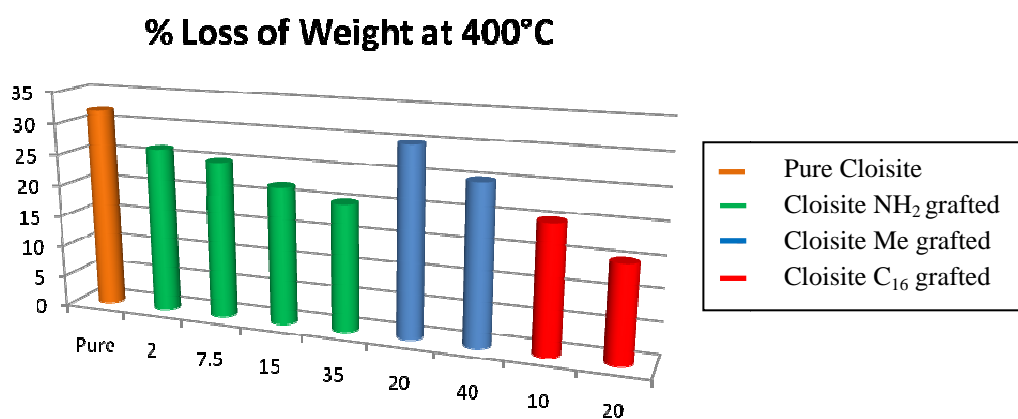


Figure 78: Effect on the graft on the intercalated ion degradation in montmorillonite

Regarding the loss of weight at 400°C that is caused by the thermal degradation of the interstitial ion, the silanes seem to slow it, independently by the nature of the silane used. Moreover, increasing the amount of silane inserted, a slower loss of weight is registered.

As example, in the following figure, are reported curves on the loss of weight for montmorillonite containing the 10 and 20% in weigh of silane C₁₆ in comparison with pure montmorillonite:

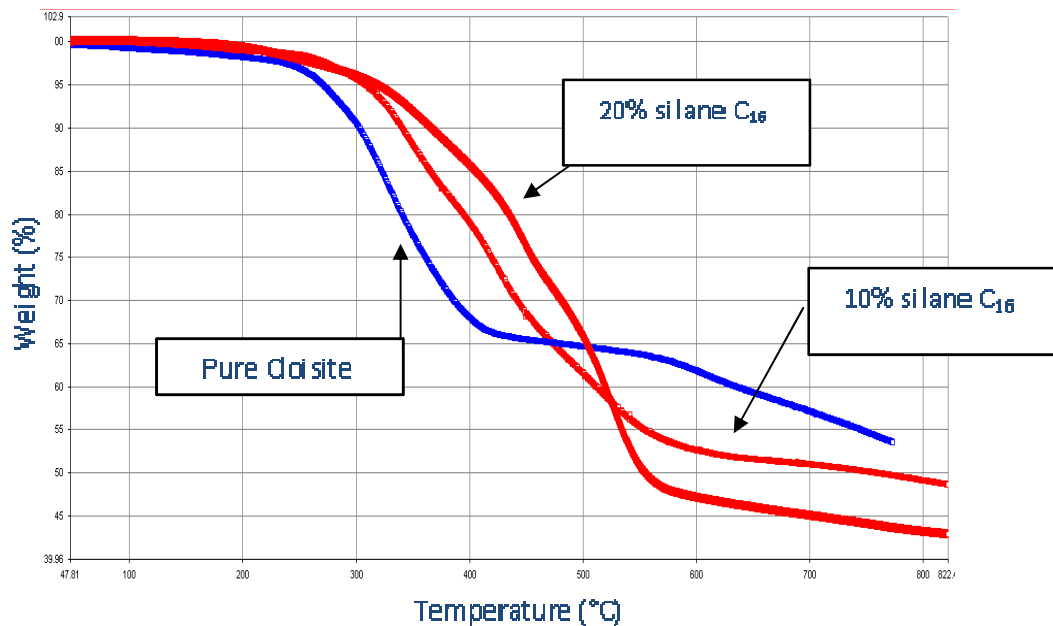


Figure 79: Effect of the graft with different amount of C₁₆ silane of TGA of montmorillonite

In the figure is possible to see that grafted fillers are more stable since loss of molecular weight occurs at higher temperature. At the end of analysis an higher loss of weight is registered for grafted fillers because it comprises also the thermal degradation of the graft.

XRD analysis of grafted montmorillonite

In the case of montmorillonite it is possible to evaluate the effect of the graft on the diffraction properties of the material.

The starting point is the XRD analysis performed on the pure Cloisite 15 A[®].

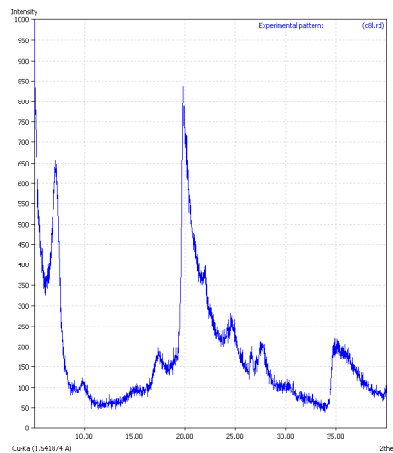


Figure 80: XRD analysis on pure Cloisite 15A[®]

The analysis shows the presence of the main peak at 20°, and a series of peak with lower intensity, around the principal one.

The graft with low dimension silanes, as the methyl silane, doesn't cause variation in the resulting diffractogram. Moreover there are not significant variations if the amount of inserted silane is increased:

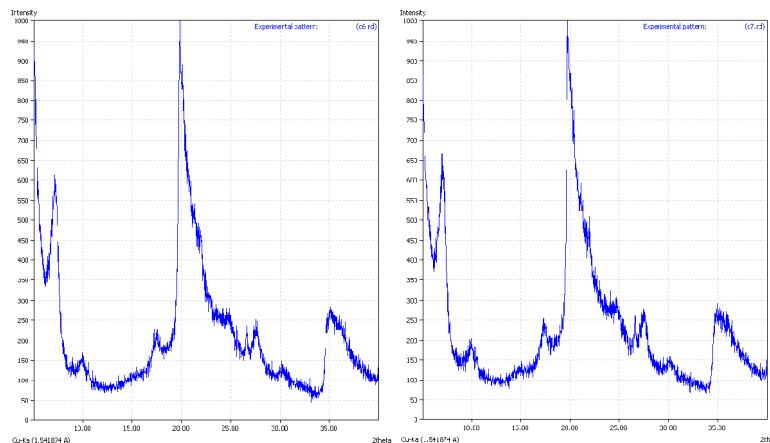


Figure 81: XRD analysis on montmorillonite modified with 20% (left) and 40% (right) of methyl silane

In the case of insertion of a silane with medium dimension (as the amino silane) an effect on the property of diffraction of the final material is observed: the loss of regularity in the crystalline order leads to a widening of the main peak and the diminution of intensity in the secondary ones:

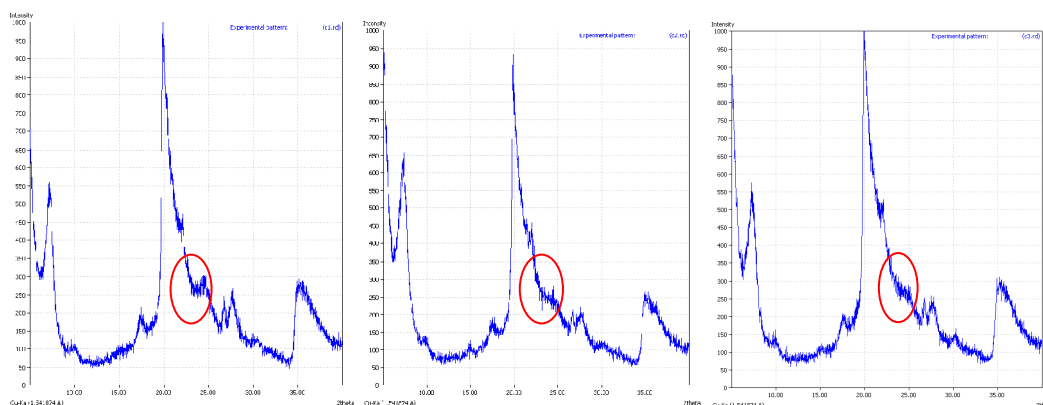


Figure 82: XRD analysis on montmorillonite modified with 7.5% (left), 15% (middle) and 35% (right) of amino silane

This effect increases in increasing the amount of inserted silane. In the case of graft with a silane with high dimension (in our case C_{16} silane), the effect on the XRD analysis is more evident. Secondary peaks disappear and near the main peak appears a second one that, in the case of graft with 20% of C_{16} silane, reaches the same intensity of the main one:

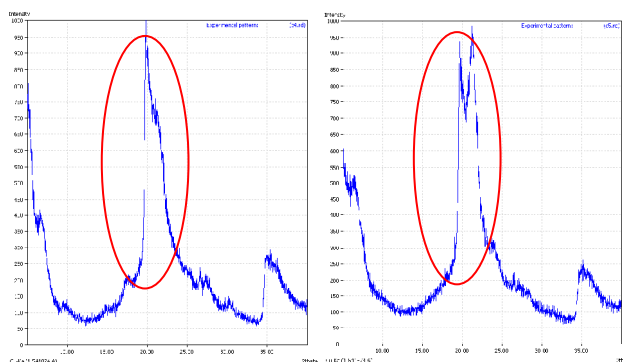


Figure 83: XRD analysis on montmorillonite modified with 10% (left) and 20% (right) of C_{16} silane

In this case the used silane have a dimension comparable to the one of the aliphatic chains bonded to the ammonium ion that is placed between two lamellae.

The hypothesis for the changing of the x-ray diffraction is the insertion of the silane in the internal part, between two lamellae, resulting in a different interaction with the intercalated ion that causes the variation in interlamellar distance.

Synthesis of nanocomposites obtained by in situ polymerization of nanosilica with polyamide 6

As presented in previous paragraphs, a series of nanosilicas with 4 different amounts of grafted amino silane have been prepared. The study on nanocomposite materials consists in the synthesis of 3 materials containing 1 2 and 5% of each nanosilica, according to the following table:

Polymer	Amount of Nanosilica (%)				
	Pure	2% NH₂	7,5% NH₂	15% NH₂	35%NH₂
Nylon 6					
1%N	1				
2%N	2				
5%N	5				
1%N-2NH ₂		1			
2%N-2NH ₂		2			
5%N-2NH ₂		5			
1%N-7,5NH ₂			1		
2%N-7,5NH ₂			2		
5%N-7,5NH ₂			5		
1%N-15NH ₂				1	
2%N-15NH ₂				2	
5%N-15NH ₂				5	
1%N-35NH ₂					1
2%N-35NH ₂					2
5%N-35NH ₂					5

Table 33: Nanocomposites synthesized in presence of Nanosilica

In the following pages results obtained in the presented materials will be explained.

The DSC of nanocomposites containing nanosilica

In chapter 9 the effect of the insertion of extraneous elements in the macromolecular chain has been presented. In this case effects obtained on the crystallinity of the material through the insertion of a nanofiller are investigated.

As example in the following figure are reported curves obtained by DSC analysis of nanocomposites obtained by the insertion of 1 2 and 5% of pure nanosilica, values of T_m and ΔH_m are evidenced in the table:

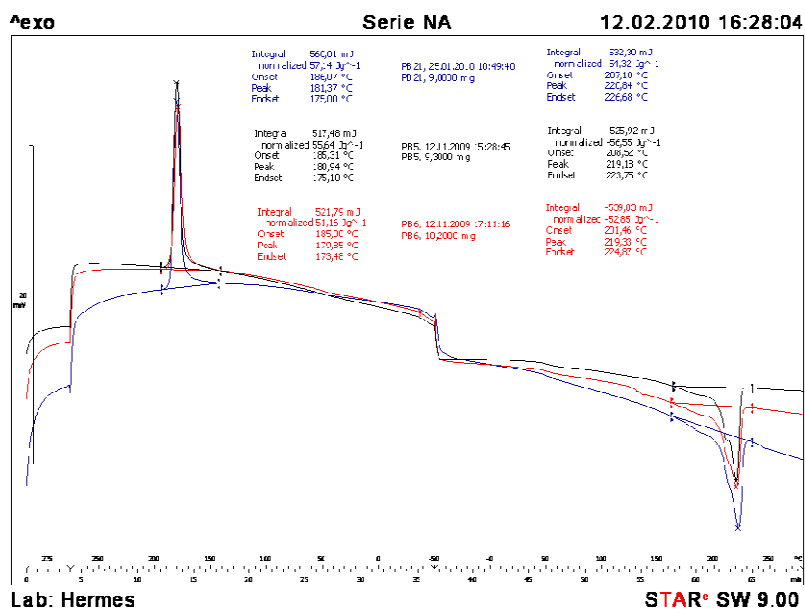


Figure 84: DSC curves of nanocomposited containing pure nanosilica

Polymer	T_m (°C)	ΔH_m (J/g)
PA 6 STD	219.0	-48.9
1% N	220.8	-54.3
2% N	219.2	-56.6
5% N	219.3	-52.8

Table 34: DSC data on nanocomposites containing pure nanosilica

As evidenced by reported data, the nanofiller works as nucleating agent, because all the composites materials have a value of enthalpy of fusion higher than pure PA 6. Moreover the presence of the external agent doesn't disturb the crystallization process; T_m is the same for pure PA 6 and the composites.

SEC analysis of composites containing nanosilica

SEC analysis of a nanocomposite material is a very delicate analysis. The insertion in a column of the filler, even if dispersed at nanometric level, can compromise the chromatographic apparatus, because it is a sort of filtration under pressure of a material than can organize itself in aggregates able to obstruct the pores of the silica gel.

Analysis have been performed on samples dissolved in the chromatographic mobile phase, and previously filtered with filters having pore dimension of 0,25 μ m diameter; this step permits to avoid problems for the columns but can exclude some species by the detection, because a fraction of the polymer, bonded to the filler can remain on the filter and consequently not analyzed.

The SEC analysis of these materials evidences 3 main behavior of this class of materials:

1. Nanocomposites materials obtained by in situ polymerization of modified nanosilica present a curve similar than pure PA 6. This data confirms that the presence of the nanosilica doesn't disturb the polymerization process:

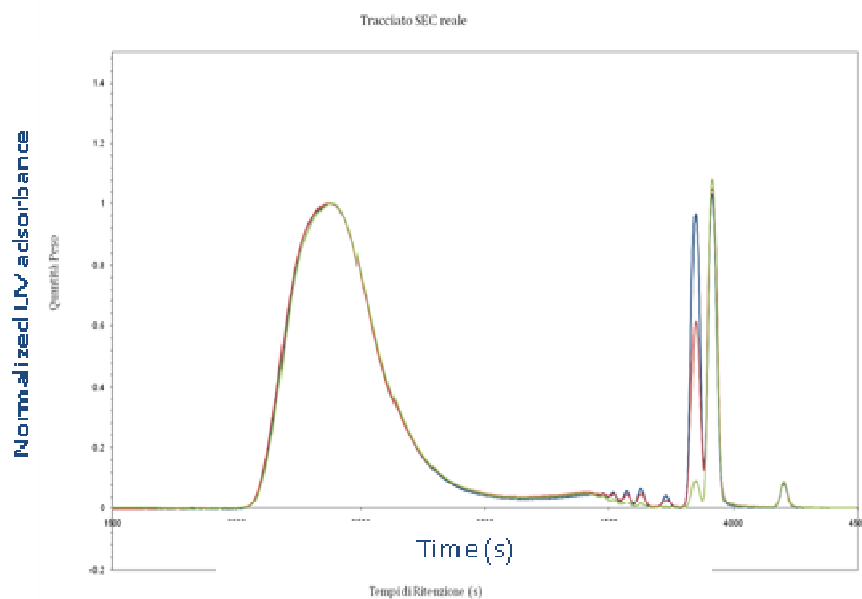


Figure 85: SEC curves of nanocomposites containing pure nanosilica (1 and 2%) compared with pure PA 6

2. The insertion of nanosilica with high amount of grafted silane causes a variation of the shape of the peak, also if the molecular weight is maintained similar to the one of pure PA6. This deformation of the peak can be explained by the interaction between the nanofiller bonded to the macromolecular chain and the chromatographic apparatus:

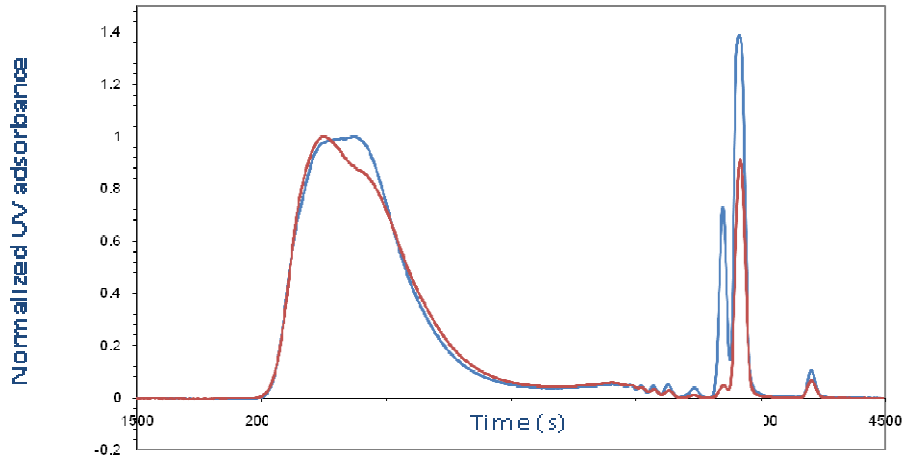


Figure 86: variation in main peak in SEC curves of nanocomposites containing grafted nanosilica compared with pure PA 6

3. In nanocomposite materials obtained with an high amount of nanofiller (5%), higher amounts of monomer and oligomers are detected in the final material. Considering that all materials are subjected to the same washing process, this means that the presence of high amount of nanofillers makes it harder for water to penetrate and so to remove monomer and oligomers. This results can be considered a proof of the improved barrier effect to water permeation of the polymer in presence of an high amount of nanofiller. In the following Figure an example is reported, that shows the presence of the caprolactam peak:

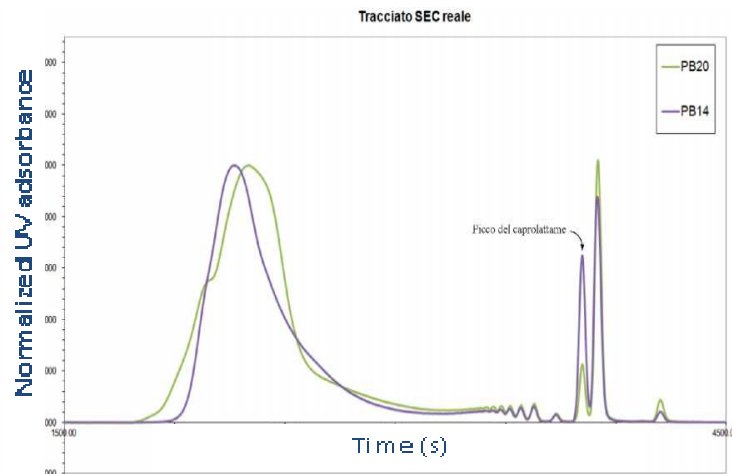


Figure 87: Presence of the peak of caprolactam in polymers with high amount of nanosilica compared with pure PA 6

Rheological properties of nanocomposites materials with nanosilica

Rheological properties of nanocomposites materials have been investigated: in particular the effect of the presence of different amount of silanes have been considered.

Nanocomposites containing 1% of grafted nanosilica

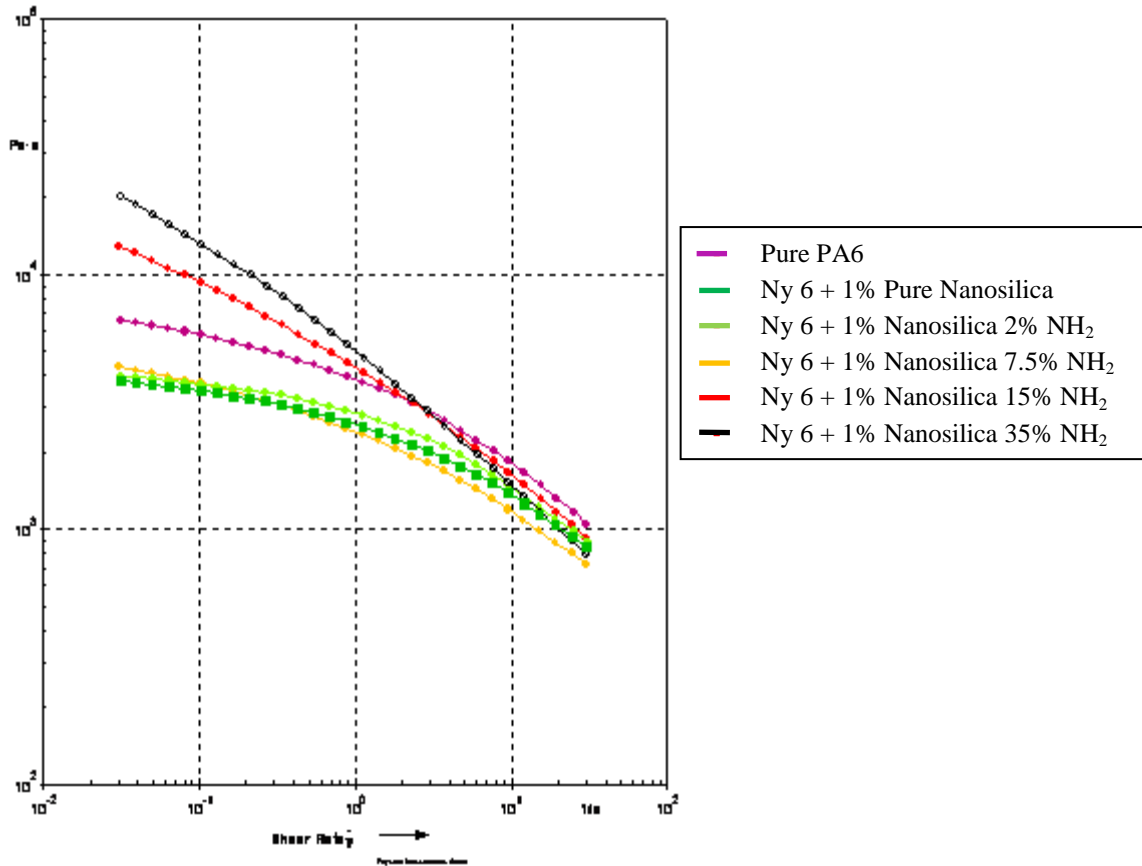
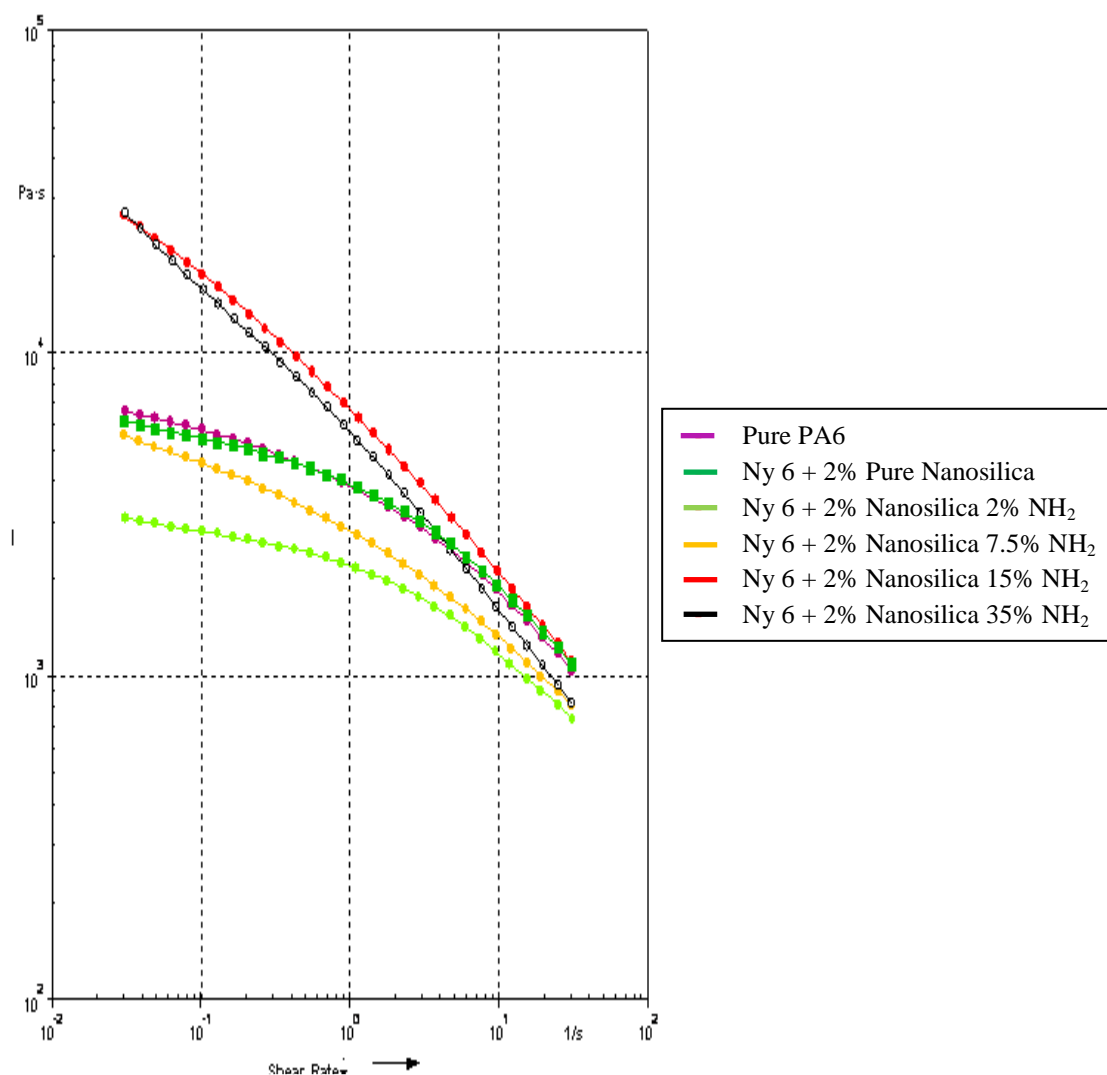


Figure 88: Rheological curves of polymers containing 1% of nanosilica grafted

In the graph the effect obtained in comparison with pure PA 6 (purple curve) is reported. While at high shear rate values, the behavior is similar for all the materials but at low values of shear rate the curve of standard nylon 6 is halfway behavior between the obtained with nanofillers without graft or with low percentages (that have lower viscosity) and the one of nanocomposites with high amount of graft (that have higher viscosity).

Nanocomposites containing 2% of grafted nanosilica



In this case the behavior registered for the previous series is confirmed. The same values of viscosity are measured at high shear rate, while in the left part of the graph, the viscosity increases for nanocomposites with high amounts of graft, and decreases when pure nanofiller, or low amount of graft are present

Nanocomposites containing 5% of grafted nanosilica

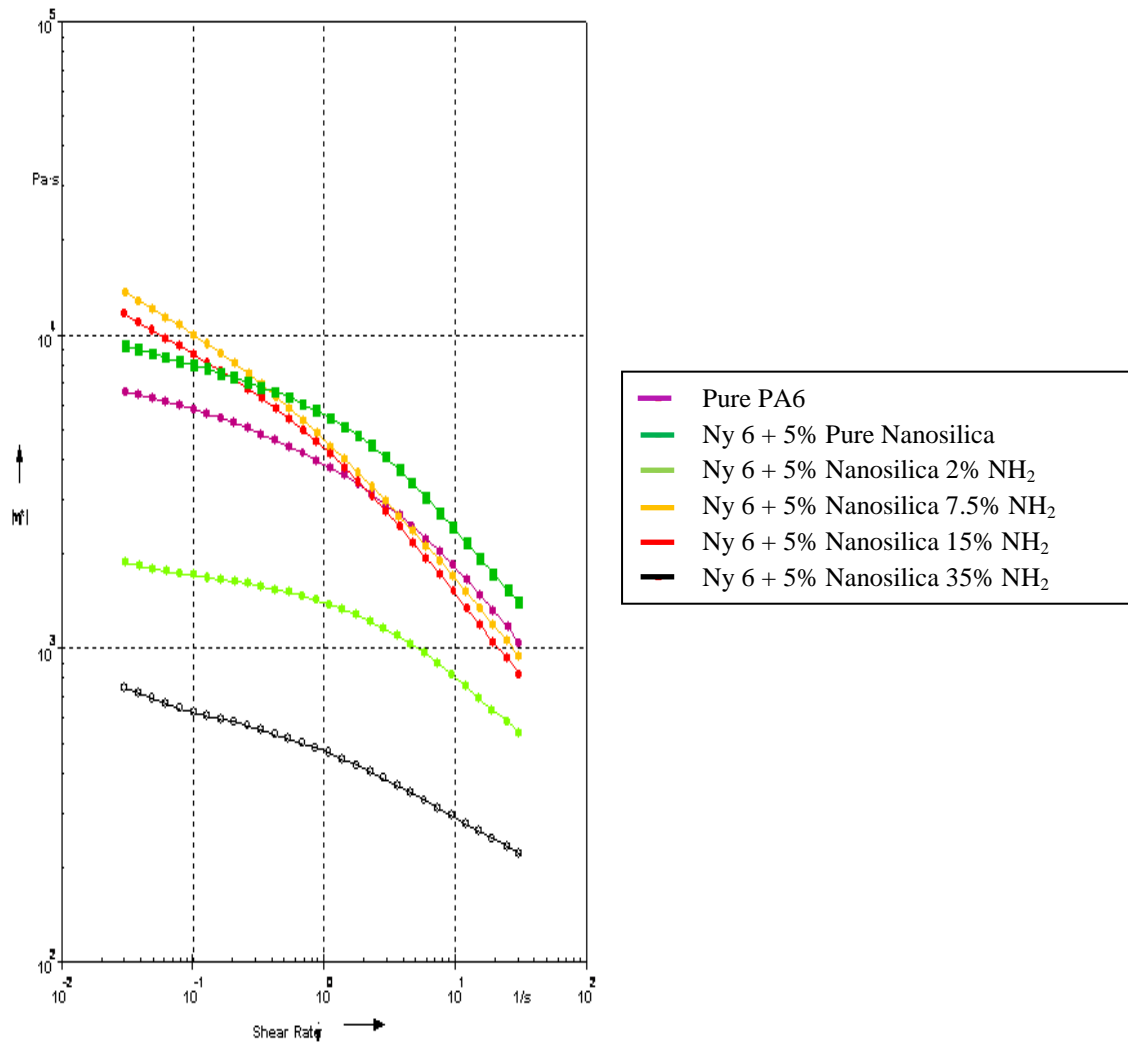


Figure 90: Rheological curves of polymers containing 5% of nanosilica grafted

In this case the high amount of nanofiller inserted causes a peculiar effect in the materials obtained. In particular nanofillers with high amount of graft have a viscosity that is much lower than standard PA6. The reason is in the high amount of a species that can work as multifunctional agent, causing the formation of star shaped molecule, that causes a decrease of the melt viscosity, as explained in chapter 9 for other materials.

Synthesis of nanocomposites obtained by in situ polymerization of montmorillonite with polyamide 6

The work on the nanocomposite materials containing modified montmorillonite has been performed synthesizing 3 polymers containing 1, 2 and 5% of each modified nanofiller, as reported in following tables, the first one contains materials obtained with cloisite modified with amino silane:

Polymer	Amount of Montmorillonite (%)				
	Pure	2% NH ₂	7,5% NH ₂	15% NH ₂	35%NH ₂
Nylon 6					
1%C	1				
2%C	2				
5%C	5				
1%C-2NH ₂		1			
2%C-2NH ₂		2			
5%C-2NH ₂		5			
1%C-7,5NH ₂			1		
2%C-7,5NH ₂			2		
5%C-7,5NH ₂			5		
1%C-15NH ₂				1	
2%C-15NH ₂				2	
5%C-15NH ₂				5	
1%C-35NH ₂					1
2%C-35NH ₂					2
5%C-35NH ₂					5

Table 35: Nanocomposites synthesized in presence of Montmorillonite and 3 amino-propyl-silane

The second one contains materials obtained starting from cloisite modified with methyl silane and silane C₁₆ :

Polymer	10% C₁₆	20% C₁₆	20% Me	40%Me
Nylon 6				
1%C-10 C ₁₆	1			
2%C-10 C ₁₆	2			
5%C-10 C ₁₆	5			
1%C-20 C ₁₆		1		
2%C-20 C ₁₆		2		
5%C-20 C ₁₆		5		
1%C-20 Me			1	
2%C-20 Me			2	
5%C-20 Me			5	
1%C-40 Me				1
2%C-40 Me				2
5%C-40 Me				5

Table 36: Nanocomposites synthesized in presence of Monmorillonite and methyl or C₁₆ silane

Through these synthesis both the effect of different grafts and different amount of nanofiller have been investigated.

The analysis on the thermal behavior of nanocomposites through DSC

DSC curves obtained for nanocomposites materials in presence of 1, 2 and 5% of pure Cloisite 15A are reported in the following figure, and data of melt temperature and enthalpy of fusion are evidenced in the table:

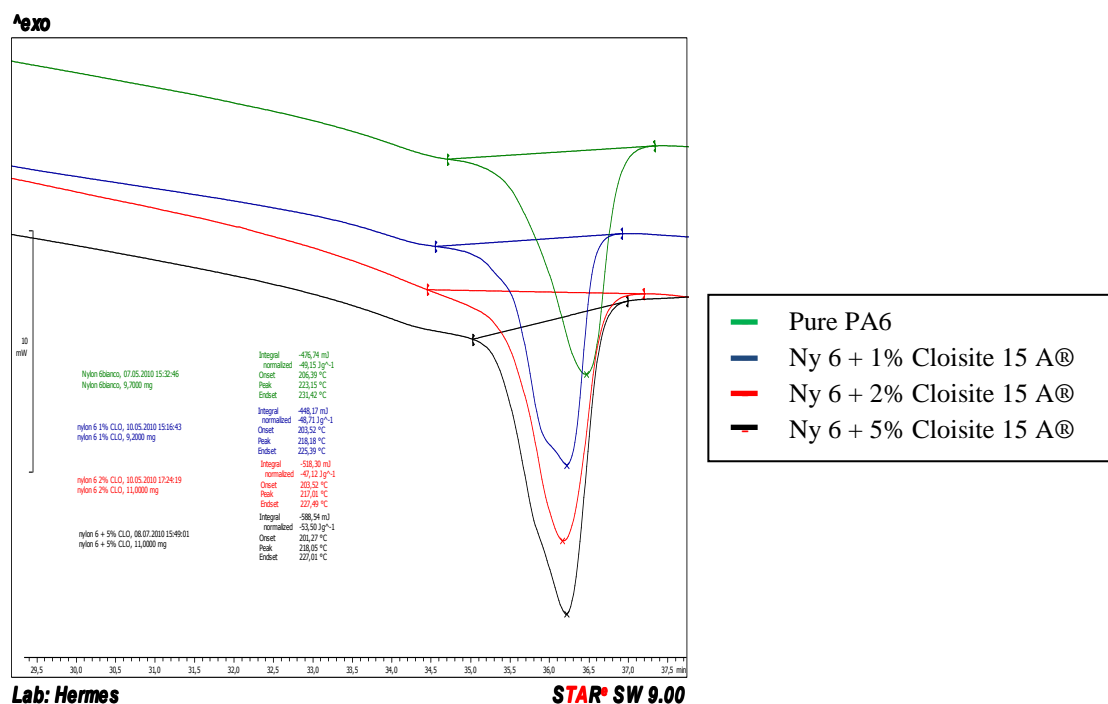


Figure 91: DSC curves of polymers containing pure montmorillonite

Polymer	Tm (°C)	ΔHm (J/g)
PA 6 STD	219.0	-48.9
1% C	218.2	-48.7
2% C	217.0	-47.1
5% C	218.1	-53.5

Table 37: DSC data of nanocomposites obtained with pure montmorillonite

Data show that neither crystallinity amount nor regularity of the lattices is disturbed by the presence of the montmorillonite. Values comparable with the ones of nylon 6 standard are registered for all the melting temperatures; regarding the value of enthalpy

of fusion, only in the case of high amount of montmorillonite (5%) a little improvement is registered.

In the case of the analysis of nanocomposites in presence of high amount of graft a similar behavior is observed; in the following figure and table, curves and data obtained by the DSC analysis of nanocomposites containing montmorillonite modified with 35% of amino silane are reported:

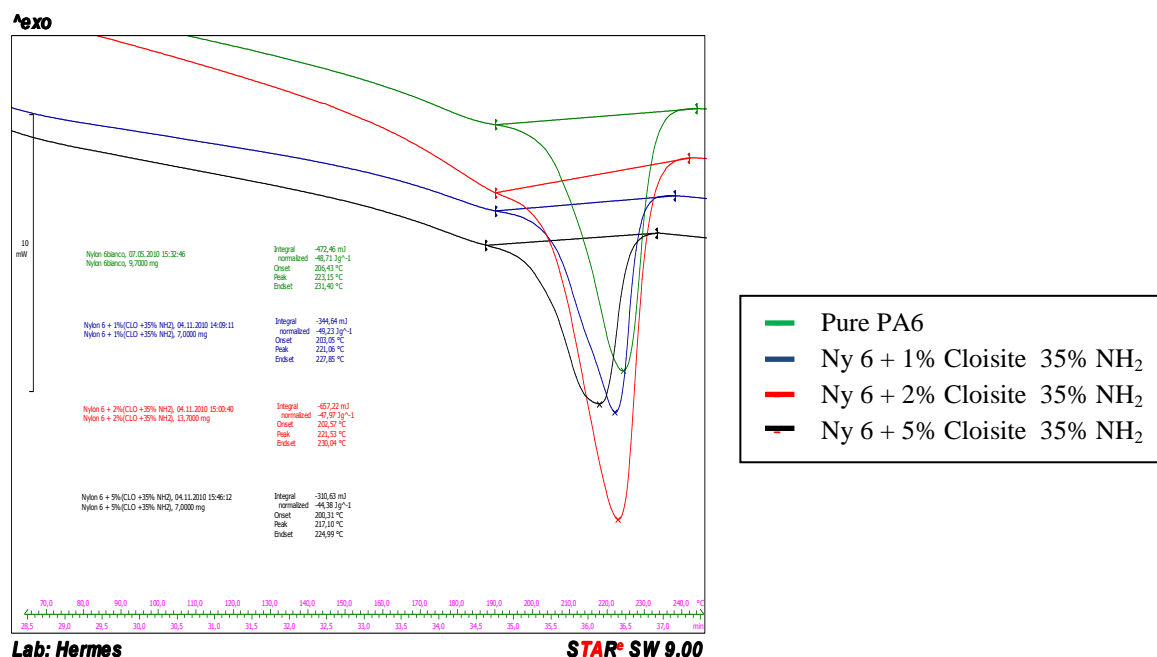


Figure 92: DSC curves of polymers containing modified monmorillonite

Polymer	Tm (°C)	ΔHm (J/g)
PA 6 STD	219.0	-48.9
1% C-35NH ₂	221.0	-49.2
2% C-35NH ₂	221.5	-47.9
5% C-35NH ₂	217.1	-44.4

Table 38: DSC data on nanocomposites obtained in presence of montmorillonite grafted 35% w/w amino silane

Also in this case the modification of the surface doesn't change the crystallization process; similar values of melt temperature and enthalpy of fusion are measured for nanocomposites with 1% and 2% of highly modified montmorillonite. In the case of the use of 5% of montmorillonite an effect of disturb of the crystallization is registered, with a decrease both of the melting temperature and enthalpy of fusion.

Results in SEC analysis of nanocomposites containing montmorillonite

Some of materials synthesized have been analyzed through SEC chromatography, giving values of molecular weight comparable to the ones of pure polyamide 6. In the following figures are reported some examples of curves obtained in presence of 2% of cloisite with different amount of graft in comparison with the one of pure nylon 6:

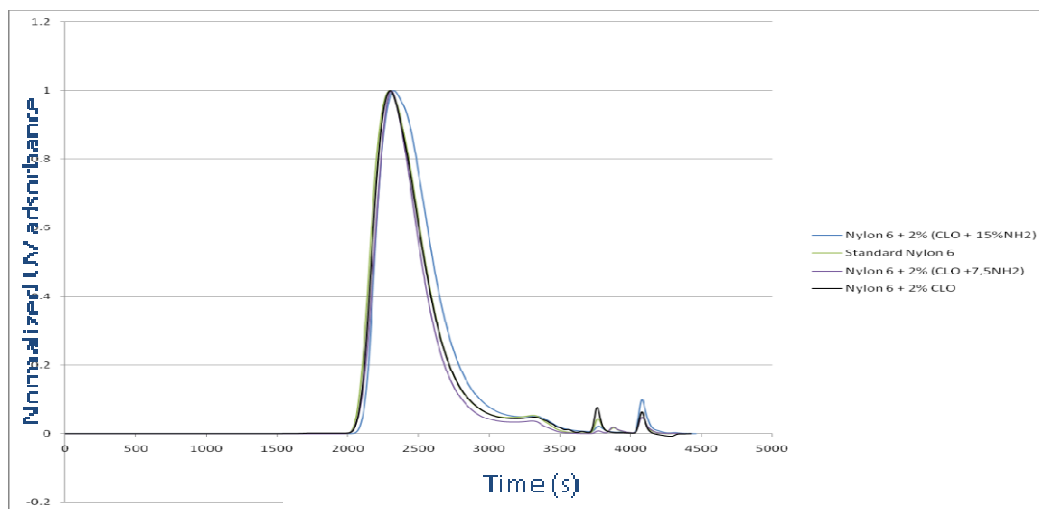


Figure 93: SEC curves of polymers containing 2% of modified montmorillonite compared with PA6

The result obtained shows that the presence of the mineral nanofiller doesn't disturb the polymerization process. Unfortunately an interference during the analysis between the chromatographic apparatus and some of the nanocomposite materials was observed, resulting in an increase of the column pressure

A manual filtration of the samples has been tried but without success and therefore the series of analysis has not been completed.

Rheological analysis on nanocomposites containing montmorillonites

Amino silane grafted montmorillonites

In the following graphs are reported curves obtained from the rheological analysis of nanocomposites containing the same amount of differently modified montmorillonites.

Nanocomposites with 1% of montmorillonite

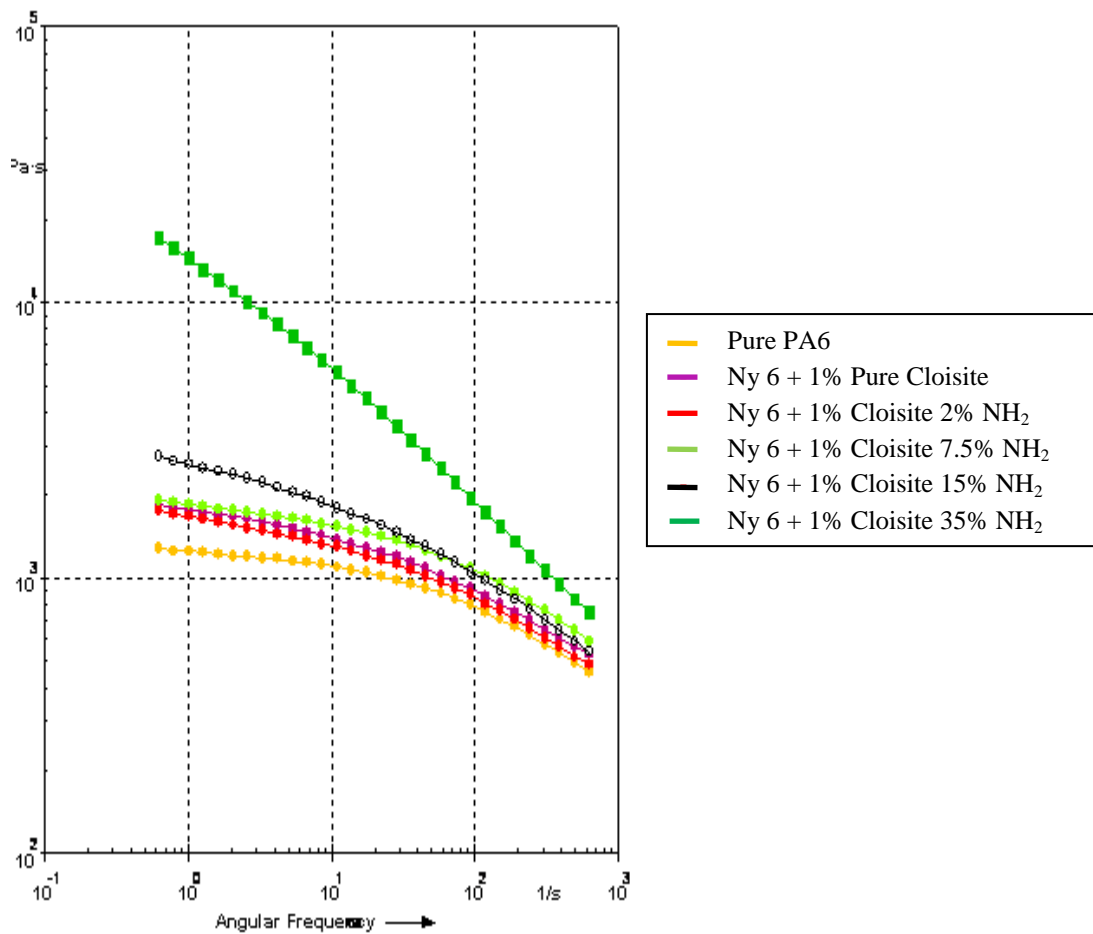


Figure 94: Rheological curves of nanocomposites in presence of 1% montmorillonite grafted with amino silane

In this series the behavior observed is an increase of the viscosity (in particular at high shear rate value) in increasing the amount of amino silane present on the nanoparticle surface. The better interaction between nanofiller and matrix causes an higher dragging effect and therefore an higher resistance to the shear.

Nanocomposites with 2% of montmorillonite

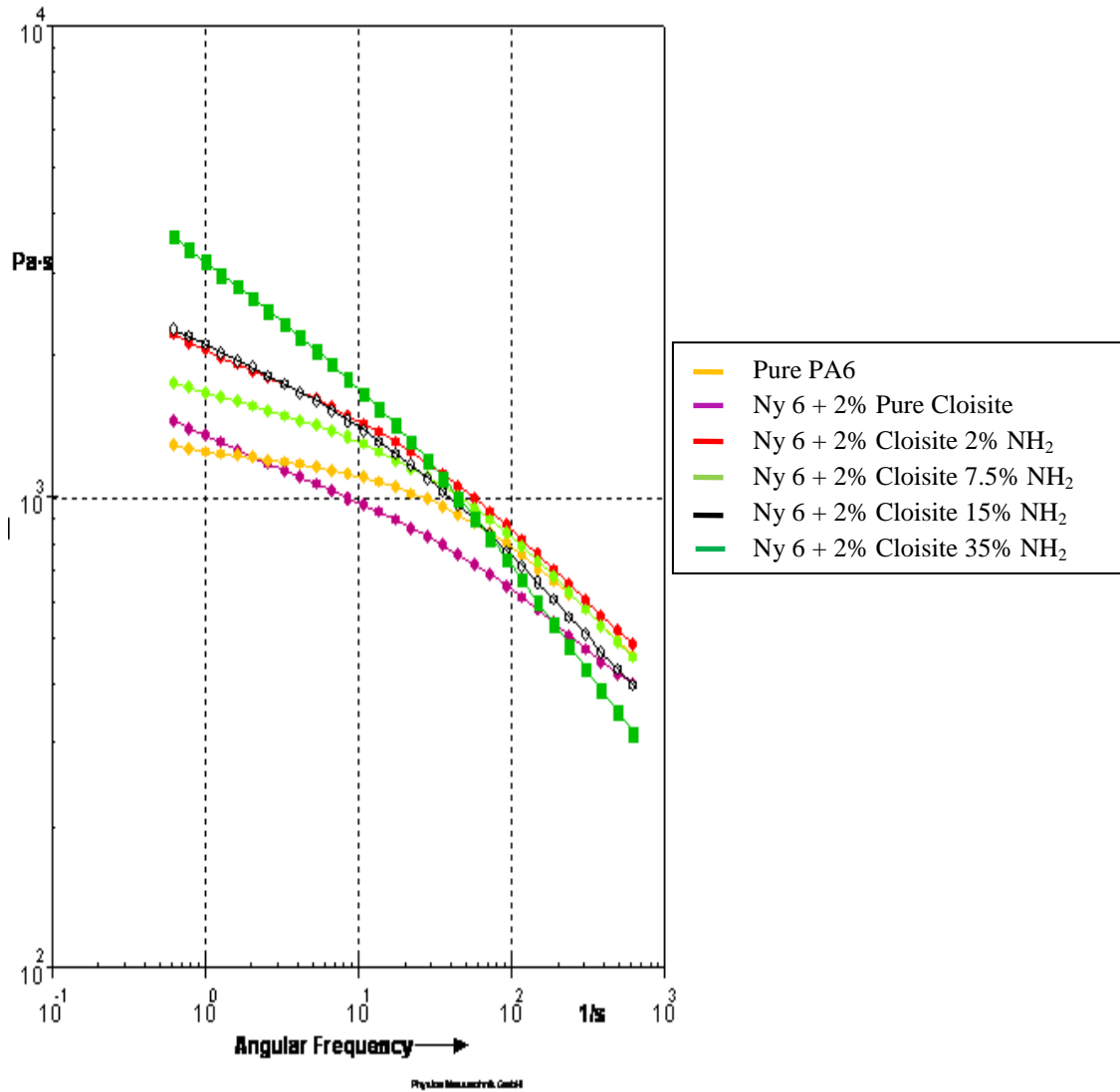


Figure 95: Rheological curves of nanocomposites in presence of 2% montmorillonite grafted with amino silane

The behavior registered is the same of the previous series. The material tends to an increase of the viscosity when increasing the amount of the graft and, while the tendency of pure nylon 6 is to reach a plateau at low values of shear rate, in presence of the nanofiller this tendency change and the effect is the higher, the higher the amount of the graft.

Nanocomposites with 5% of montmorillonite

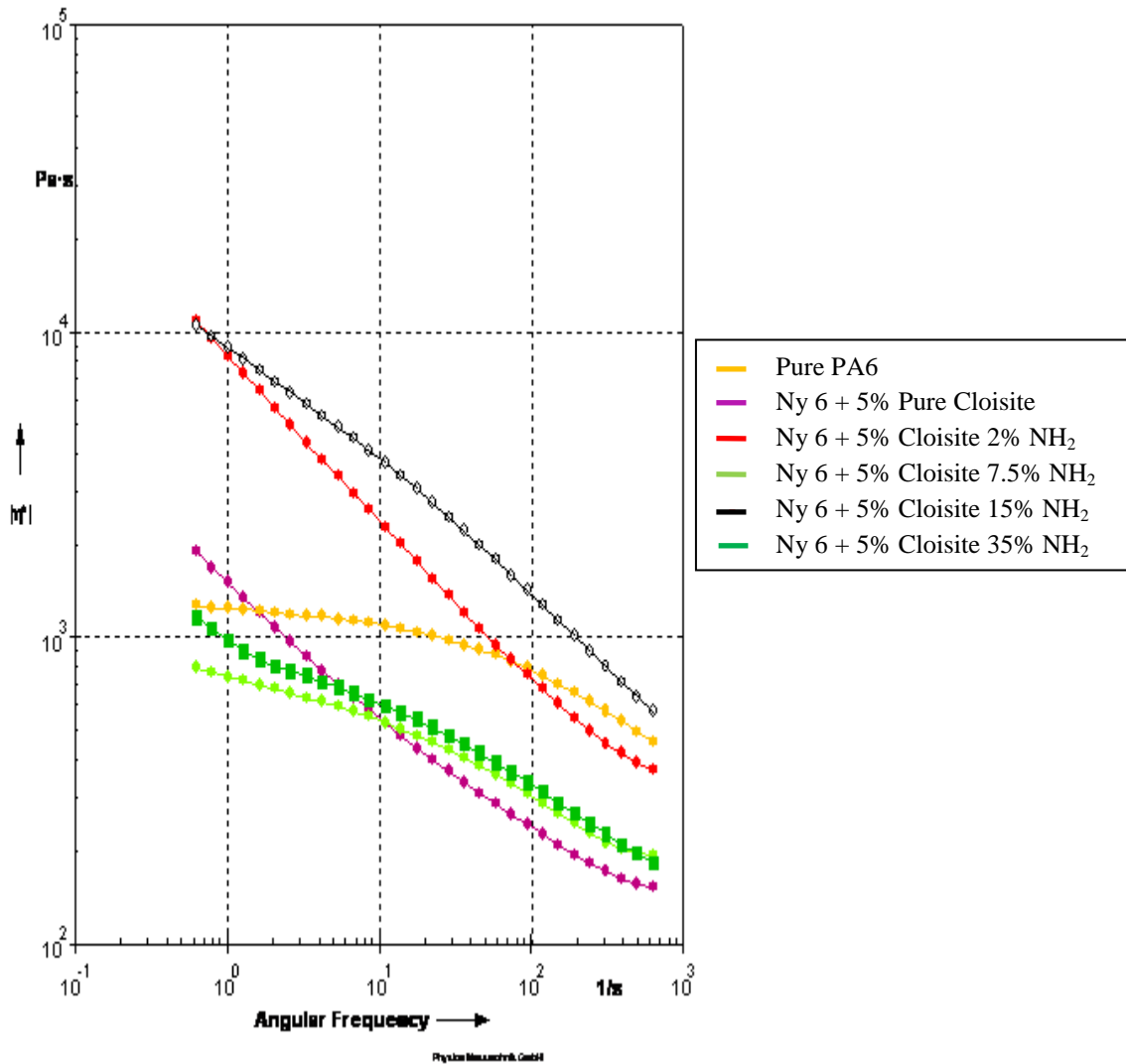


Figure 96: Rheological curves of nanocomposites in presence of 5% montmorillonite grafted with amino silane

In this case the high amount of nanofiller inserted causes rheological properties that are very different for all nanocomposites in comparison with pure PA 6. The average viscosity for all the series is lower than in the case of previous series. The polymer with higher amount of graft has the lowest viscosity, meaning that an effect of star shaping of the molecule happens, with the consequent decrease of the viscosity value.

Methyl silane grafted montmorillonites

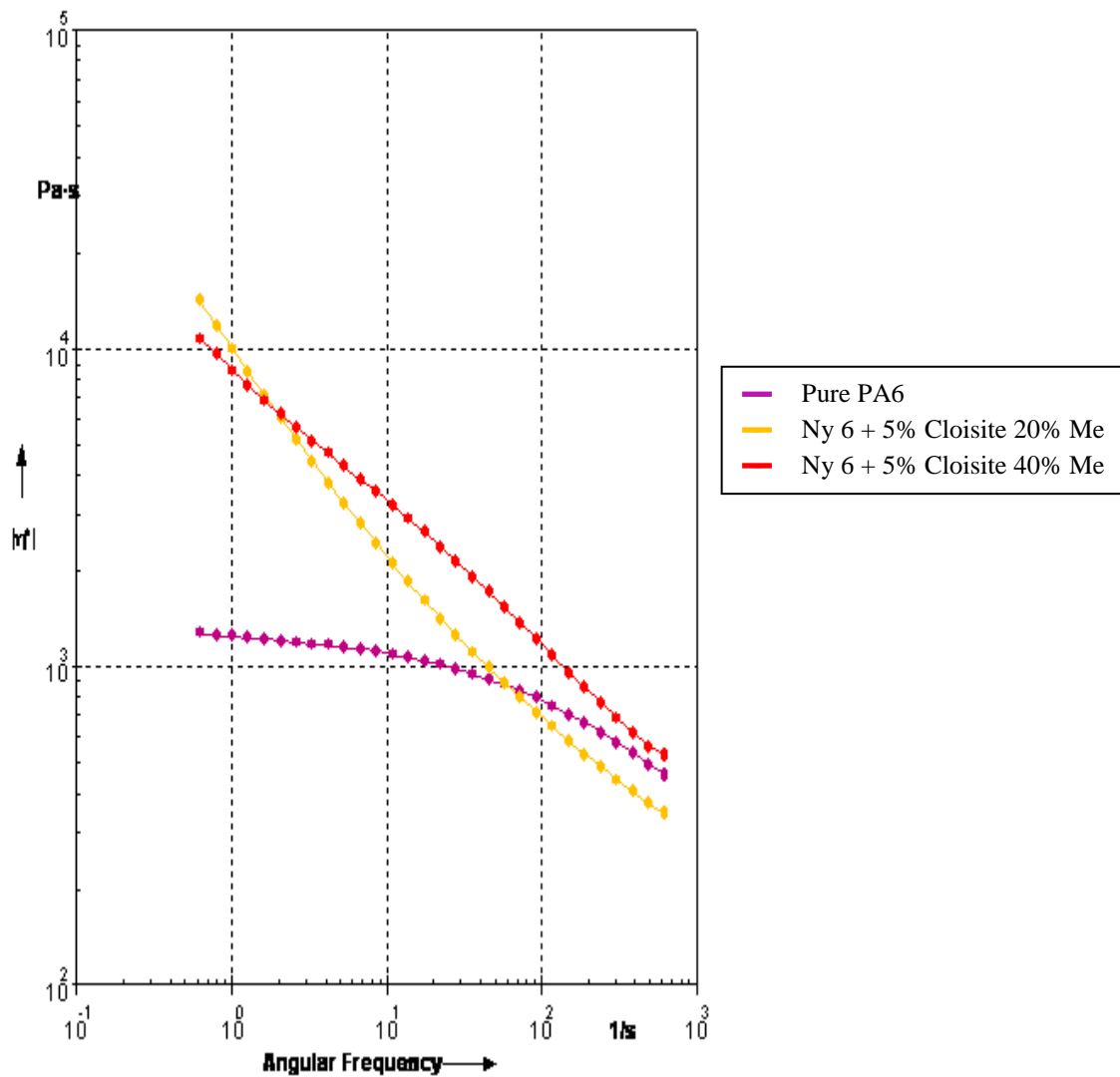


Figure 97: Rheological curves of nanocomposites in presence of montmorillonite grafted with methyl silane

In the case of the graft with methyl silane no difference as registered in comparison with pure montmorillonite, both in nanocomposites with 1 2 and 5% of nanofiller inserted. The low amount of organic matter inserted with the use of this silane doesn't cause sensible variations in the rheological behavior.

C₁₆ silane grafted montmorillonites

Nanocomposites with 1% and 2% of montmorillonite

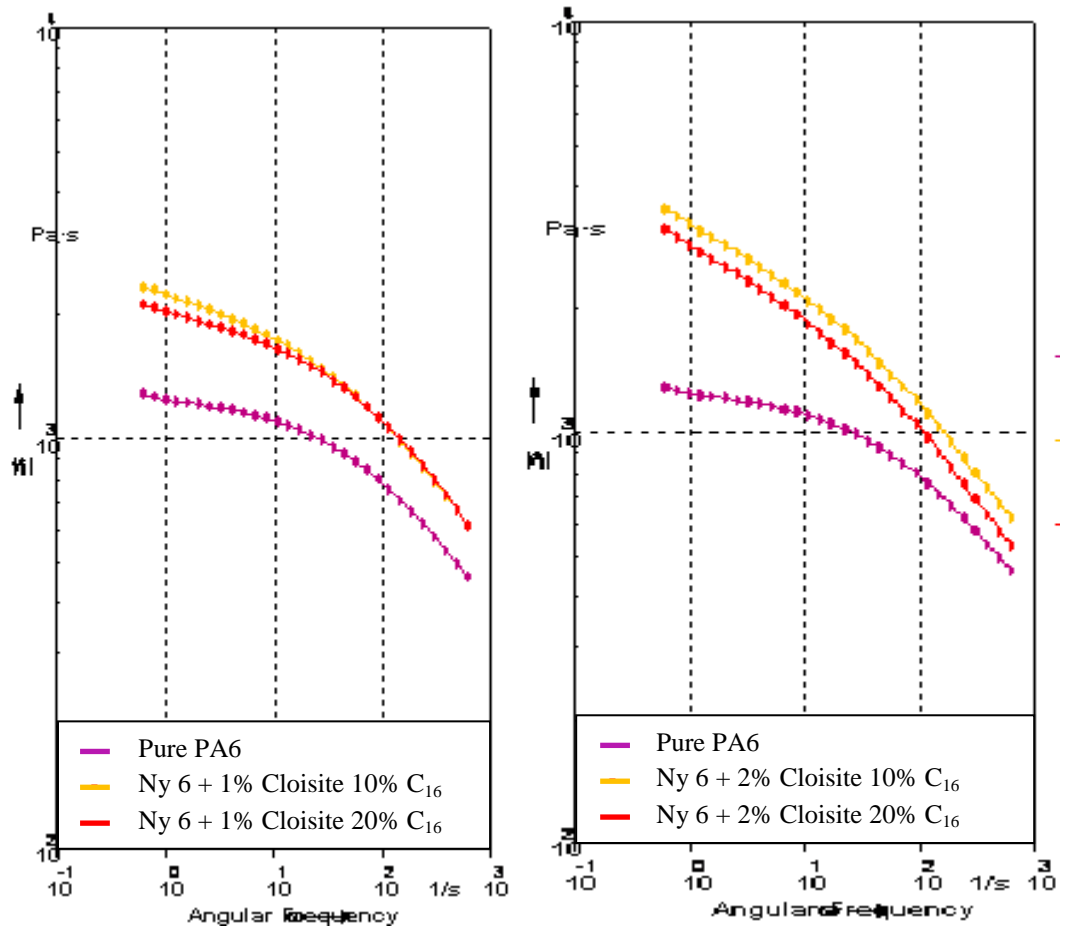


Figure 98: Rheological curves of nanocomposites in presence of montmorillonite grafted with 1 and 2% of C₁₆ silane

The presence of the silane doesn't influence the behavior of the nanocomposites, also changing the graft amount. Even if this silane leads an high amount of organic matter, there is no appreciable result in observing the rheological property of the final nanocomposite.

Nanocomposites with 5% of montmorillonite

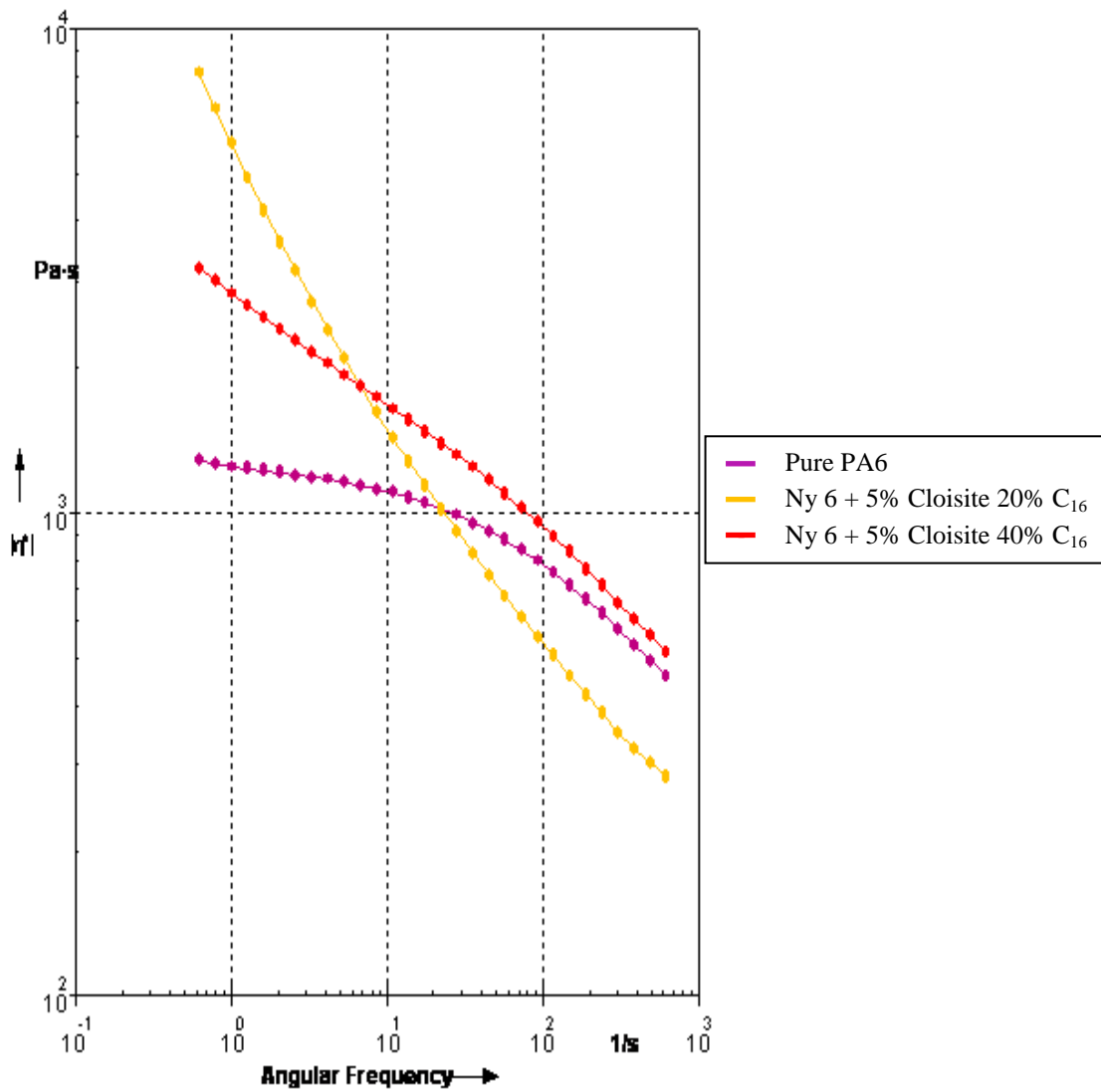


Figure 99: Rheological curves of nanocomposites in presence of montmorillonite grafted with 5% of C₁₆ silane

In this series the montmorillonite with the lower amount of C₁₆ silane gives results similar to the pure montmorillonite, while in the case of the graft with higher amount of silane, a different trend is observed, since there is a decrease of the value of viscosity similar to the one obtained with the graft with high amount of amino silane.

Conclusions:

In this chapter the preparation of nanofillers with surface modification has been investigated; regarding the effect of these modification on the filler, the main results are:

- in the case of nanosilica, the presence of the graft prevents the high water adsorption, typical of this filler (up to 12% w/w).
- In the case of montmorillonite, the use of amino silane for the grafting process causes an increase of water adsorption, while methyl silane and C₁₆ silane lower it.
- When montmorillonite is used, the presence of the graft reduces the degradation of the intercalated ammonium ion; the higher is the amount of graft present, the higher the decomposition temperature.
- XRD analysis of grafted montmorillonite shows a loss of regularity in the lattices of the filler in comparison with the non-grafted one; this effect is increased by increasing the amount and the molecular weight of silane. The loss of regularity is caused by the insertion of the silane on the surface of the filler and between two lamellae, disturbing the interaction between them, and allowing a better separation.

Regarding the results in nanocomposite materials:

- Both in the case of montmorillonite and nanosilica the crystallization process of the polymer is not disturbed or enhanced by the presence of the filler.
- SEC analysis shows that molecular weight is not affected by nanofillers; but their presence causes problems to the chromatographic apparatus: the preventive filtration operated is not efficient, and the integrity of the is not guaranteed when analyzing these materials.

About the rheological properties in presence of nanosilica:

- In the case of 1% and 2% w/w of nanosilica, the presence of the pure nanosilica or nanosilica with low amount of graft causes a lowering of melt viscosity at high value of shear rate in comparison with standard PA6, since the presence of a spherical nanofiller not bonded with the polymeric matrix causes a better flow of melt macromolecules, and decreases the viscosity. When an high amount of graft is present, the viscosity increases at high value of shear rate: this phenomenon is caused by the presence of a chemical bond between the filler and the matrix that is strong enough to drag the filler during the rheological analysis, causing the increase of the viscosity.
- In the case of 5% of nanosilica there is a decrease of the viscosity at high values of shear rate, that is clear in the case of grafting with high amount of silane. In this case the effect of a star shaped molecule is registered where surface modified nanofillers are considerable as multifunctional agents.

About the rheological properties in presence of montmorillonite:

- In the case of low amounts of montmorillonite (1 or 2%) , rheological properties of nanocomposites are in all cases higher than pure nanosilica. The effect of the graft is an increase of the viscosity proportional to the inserted graft: its presence allows the formation of a chemical bond between the matrix and the filler, increasing the viscosity of the material.
- In the case of the insertion of 5% of montmorillonite, the behavior registered is completely different from the one of PA6. Viscosity increases very rapidly when increasing the shear rate both with pure montmorillonite and low grafted ones. The high amount of a lamellar shaped filler causes a great effect of flow resistance to the applied shear, that gives a high viscosity. In the case of high amount of graft, a star shaping effect is obtained: the filler works as multifunctional agent and the viscosity of the material is lower than the other ones.
- Using methyl silane, no effects are evidenced and rheological results are comparable to the ones observed for the pure montmorillonite, considering all percentages of silane inserted and all amounts of graft. This result can be explained by the low dimension of the silane, that is not enough to cover the filler and to have effect on rheological properties.

- Using C₁₆ silane on the filler inserted in 1 and 2% w/w in the nanocomposite, the results is an increase of the viscosity of the material, but the tendencies are the same ones registered for the pure montmorillonite. The cover of the inorganic filler allows a better superficial interaction, but there isn't the effect that is obtainable making a chemical bond as in the case of amino silane.

When the 5% of nanofiller is inserted, when a higher amount of graft is present, a great difference in comparison with pure montmorillonite is observed; the high amount of organic matter that covers the filler permits a better flow of macromolecules and the viscosity is not highly increased as in the case of pure filler.

CHAPTER 11: Evaluation of the thermal stability of polymeric materials coupled with IR spectroscopy of the degradation products

As explained in chapter 1 thermal degradation in the condensed phase is one of the most important phenomenon influencing the production of volatile products that feed the flame.

The evaluation of thermal stability of the material gives an indication of the behavior of the polymer in conditions similar to the ones obtained immediately before and during the combustion process; however the behavior during the thermal degradation must not be confused with the flame retardancy, because it evaluates only one process of the more complex phenomenon “combustion”.

The thermal degradation of a polymeric material is evaluable through the thermogravimetric analysis (TGA): the analysis measures the loss of weight of the analyzed sample during an increasing of temperature.

The weight of the sample is measured by a microbalance with a precision of 1 μg , while the scansion of temperature can be performed from 25 to 900°C. The analysis is conducted in controlled atmosphere (usually with inert atmosphere or oxidant one).

At the exit of the oven where the thermal degradation occurs, it is possible to connect instruments giving the spectroscopic analysis on volatile products developed; usually they are a mass spectrometer that, giving values on the mass of developed products, allows the comprehension of the degradation mechanism, or the IR spectrometer that analyzing the IR adsorption of volatile products permits to understand their nature.

During this work a TGA coupled with an IR spectrometer has been used. The connection is obtained by a transfer line that carries degradation products to the IR permitting the analysis of IR adsorption in any moment.

The transfer line has an heated cover that maintains the high temperature during the transfer of the volatile products avoiding their condensation or precipitation.

The transfer line has also a suction pump, that collects the fumes emitted with a controlled flux for the transportation to the IR cell: the suction flux is lower than the purge gas flow to permit the collection of degradation products emitted by the furnace without the aspiration of external gases.

Thermal degradation of PA 6

The starting point for the thermal degradation analysis of PA6-based nanocomposites, is the study of the behavior of the pure polymer.

The loss of weigh curve of an industrial PA6 sample is reported in the following figure:

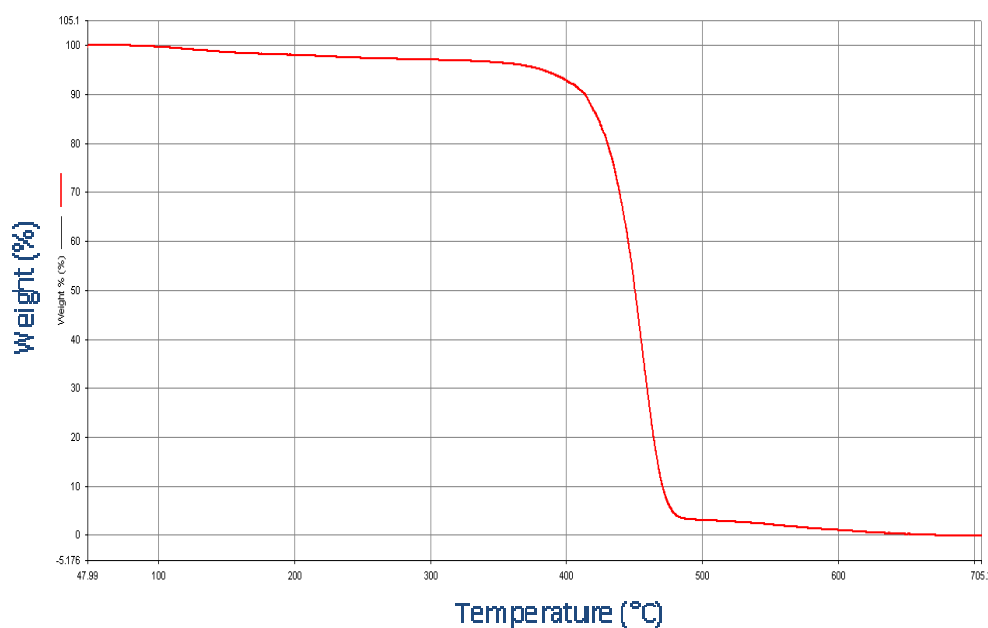


Figure 100: TGA curve of PA6

The thermogravimetric curve presents 2 principal transitions: the first one corresponds to the loss of the adsorbed water while the second one is the loss of weight caused by the thermal degradation of the macromolecular chain:

	Start T (°C)	End T (°C)	Loss of weight (%)
1	100	200	1.6
2	200	500	95.0

Table 39: Degradation phenomena in TGA analysis of pure PA6

The IR spectroscopy of the evolved products confirms the degradation mechanism proposed:

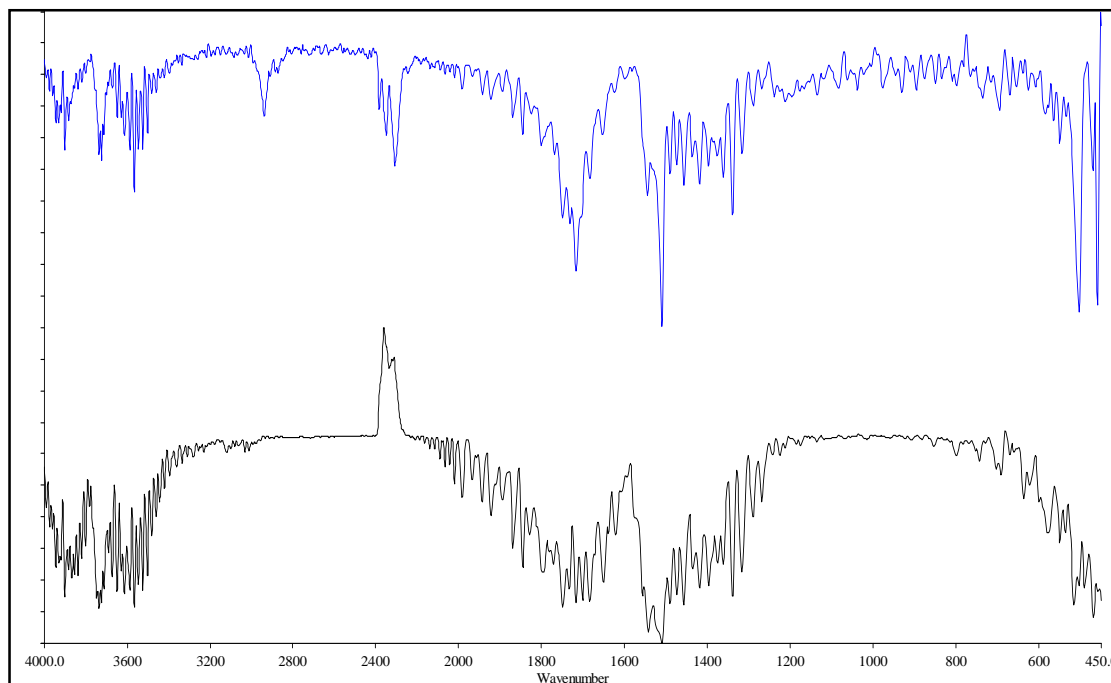


Figure 101: IR spectra of (black) degradation product at 190°C of PA 6 and (blue) water

Analyzing the IR spectrum of the products emitted at 180°C, signals typical of water molecule in gas phase are found: in the figure, blue curve represents the adsorption of pure water, while the black curve the adsorption of the emitted fumes.

In the following figure the IR spectra registered during the second transition is reported:

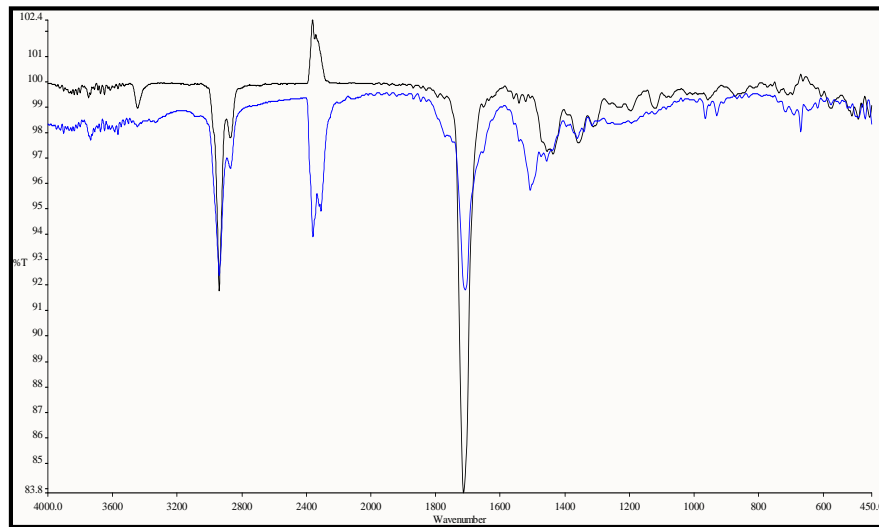


Figure 102: IR spectra of (black) degradation product at 450°C of PA 6 and (blue) aminohexanoic acid

The second transition is the most important phenomenon of loss of weight in this material (it interests the 95% of the total weight); the IR spectrum registered shows that the main product developed is the monomer (in blue is reported the spectrum of pure aminoacid, in black the mixture evolved during the analysis) confirming the unzipping process of degradation of the polyamide.

This mechanism consists in the demolition of the macromolecular chain starting from one of the ends of the chain, losing a single repetitive unit after the other.

Comparison between the thermal behavior of nylon 6 synthesized in our laboratory and the industrial one

Our method of synthesis of standard nylon 6 gives a polymer having molecular weight and rheological properties similar than the industrial one. In the evaluation of the thermal stability of materials synthesized, one of the first step is the comparison between the pure matrix synthesized in our laboratory and the industrial one; in the following figure in blue is reported the thermal degradation of industrial standard PA6, while in red is presented the behavior of the polymer synthesized in our laboratory.

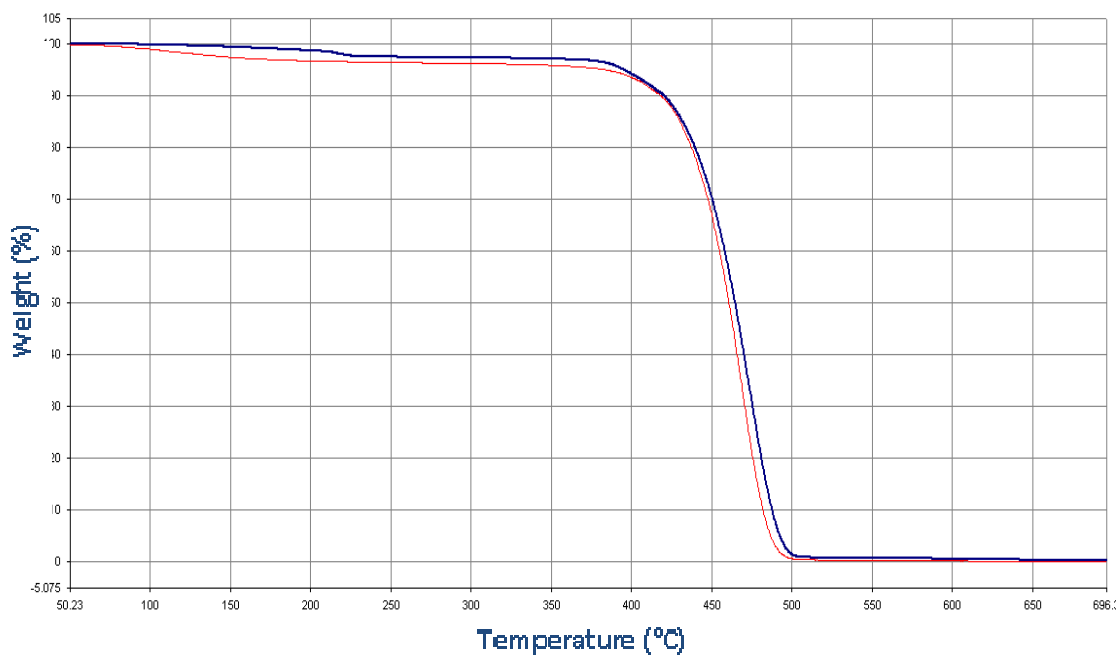


Figure 103: TGA curves of (blue) PA6 from industrial synthesis and (red) PA6 produced in our laboratory

The two behaviors are comparable but the industrial sample presents higher thermal stability, probably due to the insertion of a small amount of stabilizers usually added on all polymers industrially synthesized to prevent degradation phenomena caused by manufacture processes (extrusion, moulding etc..).

Influence of the molecular weight on the thermal degradation of polyamides

Considering that materials synthesized in our laboratory, that will be analyzed by thermal degradation, have an average molecular weight lower than the standard polyamide 6, the evaluation of the effect of molecular weight on the degradation has been investigated

A series of linear nylon 6 with a M_n of 3000, 10000, and 18000 has been analyzed by thermogravimetric analysis; in the following figure the resulting curves are presented (red curve PA6 M_n 3000, green curve PA6 M_n 10000, blue curve PA6 M_n 18000).

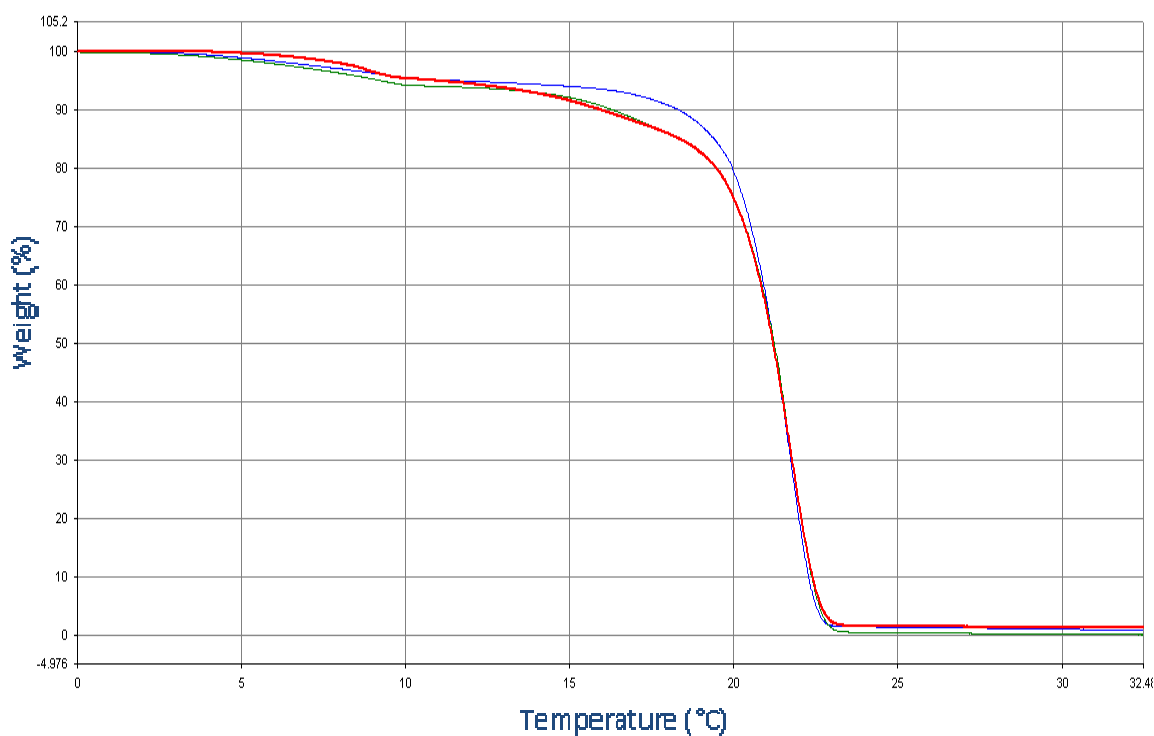


Figure 104: TGA curves of Pas 6 with different molecular weight

The degradation process starts early in the case of polymers with lower molecular weight, but after the beginning of the process, curves are similar for all the tested polymers.

Analysis of industrial flame retarded polyamides 6

In this paragraph two flame retarded polyamides 6 obtained by compounding process have been analyzed:

1. Nylon 6 + 20% of melamine cyanurate, a typical example of NHFR used in polyamide field (blue curve)
2. Nylon 6 + 21% of polybromostyrene (PBS) and the 6% of aluminum trioxide (used as synergic): also this formulation is commonly used

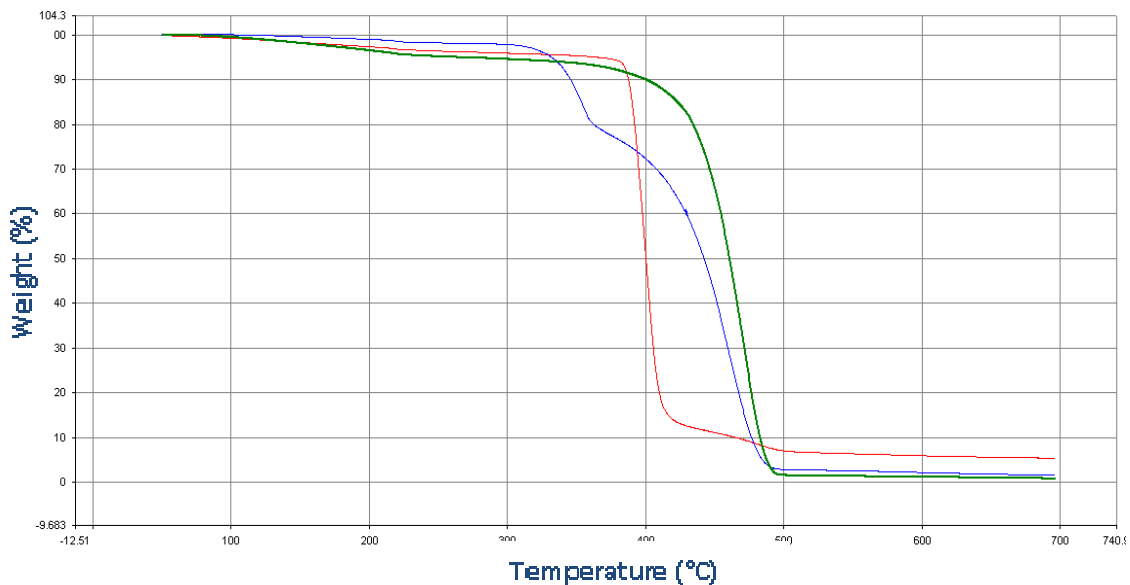


Figure 105: TGA curves of industrial Pas 6 FR

Regarding the matrix mixed with melamine cyanurate a well defined changing of direction is registered in the curve at 360°C that signs the loss of weight of the 20% of the polymeric material.

This loss of weight is related to the loss of molecules of melamine cyanurate, inserted by compounding, without chemical bond to the polymeric material. Its effect is evident on the remaining part of the material that degrades more slowly.

The material modified with brominated flame retardant and synergic has an higher stability to thermal degradation. This thermal degradation occurs at lower temperature and with higher speed than in the case of PA6.

The flame retardant effect is in this case observed only in the last part of the analysis, when the curve change his slope (just before 10% of remaining material). The rate of degradation slows down because of the formation of *char*.

Moreover in the evaluation of the behavior of this material is important to remember that in the case of combustion, the formation of char is coupled with a radical action in gas phase that is very important for the flame retardancy and is not evaluable through the TGA analysis.

Both the materials have a temperature of thermal degradation that is lower than the corresponding pure PA 6, this feature is classical for these kind of materials because the flame retardant, acts before the thermal degradation of the polymeric matrix in which is inserted.

Results obtained through TGA analysis of nanocomposites in presence of nanosilica

All materials obtained through in situ polymerization are been analyzed by TGA analysis in atmosphere with oxygen using temperature scanning between 50 and 700°C at the rate of 20°C/min.

The insertion of the mineral filler slightly increases the thermal stability of the standard PA 6 as shown in the following pictures (red curve correspond to PA 6, while the black curve is relative to the nanocomposite containing 1% of pure nanosilica)

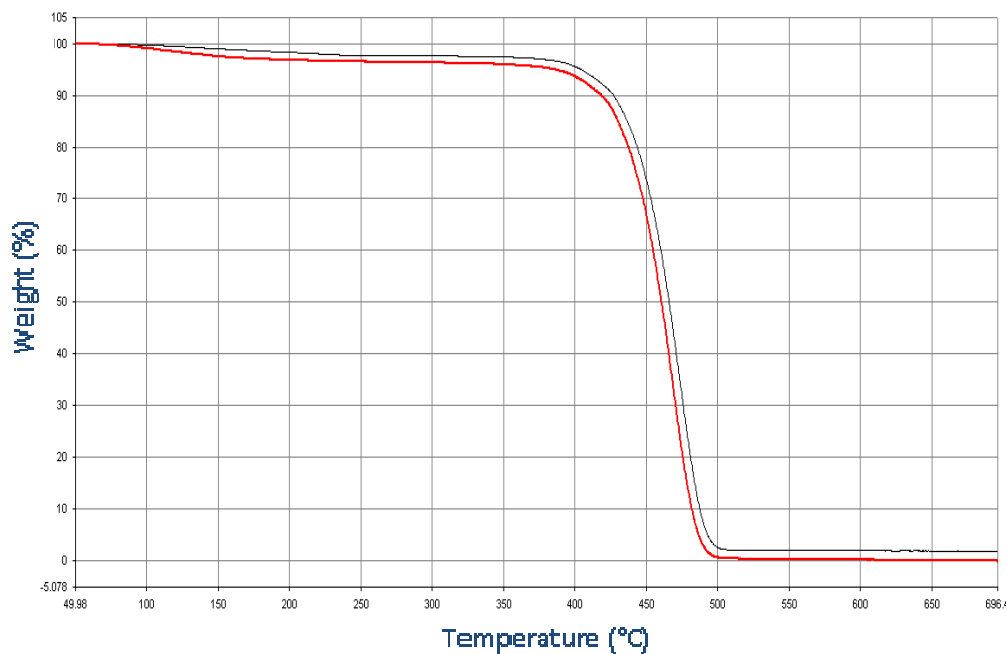


Figure 106: TGA curves of PA6 (red) and 1% nanosilica

The loss of weight at the temperature of 450°C are reported in the following table:

Sample	Residual weight at 450°C (%)
Pure PA 6	67.2
1%N	73.9
1%N 2%NH ₂	69.5
1%N 7.5%NH ₂	68.4
1%N 15%NH ₂	67.1
1%N 35%NH ₂	72.4
2%N	74.2
2%N 2%NH ₂	74.0
2%N 7.5%NH ₂	65.5
2%N 15%NH ₂	72.6
2%N 35%NH ₂	73.0
5%N	68.7
5%N 2%NH ₂	62.7
5%N 7.5%NH ₂	69.1
5%N 15%NH ₂	71.7
5%N 35%NH ₂	73.4

Table 40: Loss of weight data in containing-nanosilica nanocomposites at 450°C

Generally the best values are obtained for nanocomposites containing the 2% of nanosilica both pure and with surface modification. Values are very similar for all the nanocomposites, but some trends are identifiable:

1. When a low amount of nanosilica (1-2%) is inserted, best results are obtained for pure nanosilica or with a low level of surface modification.
2. When an high amount of nanosilica (5%) is inserted the trend is the opposite and best results are obtained with high amount of the graft.
3. Nanocomposites with low amount of graft tend to lose their thermal stability when increasing the amount of nanofiller inserted; if an high amount of graft is present a better result is obtained increasing the amount of nanofiller.

Results obtained through TGA analysis of nanocomposites in presence of montmorillonite

In this case the insertion of pure montmorillonite causes a decrease of the thermal stability, that gets higher, as the amount of filler inserted increases; in the following figure this behavior is evidenced focusing on the zone of loss of weight a 450°C:

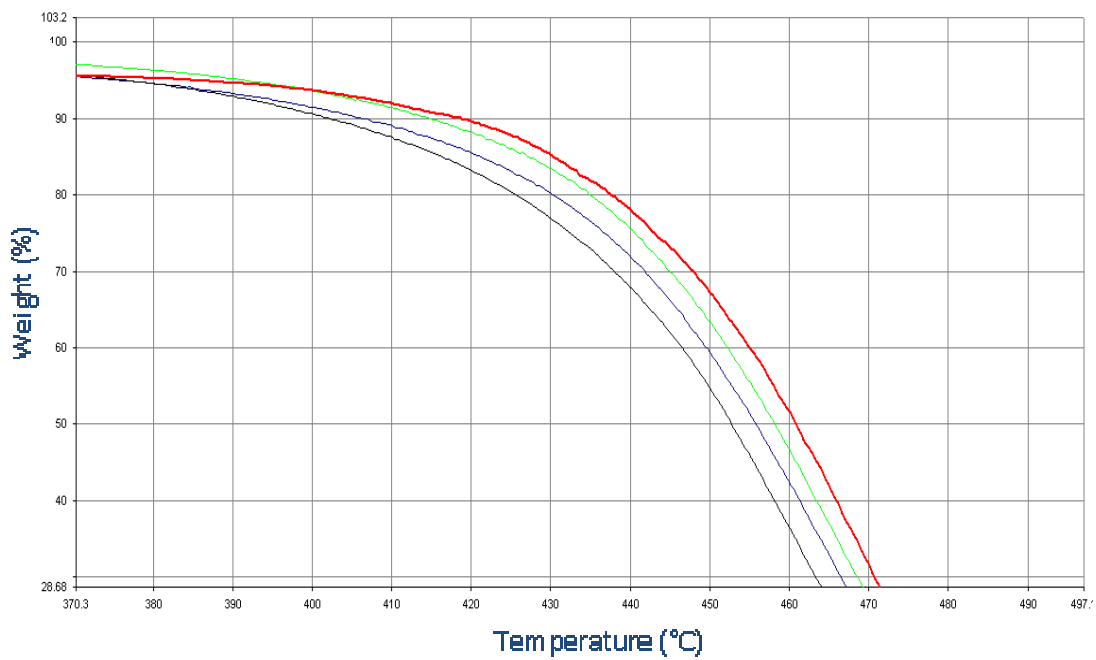


Figure 107: TGA curves of nanocomposites in presence of pure montmorillonite

Red curve correspond to pure PA6, the green one nanocomposite with 1% of montmorillonite, the blue one the 2% and the black one 5%.

All nanocomposites synthesized have been analyzed using TGA, and the values obtained for their loss of weight at 450°C are reported in the following table:

Sample	Residual weight at 450°C (%)
Pure PA 6	67.2
1% C	63.4
1%N C 2%NH ₂	66.3
1%N C 7.5%NH ₂	64.6
1%N C 15%NH ₂	66.8
1%N C 35%NH ₂	69.6
2% C	59.4
2% C 2%NH ₂	63.4
2% C 7.5%NH ₂	60.4
2% C 15%NH ₂	66.4
2% C 35%NH ₂	66.1
5% C	54.8
5% C 2%NH ₂	64.6
5% C 7.5%NH ₂	58.6
5% C 15%NH ₂	65.4
5% C 35%NH ₂	67.0
1% C 20% Me	64.9
1% C 40% Me	68.5
1% C 20% C ₁₆	68.8
2% C 20% Me	56.5
2% C 40% Me	64.4
2% C 20% C ₁₆	66.6
5% C 20% Me	64.9
5% C 40% Me	59.5
5% C 20% C ₁₆	66.7

Table 41: Loss of weight data in containing-montmorillonite nanocomposites at 450°C

From this group of analysis, several data on the effect of the graft on the thermal stability of the final material is observed:

1. The general tendency of loss of thermal stability in the nanocomposite when increasing the amount of nanofiller inserted increases, is maintained also with grafted fillers.
2. The use of a graft able to make a chemical bond with the polymeric matrix (silane) increases the thermal stability of the final material, and this increment is proportional to the amount of graft used. (in the series an exception is the montmorillonite grafted with the 7.5% of amino silane, that gives worst results in all nanocomposites).

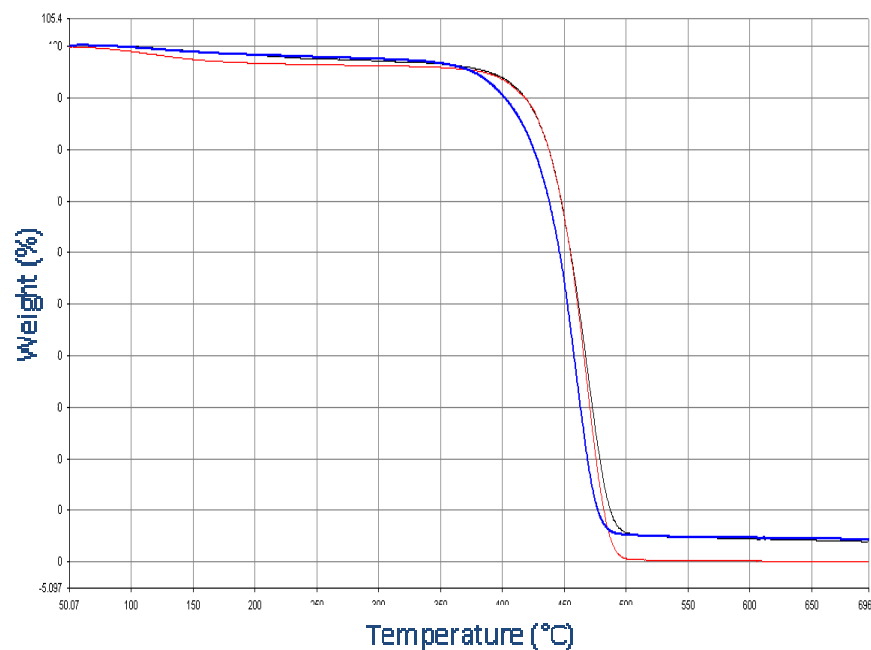


Figure 108: TGA curves of nanocomposites with 5% of pure montmorillonite (blue) and grafted with 35% of amino silane (black) compared with standard PA6 (red)

In the graph the red curve represent the standard PA6, the blue one is the nanocomposite with 5% of pure montmorillonite and the black one is obtained with 5% of montmorillonite grafted 35% NH_2

3. The use of Methyl silane in low amount (20%) gives results similar than the pure montmorillonite. Increasing the amount of methyl silane a better thermal stability is obtained.
4. The behavior when silane C_{16} is present is similar to the one obtained with the high amount of Methyl silane inserted.

**Results obtained through TGA analysis of materials with modified
molecular architecture and CEPP**

Polymers obtained by the copolymerization of the caprolactam with a multifunctional agent, and the ones obtained in presence of the CEPP have been evaluated by TGA.

The results are reported in the following table where the temperature of 90% loss of weight and the 10% one are presented together with the gap between these two temperatures:

Sample	Temperature of the loss of 10% of weight	Temperature of the loss of 90% of weight	ΔT (°C)
PA6	420.7	487.9	67.2
160 HBHT	426.4	488.9	62.5
255 HBHT	427.9	484.6	56.7
460 HBHT	423.8	487.0	63.1
160 POSS	426.9	486.0	59.1
255 POSS	431.3	505.6	72.3
460 POSS	425.0	499.6	74.4
160 HBHT + CEPP	385.3	466.1	80.7
255 HBHT + CEPP	381.7	448.8	67.2
460 HBHT + CEPP	374.3	455.1	80.8
160 POSS + CEPP	391.7	468.1	76.4
255 POSS + CEPP	385.3	469.8	84.4
460 POSS + CEPP	378.1	467.0	88.9

Table 42: Loss of weight data in polymers with modified molecular architecture

The use of inorganic matter highly compatibilized with the polymeric matrix causes an increase of the thermal stability, as shown in the following graph:

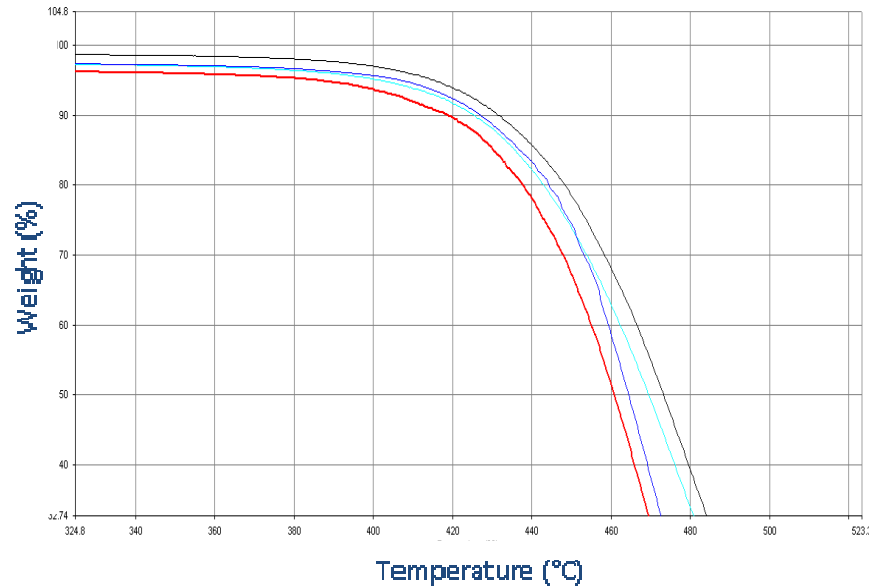


Figure 109: TGA curves of star shaped PA6 obtained with POSS

The presence of CEPP causes the decrease of the thermal degradation temperature; this decrease is higher, when the amount of CEPP inserted is increased; the following figure presents the difference between PA6 (red curve), materials containing CEPP and HBHT (black curves) and materials containing POSS and CEPP (green curves):

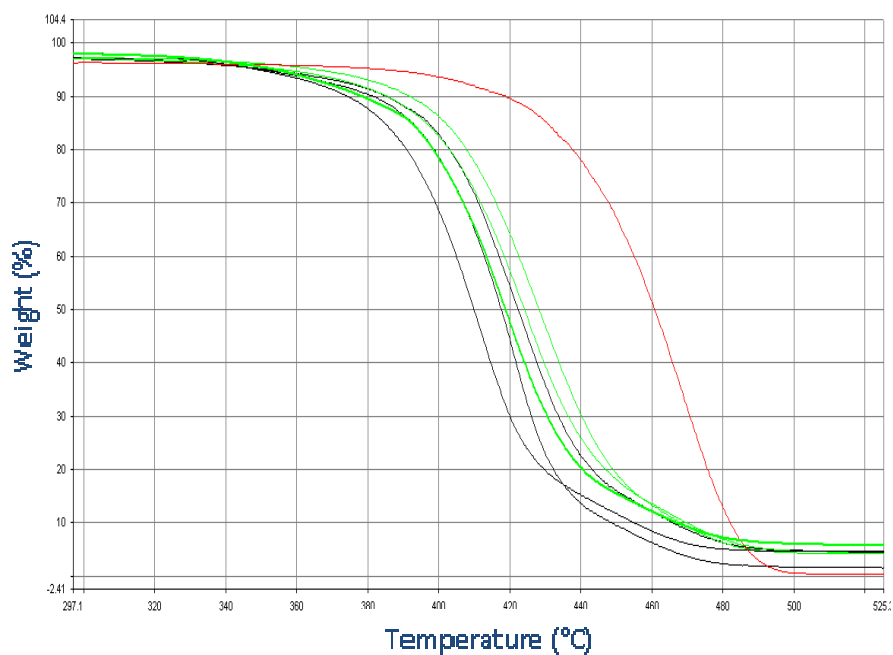


Figure 110: TGA curves of star shaped PA6 obtained with CEPP

Moreover a synergic effect between the inorganic multifunctional agent and CEPP is evidenced, resulting in higher thermal stability than in the case of the use of HBHT as multifunctional agent.

The bond between the CEPP and the material is evidenced in the increase of the temperature of thermal degradation in comparison with the pure molecule; in the following figure the final material curve is the red one, while the blue is relative to pure CEPP:

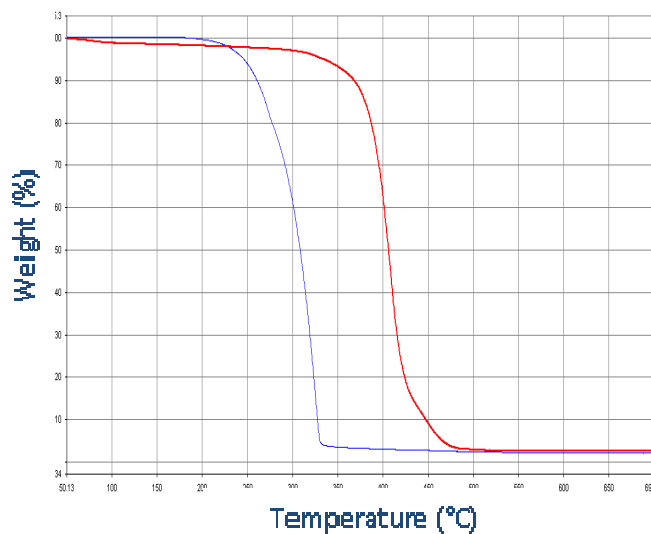


Figure 111: TGA curves of star shaped PA6 obtained with CEPP and pure CEPP

On the contrary, in the case of the addition by compounding process, the thermal properties of the molecule added is the same of the pure one; in the following figure is reported the curve relative at the material obtained by the compounding of melamine cyanurate with nylon 6 (red curve) with the one of pure flame retardant (blue curve)

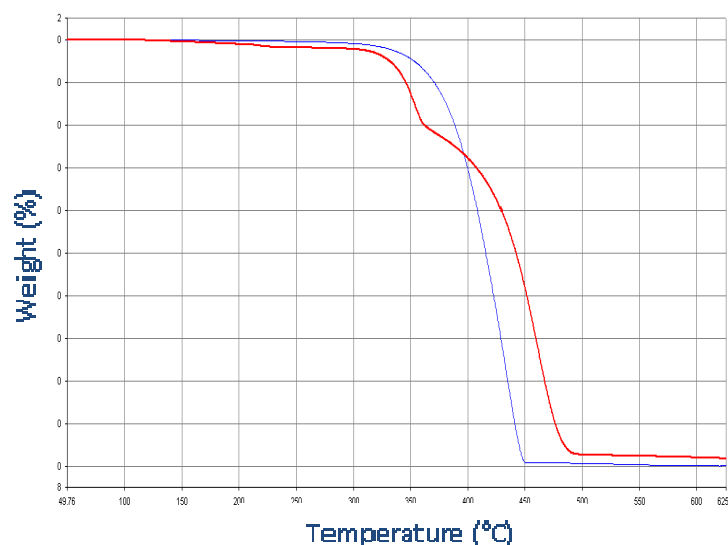


Figure 112: TGA curves of PA6 with 20% of melamine cyanurate and pure FR

Another important aspect is the increase of the temperature range necessary to pass from the 10% of loss of weight to the 90%. This range is increased in the case of the presence of CEPP of an amount of 50%. If 67,2°C are needed to consume the 80% of the pure PA6, in presence of CEPP this range can reach the 88,9°C. This phenomenon is caused by the formation of a char protecting the polymer, that slows down the thermal degradation.

The formation of the residue is confirmed in the final part of the TGA analysis; when CEPP with POSS and HBHT is present, an higher residue is registered; an higher amount matter in the case of CEPP with POSS (green curve) than HBHT (black curve) while in the case of pure PA6 (red curve) all the matter is consumed.

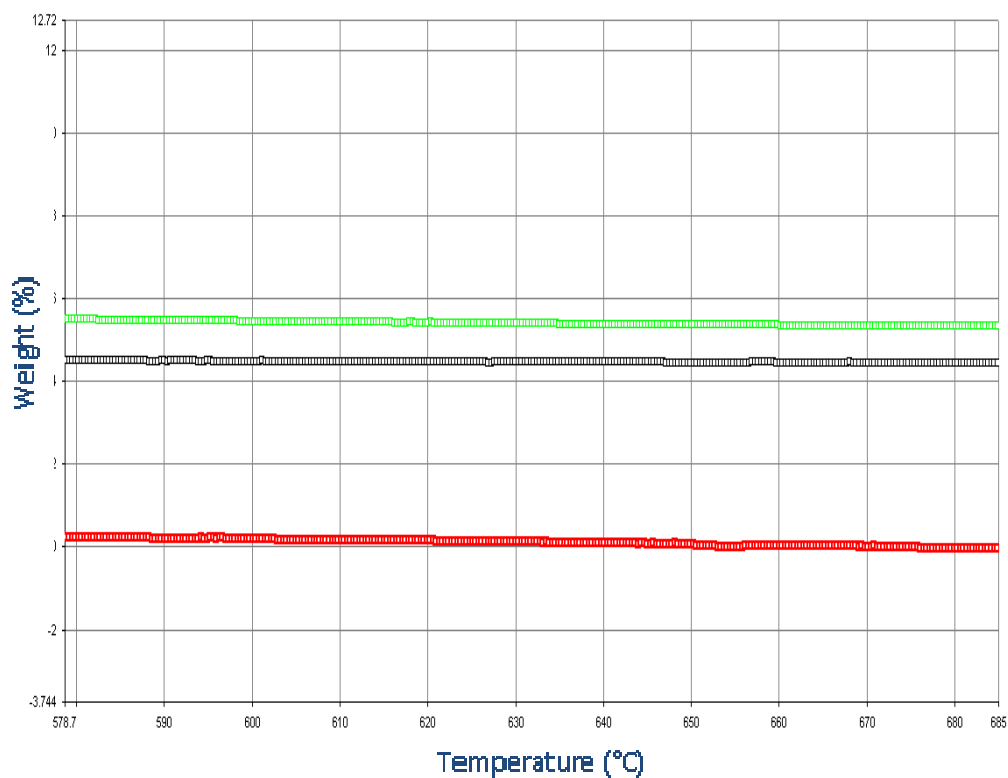


Figure 113: Residual weight of polymers in presence of CEPP at the end of thermal degradation

Cone calorimeter tests on polymers with HBHT and CEPP

The series of materials obtained using HBHT as multifunctional agent and CEPP as monofunctional chain ender has been chosen for a synthesis on large scale 700-1000g to perform the production of sample analyzable by cone calorimeter.

In fact the production of samples for the flame retardant tests needs a minimum amount on the order of few kilograms.

The series has been chosen because of its higher stability and the possibility to predict its behavior during the synthesis (that is not possible in the case of the use of POSS as explained in the chapter 9).

Cone calorimeter has been chosen as flame retardant test: it gives an higher amount of information on the behavior of the material in combustion conditions in comparison with LOI and UL94.

The value reported in literature for the peak of rate of heat release for PA6 is fixed on 2049 kJ/sm^2 for an analysis performed with a heat flux with 50 kW/m^2 ^[33].

In our case the value registered for three materials are:

Sample	PRHR (KJ/sm²)
160 HBHT + CEPP	714
255 HBHT + CEPP	640
460 HBHT + CEPP	638

Table 43: PRHR for polymeric materials containing HBHT and POSS

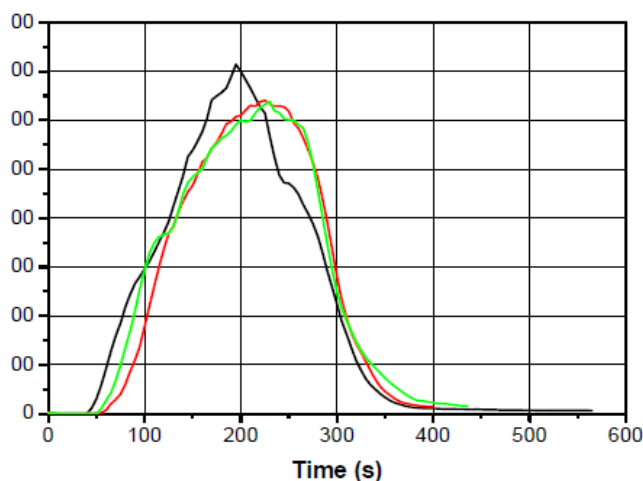


Figure 114: RHR graphic for polymers containing HBHT and CEPP

The result reported shows that the polymers synthesized have a maximum of heat release that is 3 times lower than the standard PA6 confirming the very good results of synthesized polymers.

Moreover the flame retardancy of the materials improved increasing the amount of CEPP inserted:

1. The reported value of PHRH decreases increasing the amount of CEPP inserted
2. Time of peak of heat release and average rate of heat release (ARHR) confirm the higher flame retardancy of the material with higher CEPP content, that ignites later than the other ones and with a lower rate of combustion.

The following table reports the values of peak of heat release and ARHR for our polymers:

Sample	Time of PRHR (s)	ARHR (KJ/sm ²)
160 HBHT + CEPP	146	446
255 HBHT + CEPP	159	437
460 HBHT + CEPP	170	425

Table 44: Time of PRHR and ARHR for polymeric materials containing HBHT and POSS

Conclusions

The complete characterization by thermal degradation analysis of all the synthesized polymers has been performed. Here are presented the conclusions on the results obtained:

- Regarding nanocomposites containing nanosilica, in all the samples the presence of the filler (with the exception of nanocomposite 5%N 2%NH₂) increases the thermal stability of the material. Good results are obtained in the case of insertion of 2% of nanosilica with all amounts of graft and with 5% of nanosilica grafted with high amounts of silane. This result is obtained because an high amount (5%) of non grafted filler (that is not compatible with the organic matter) disturbs the regularity of the material favouring the thermal degradation of the polymer. If an high amount of filler is inserted, an high percentage of graft is needed because the improved compatibility leads to higher thermal stability.
- Regarding nanocomposites containing montmorillonites, the insertion of the pure filler causes a decrease of the thermal stability. This decrease is higher when the amount of filler is increased since the low compatibility between the filler and the matrix, at the inter-phase can be the starting point of the degradation process. When the graft is inserted, thermal stability is improved; if the inter-phase filler/matrix is the starting point of the thermal degradation, a better compatibility between the two elements causes the slowing of the process. The results is further improved when the nanofiller is grafted with a silane that can react with the matrix (in our case amino silane); when the silane cannot react, the better result is obtained increasing the amount of organic molecules covering the filler (C₁₆ silane gives better results than methyl silane, and an higher amount gives better results than a lower amount).

- Regarding polymers containing CEPP, several behaviors are evidenced:
 1. Thermal degradation of polymers containing CEPP occurs at temperature lower in comparison to the pure PA6; this temperature decreases when the amount of CEPP is increased. CEPP is the first molecule to degrade and its degradation affects all the material.
 2. The degradation of polymers containing CEPP doesn't present changes on the slope of the curve and occurs at higher temperature than pure CEPP, meaning a chemical bond of the molecule with the polymeric matrix.
 3. The residual weight obtained when a polymer containing CEPP is burned, shows the effect of char formation, that protects the residual part of the polymer
 4. CEPP degradation acts slowing the degradation of the polymeric material that degrades with lower rate than standard PA6
 5. A synergic effect is registered in there is the presence of both inorganic matter (POSS) and CEPP; in this case all effects of flame retardancy evidenced are improved.

Regarding cone calorimeter tests performed on the series of polymers containing HBHT and CEPP, results obtained show that:

- The peak of rate of heat release is three time lower than standard PA6 in the case of our polymers; flame retardant effect is through this data confirmed.
- The flame retardancy effect of CEPP is confirmed by the increase of the time of ignition when the amount of CEPP increases; the same tendency is obtained for the value of average rate of heat release.

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