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Cyclophosphazenes as Polymer Modifiers

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Summary: The utilization of cyclophosphazenes as polymer modifiers is reviewed, with particular concern to their exploitation as versatile chain extenders, possibly for recycle problems, crosslinkers, to enhance mechanical properties of polymeric materials, branchers, to selectively introduce ramifications in linear polymers, and compatibilizers, to favor the formation of blends between originally incompatible organic macromolecules. The great versatility of the synthetic methods put forward for these substrates, together with the ease of controlling their modification, functionalization and reactivity are important parameters for the evaluation of which type of use is more feasible for these trimers. The importance of cyclophosphazenes bearing organic polymeric chains, azide groups, 2-oxazoline derivatives and oxirane rings in connection with organic conventional macromolecules is critically highlighted.

Keywords: chain-extenders; compatibilizers; cyclophosphazenes; epoxide; 2-oxazoline

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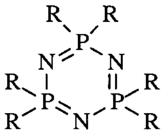
Introduction

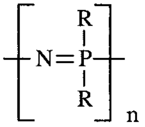
Cyclophosphazenes (CPs) are relevant phosphazene compounds[1-3] having the structure reported below:



FORMULA 1

in which the phosphorus atoms in the cycle bear two substituent groups.

The large majority of cyclophosphazenes are formed by three -P=N- units[4], although less frequent superior cyclic homologues, formed by four[5-7], five[8,9], six [8-11], seven[12], etc., phosphazene units are known. The scientific importance of these products was restricted for long time to act as model compounds for the high molecular weight poly(organophosphazenes) (POPs)[13,14]



$$\left[N=\overset{\displaystyle R}{\underset{\displaystyle R}{P}} \right]_n$$

FORMULA 2

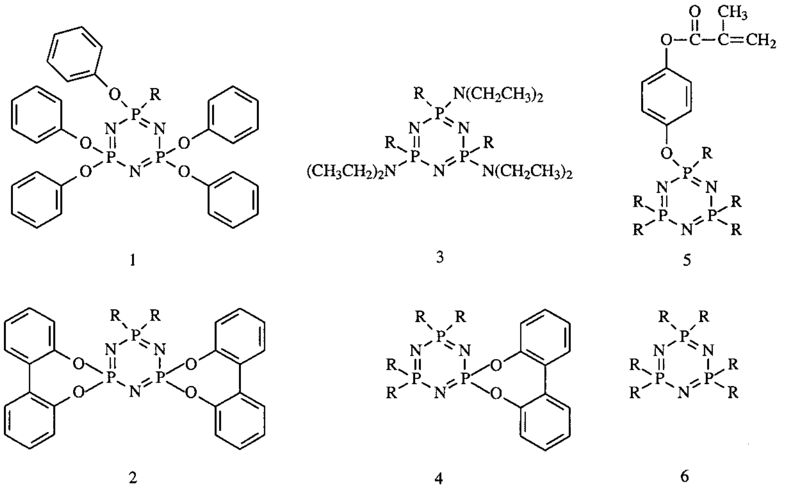
in the sense that research on the chemical reactivity, substitutional kinetics, spectroscopic, photochemical, thermal, biological, etc. properties of these polymers was preliminary carried out at trimeric level, and only subsequently the results obtained were extended to the corresponding macromolecules.

However, it was realized very soon that cyclophosphazenes are very versatile materials, able to cover themselves a large variety of different applications[15]. Thus, they are excellent materials for the preparation of cyclomatrix[4] and cyclolinear[16,17] polymers; biologically important substrates (as antitumors[18-20], pesticides[21], insect chemosterilant[1,2], fertilizers[1,2,22-24]); products that show photochemical (as photoinitiators[25,26], photostabilizers[27-34]), antioxidant[35,36], and flame retardant[2,37] activity, with possibility of forming clathrates[38-40], and high temperature resistant fluids[41,42]. They are also important in supramolecular chemistry[43-48], electric conductivity[46,49], dendrimers[50-52], star polymers[50,53], and ion receptors[54-56].

Among the applications of cyclophosphazenes, the exploitation of these compounds as modifiers for conventional organic macromolecules looks very attractive. For their practical utilization, in fact, organic polymers very often need to be crosslinked, blended, extended, branched, compatibilized, in a controlled way, and cyclophosphazenes seem to be particularly useful to fulfill these goals. In this paper we would like to report on the advances of cyclophosphazene research in these domains, focusing on those carried out in our labs.

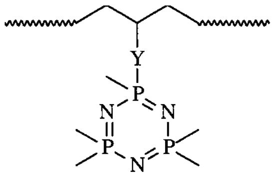
Discussion

Polymer modifiers are low-molecular weight mono- or multi-functional compounds which are reacted with conventional macromolecules both to modify the pristine structures and properties of the polymers and to introduce novel chemical and/or physical features in these materials. For this type of research, cyclophosphazenes lend themselves nicely. In fact they are multifunctional compounds containing, in the case of cyclotriphosphazenes, from 1 to 6 reactive groups "R", as reported in the formulae below:



FORMULA 3

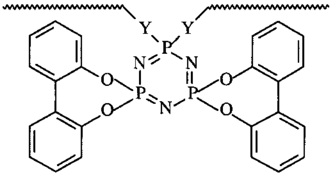
The number of reactive groups "R" in the cyclophosphazenes is able to determine the possible practical utilization of these substrates. In fact, cyclophosphazenes containing just one functional groups[57] can be used as monomers or as ***polymer modifiers***, as reported below:



FORMULA 4

in which the trimeric substrate, attached to the polymer chain as a side group, may be able to impart to the macromolecule properties initially belonging to the trimer exclusively.

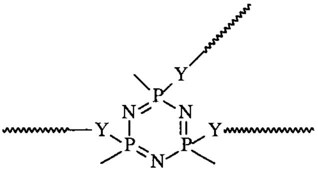
Cyclophosphazenes with two reactive substituents[58], may act as ***chain-extenders***, according to the following Formula:



FORMULA 5

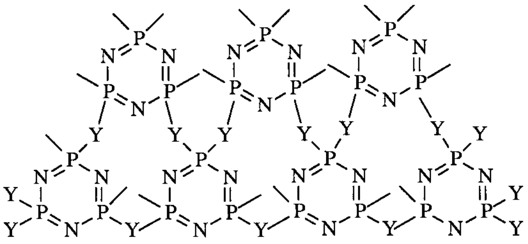
in which two polymeric chains are linked together through the cyclophosphazene thus inducing the increase in the molecular weight of the material and possibly recovering of mechanical properties.

In the case of cyclophosphazenes bearing from 3 to 6[57,59,60] reactive substituents, they can be used as ***branchers*** to introduce ramification of polymer chains in a controlled way, as illustrated in Formula 6 in which three polymer chains are bonded to the trimer;



FORMULA 6

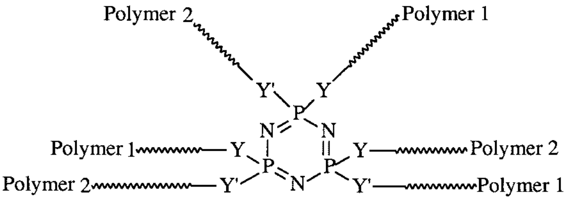
the same materials, moreover, may act ***crosslinkers*** inducing the complete reticulation of polymeric substrates through the formation of tridimensional networks having the general structure below:



FORMULA 7

where "Y" represent the polymer chains included between two cyclophosphazene rings.

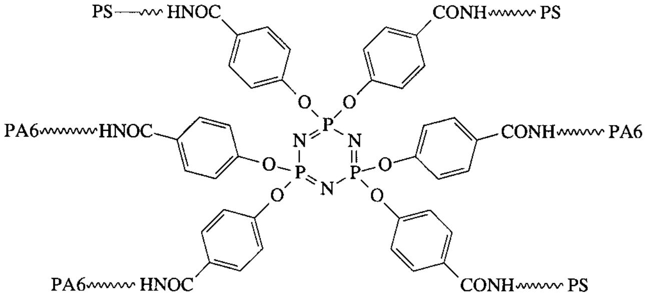
Finally, when on the same cyclophosphazene substrate are simultaneously present two different reactive groups[58], *e.g.* "R" and "R' ", these molecules can be exploited as ***polymer compatibilizers***, for instance, in reactive blending processes, linking chains of different polymers to the same cyclophosphazene ring and forming very efficient compatibilizing agents with the following general structure:



FORMULA 8

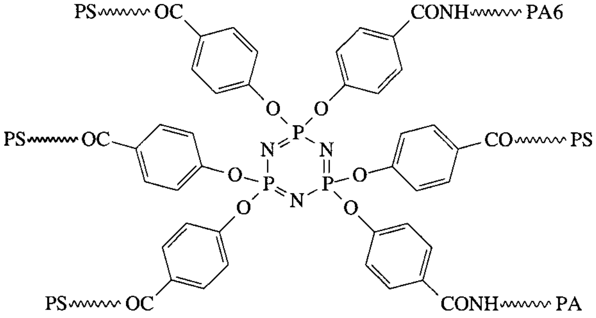
Having in mind the guidelines exposed above, research on cyclophosphazenes as polymer modifiers started in 1996 when K.Inoue[61] proposed the use of cyclophosphazenes as compatibilizers for immiscible poly(2,6-dimethylphenylene-oxide) (PPO) and Nylon-6 (Polyamide-6, PA6) by means of the use of specially designed trimers containing polystyrene (PS) and polyamide chains in their chemical structure.

The cyclophosphazenes used as compatibilizers were prepared starting from hexakis(4-carboxyphenoxy)cyclophosphazene, $[NP(OC_6H_4\text{-}COOH)_2]_3$, chlorination of the compound to $[NP(OC_6H_4\text{-}COCl)_2]_3$ by treatment with thionyl chloride, and reaction with amino-terminated polystyrene, $PS\text{-}NH_2$, or with polystyrene anion, PS^-Li^+, to obtain cyclophosphazenes partially substituted at the phosphorus with PS chains. The materials obtained (still containing -COCl functions) was hydrolyzed with alkaline water to reform the original carboxylic groups, and eventually reacted with ε-caprolactame, to graft polyamide chains onto the cyclophosphazene platform. The chemical structures of the cyclophosphazenes obtained are reported below.



FORMULA 9

and



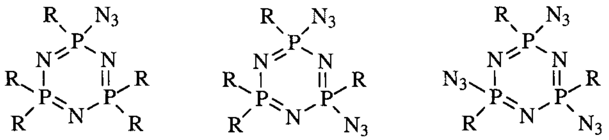
FORMULA 10

showing both polystyrene and polyamide chains attached to the phosphorus atoms of the cyclophosphazene ring.

The successive blending of PPO and Polyamide-6 polymers with variable percentages of these CPs induced the strong reduction of the surface tension between the two polymers due to the onset of interactions between the polystyrene and polyamide side arms of the cyclophosphazene with PPO and Polyamide-6 polymers, respectively. These facts were reflected by the presence of an unique T_g in the thermograms of blends prepared with a different

PPO/PA6/CP composition, by the decrease of the thermal stability of the final blends with the increase in the polystyrene content, and by the enhancement of tension modulus, strength and elongation of these products. After this initial step, research on the practical exploitation of CPs as modifiers for conventional polymers evolved towards the use of cyclophosphazenes substituted with azide groups.

Although in the past several articles have been published dealing with phosphazene substrates functionalized with azides[62-68], the use of these compounds as polymer crosslinkers was addressed a few years ago by H.R.Allcock[69-71] who succeeded in synthesizing the following series of compounds:



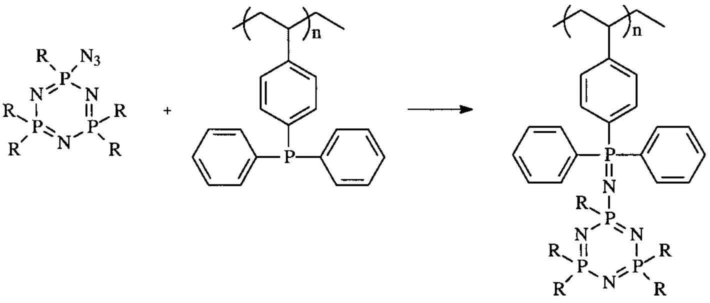
where: R may be C_6H_5O-; CF_3CH_2O- or $(CH_3)_2N$-

FORMULA 11

The synthesis has been carried out by reacting partially substituted chlorinated cyclophosphazenes with sodium azide in 2-butanone and in the presence catalytic amounts of tetrabutylammonium bromide[69-71].

The reactivity of these CPs was tested first by using monoazide derivatives in nitrene insertion reactions[69-71] induced both thermally[69-71] and photochemically[70,71]. It could be proved that thermal nitrene insertion takes place with $N_3P_3(OC_6H_5)_5(N_3)$ in the presence of 1-phenylnonane, while photolytic nitrene insertion could occur by irradiating $N_3P_3(OCH_2CF_3)_5(N_3)$ in cyclohexane. These types of reaction have been claimed to serve as a powerful tool for crosslinking polyolefins[69,71] and to chain extend syndiotactic polystyrene[72].

An alternative way for azide-functionalized CPs to induce modifications in conventional macromolecules is based on the utilization of the Staudinger reaction between triphenylphosphine-containing polystyrene[73-75] and/or silicones[74,75] and azido-functionalized cyclophosphazenes, according to the following Scheme:



SCHEME 1

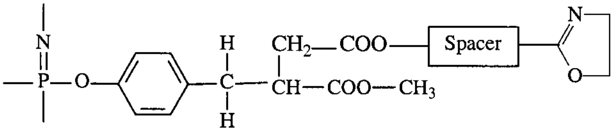
which might be extremely useful in the preparation of polymers containing high quantities of nitrogen and phosphorus atoms, particularly suitable to enhance the flame resistance and the thermal stability of these materials[73].

In our laboratory the utilization of cyclophosphazenes as polymer modifiers was faced using rather different point of view, *i.e.* by considering the synthesis of new CP derivatives functionalized with 2-oxazoline[76-81] and with epoxy groups[82].

2-Oxazolines are very interesting compounds used for many important practical applications, as monomers for polymerization processes[83], protective groups for carboxylic functions[84], core molecules for dendrimers[85,86], chain extenders[87,88] and blend compatibilizers[89-91]. A number of review articles covering the synthesis, modification, and utilization of 2-oxazolines have been published over the time[83,86,92-95].

The first combination between phosphazene materials and 2-oxazolines was reported on 1994 in the pioneering work by Chang[53,96,97], who used first an aryloxy-substituted cyclophosphazene containing six -CH_2Br functions in combination with 2-methyl-2-oxazoline to prepare star polymers[53] with a cyclophosphazene core, and successively a bromomethylated polyphosphazene to obtain POP-*g*-poly(2-methyl-2-oxazoline) grafted copolymers[96,97].

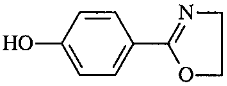
Expanding upon this research, we could succeed in inserting 2-oxazoline groups into polyphosphazene substrates by grafting a 2-oxazoline-containing maleate onto a poly[bis(4-methylphenoxyphosphazene], to obtain a grafted copolymer very reactive towards acidic compounds, that was successively blended with polyacrylic and/or poly methacrylic acids[76].



where “Spacer” is a long aliphatic chain

FORMULA 12

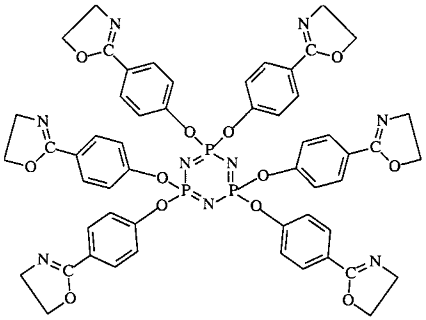
After these initial investigations, we developed a different strategy to combine 2-oxazoline derivatives and phosphazene materials, based on the use of 4-hydroxyphenyl-2-oxazoline[98]



FORMULA 13

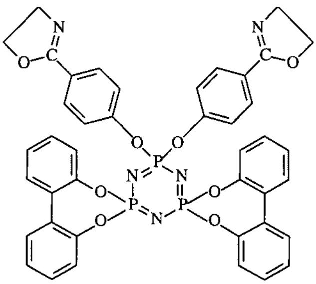
in combination with cyclophosphazenes containing a variable number of chlorine atoms[77-81,99].

Thus the reaction of 4-hydroxyphenyl-2-oxazoline with hexachlorocyclophosphazene led to the synthesis of hexakis(4-oxazolinophenoxy)cyclophosphazene (***C-6-OXA***)



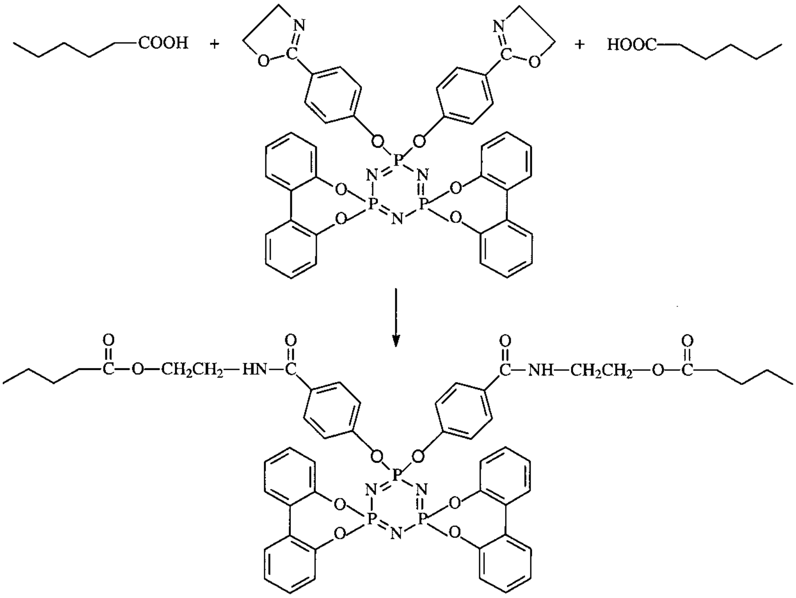
FORMULA 14

while the utilization of 2’,2”-dichloro-4,4,6,6-bis[spiro(2’,2’’-dioxy-1’,1’’-biphenyl)]cyclotriphosphazene allowed the preparation of 2’2”-bis(4-oxazolinophenoxy)-4,4,6,6-bis[spiro(2',2"-dioxy-1',1"-biphenyl)]cyclophosphazene (***C-2-OXA***).



FORMULA 15

The reaction of ***C-2-OXA*** with low-molecular weight poly(ethylene terephthalate) (PET) in the internal chamber of a Haake Rheomix 600 Mixer at 270°C in the presence of about 5% of this trimer leads to the formation of a new material. The expected reaction is reported below.



SCHEME 2

The polymers obtained showed different thermal and mechanical properties with respect to those of the starting material[81]. In fact, thermal analyses carried out by DSC on both virgin and treated PET showed that the T_g of the original polymer is always lower than that of the modified

PET, while the melt and crystallization enthalpies, and the cooling crystallization temperature of the starting polymer are always higher. At the same time, according to the data obtained by Dynamical Mechanical Thermal Analysis (DMTA), PET modified with ***C-2-OXA*** exhibited not only a higher modulus, but also a lower percentage of deformation above T_g, as reported in Figure 1:

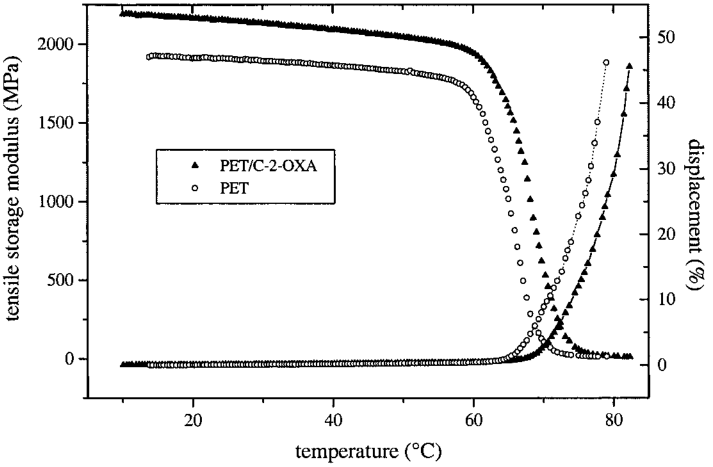
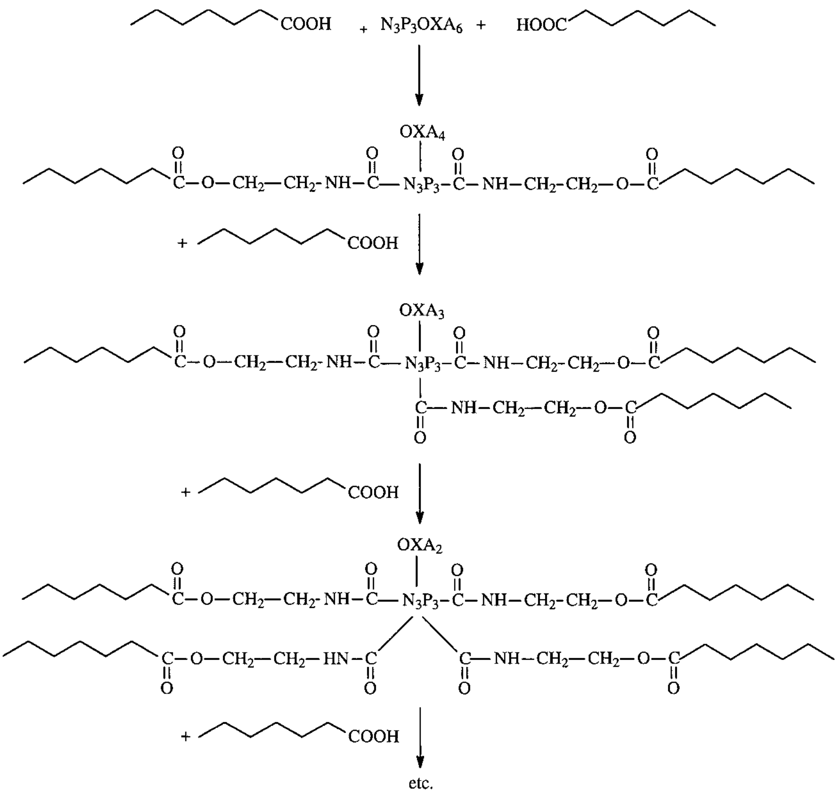


FIGURE 1. DMTA analysis for PET and PET treated with ***C-2-OXA*** (Tensile DMTA Mk II Polymers Laboratories: static stress 0.6 MPa, deformation amplitude 64 micron, frequency 1 Hz, heating rate 3 °C/min).

These experimental evidences of lower crystallinity, higher T_g, higher storage modulus, and reduction of mobility appear to be consistent with a remarkable increase of the molecular weight of the ***C-2-OXA*** modified polymers.

Even more striking are the results obtained by treating PET with ***C-6-OXA***, because of the presence of six 2-oxazoline residues in the trimer that are able to induce deep modifications in PET by simultaneously bonding several PET chains on the same cyclophosphazene ring. The general reaction is reported in the Scheme 3 below:



SCHEME 3

The rheological measurements reported in Figure 2, showed that the complex viscosity of ***C-6-OXA***-modified PET (upper curve) undergoes a dramatic enhancement with respect to that of the virgin polymer (lower curve) and that of a PET sample modified with a commercial bis-oxazoline derivative, *i.e.* (1-4 phenylene)-bis-2-oxazoline (***Ph-2-OXA***)[100] (middle curve), to suggest the onset of strong coupling processes between the cyclophosphazene and the polymer.

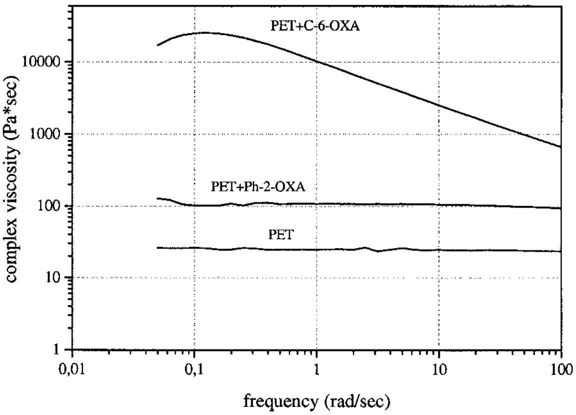


FIGURE 2. Complex viscosity variations at 270°C versus oscillation frequency of molten PET/***C-6-OXA***; PET/commercial bis-oxazoline (***Ph-2-OXA***); Virgin PET, after treatment in a mixer.

Similar results are obtained by analyzing the shear storage and loss shear moduli of molten polymers, as reported in Figures 3A and 3B where it can be easily seen that both shear storage and loss moduli of the virgin PET are much lower than those of same polymer treated with the bis-oxazoline and with ***C-6-OXA***, respectively. Moreover, the PET sample modified by reaction with ***C-6-OXA*** behave predominantly as a viscous polymer at low oscillation frequency, but it start to behave as an elastic materials when the applied frequencies increased.

The great usefulness of ***C-6-OXA*** as a polymer modifier could be confirmed also by using this trimer as a blend compatibilizer for immiscible polycarbonate (PC) and Polyamide-6 materials.

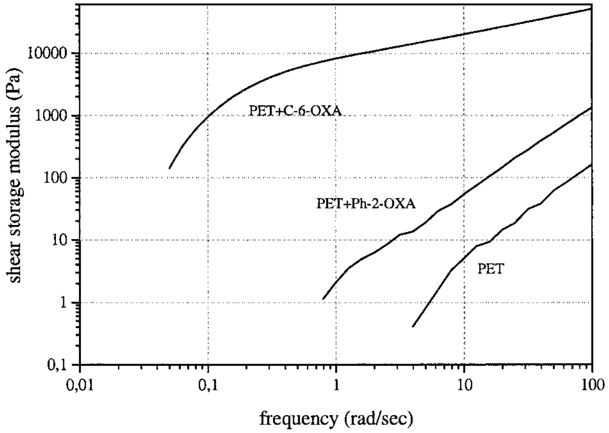


Figure 3A. Shear Storage Modulus G' variations at 270°C versus the oscillation frequency for molten PET/***C-6-OXA***; PET/commercial bis-oxazoline (***Ph-2-OXA***); virgin PET after treatment in a mixer.

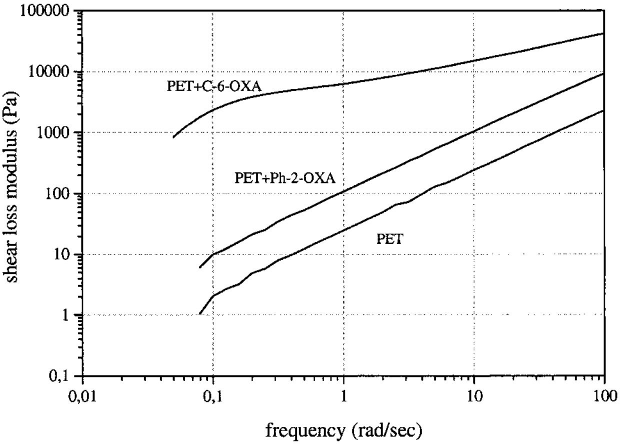
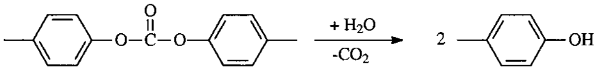


Figure 3B. Shear Loss Modulus G" variations at 270°C versus the oscillation frequency for molten PET/***C-6-OXA***; PET/commercial bis-oxazoline (***Ph-2-OXA***); virgin PET after treatment in a mixer

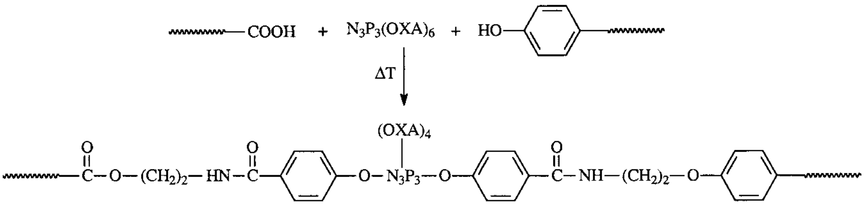
In general polyamides possess terminal -COOH groups that could react with 2-oxazolines, while PC does not contain any useful end groups on the skeleton because of the utilization of monophenols to control the molecular weight of the material during the synthesis. This polymer, however, is believed to thermally degrade during blending to produce free hydroxylic functions according to the following reaction[101,102]. These groups are reported to be reactive towards 2-oxazolines[94].



SCHEME 4

As a matter of fact, three 50:50 blends have been prepared between PC and polyamide-6 containing no additives, (1,4-phenylene)-bis-2-oxazoline (***Ph-2-OXA***) and ***C-6-OXA*** (in similar molar 2-oxazoline content), respectively, using a Haake internal mixer at 270°C, which were analyzed from a morphological and mechanical point of view[99].

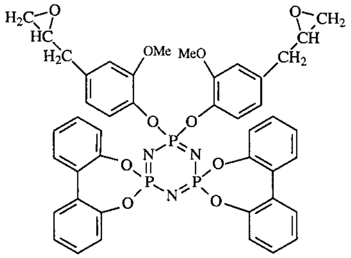
The results obtained showed that the mechanical mixture of the two polymers has a biphasic structure in which polyamide-6 acts as the matrix and PC as the dispersed phase. The structure becomes co-continuous when the commercial bis-oxazoline is added to the blend, while by treatment with ***C-6-OXA*** the situation is inverted, PC becoming the matrix and polyamide-6 the dispersed phase. At the same time, mechanical characterization revealed that the formation of PC/PA6/***C-6-OXA*** blend leads to an enhancement of the elastic modulus (possibly due to phase inversion and decreased effect of water as a plasticizing agent), while the toughness of the blends produced is substantially kept at a good level. These preliminary findings seem to indicate that the addition of ***C-6-OXA*** to the PC/PA6 blends alters in a significant way both the morphology and the physical properties of the mechanical mixture of the two polymers, possibly due to the formation in the reaction chamber of the internal mixer of a compatibilizing agent, according to the following Scheme:



SCHEME 5

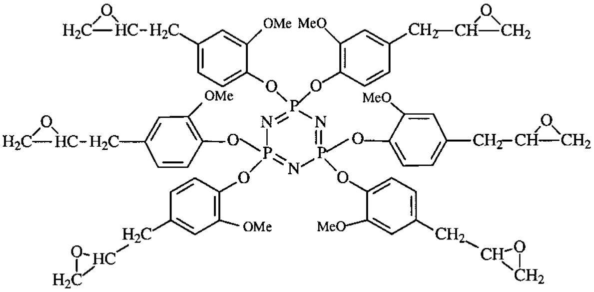
This hybrid compound might be able to reduce the surface tension between the two partners of the blend allowing the preparation of new materials.

Almost simultaneously to the research on the use of cyclophosphazenes functionalized with 2-oxazoline groups as chain-extenders and polymer compatibilizers described above, we started investigations on the use as polymer modifiers of new cyclophosphazenes substituted with epoxide moieties. These products were prepared by reacting hexachlorocyclophosphazene and 2',2"-dichloro-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenyl)]cyclotriphosphazene with eugenol (2-methoxy-4-allylphenol) according to literature[103], and successive peroxidation of the allyl residues to oxirane rings[104] by the action of *m*-chloroperbenzoic acid. The general structures of the resulting compounds are reported below, in which 2 (***CP-2-EPOX***)



FORMULA 16

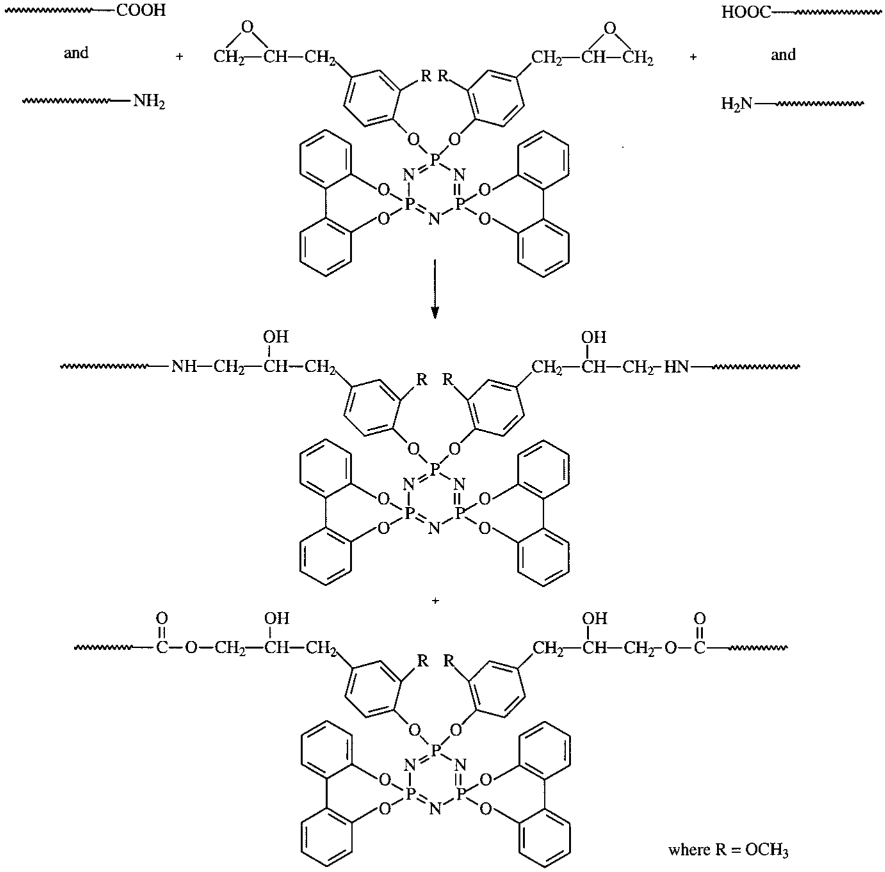
and 6 (CP-6-EPOX)



FORMULA 17

epoxide units are attached to the cyclophosphazene substrate.

These functions are known to be very reactive toward both -NH_2 and -COOH terminal groups of polyamides[105], and in this way they can act as a chain extenders in combination, for instance, with polyamide-6. The reaction between ***CP-2-EPOX*** and/or ***CP-6-EPOX*** with polyamide-6 was carried out in a Haake Minilab at 240°C, sometimes drying both polyamide-6 and the cyclophosphazene additives at 100°C prior to use to minimize the influence of hydrolytic phenomena in polyamide-6 during reactive blending. The resulting reactions between cyclophosphazenes and polyamide-6 are describe for ***CP-2-EPOX*** in the following reaction Scheme 6:



SCHEME 6

in which different polyamide chains are linked together through a cyclophosphazene molecule.

The action of ***CP-2-EPOX*** was found to be more effective than that of ***CP-6-EPOX***, possibly due to phenomena of thermal instability which are operative for ***CP-6-EPOX*** already during the preliminary drying step of the cyclophosphazenes, resulting in the thermal degradation of the additive. These facts have been evidenced by DSC and TGA measurements on the cyclophosphazenes exploited.

In spite of these facts it could demonstrated that blending in the internal mixer described above polyamide-6 with very low amounts of ***CP-2-EPOX*** (0.2% w/w) introduces strong variations with an increase in both the torque and in the melt pressure drop during blending polyamide-6 in the presence of the cyclophosphazene with respect to the same process carried out only with the starting polymer.

The same holds true for rheological measurements in the melt, as reported in Figure 4 below for complex viscosity:

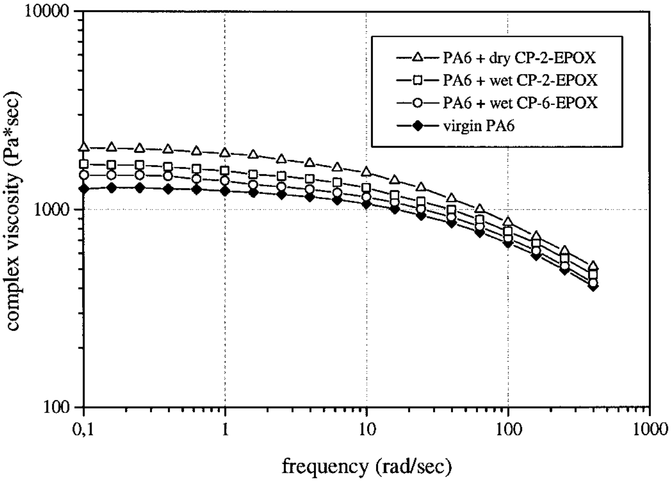


FIGURE 4. Complex viscosity at 240°C of Polyamide-6 samples treated with wet ***CP-6-EPOX*** and wet and dry ***CP-2-EPOX.***

and in Figure 5 for the shear storage modulus of polyamide-6, where it is evident that both these parameters increase very much passing from virgin polyamide-6, polyamide-6 treated with wet ***CP-6-EPOX***, polyamide-6 combined with wet ***CP-2-EPOX***, to reach the maximum value when the polyamide is mixed with dry ***CP-2-EPOX***.

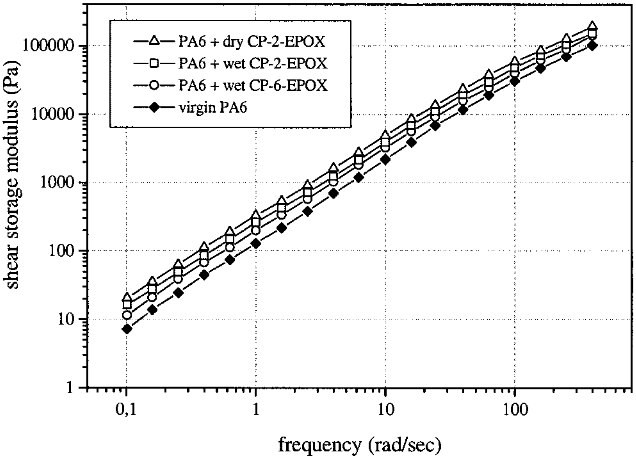


FIGURE 5. Storage and loss modulus at 240°C of Polyamide-6 samples treated with wet ***CP-6-EPOX*** and with wet and dry ***CP-2-EPOX***

Contrarily to what happens to mechanical and rheological properties, which are deeply influenced even using very low amounts of epoxide-containing cyclophosphazenes during the mixing processes, the thermal properties of the same materials seem not to be appreciably modified by the presence of cyclophosphazenes in the blend. This could be demonstrated by DSC and TGA, that showed no substantial modifications in the T_g, T_m and ΔH_m of virgin polyamide-6, compared with the value of the same parameters of the modified polymer. Moreover, during pyrolysis analysis, only ε-caprolactame production could be observed in both treated and untreated samples.

Conclusions

In this paper we highlighted literature on the utilization of cyclophosphazenes as polymer modifiers, and presented results on our activity in this field. The importance of experimental parameters such as the synthetic versatility of cyclophosphazenes, the ease of their chemical modification and/or functionalization, and the possibility of controlling the reactivity of the phosphazene trimers by carefully inserting a well defined number of chemical functions, are critically evaluated. The original work in this field carried out by K. Inoue[61] on the utilization of cyclophosphazenes containing polystyrene and polyamide chains as blend compatibilizers for poly(phenylene oxide) (PPO) and polyamide (Polyamide-6), and by H.R. Allcock[69-71,73-75] on the utilization of azide-containing trimers as crosslinkers for polyolefins, opened the route to successive research on the synthesis of cyclophosphazenes bearing new reactive functions, such as 2-oxazoline[76-81,99] and epoxide[82] groups, and on their utilization as chain extenders for polyesters (e.g. PET) and polyamides (e.g. Nylon 6), respectively, or to promote the compatibilization processes between immiscible polycarbonate (PC) and polyamides. Future developments of this research deal with the preparation of novel cyclophosphazene derivatives bearing substituents containing new reactive groups and/or with the synthesis of cyclophosphazenes containing mixed chemical functionalities.

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