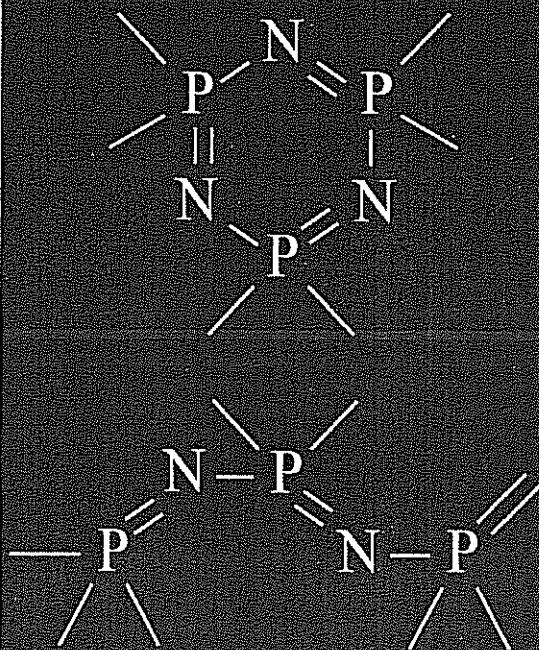


# PHOSPHAZENES

A WORLDWIDE INSIGHT

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*Chapter 19*

## PHOSPHAZENE HYBRIDS BY SOL-GEL

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### SUMMARY

In this article the application of the sol-gel technique to phosphazene substrates to obtain a novel series of hybrid materials is reviewed. Different types of phosphazenes are suitable for this goal, i.e. hexachlorocyclophosphazene and polydichlorophosphazene, alkoxy-substituted phosphazene substrates, phosphazene polymers bearing oligoethyleneoxyde or trifluoroethoxide moieties, phosphazene derivatives containing alkoxy or aryloxy groups functionalized with free hydroxyl functions, and cyclophosphazenes containing trialkoxysilane functionalities. For some of these materials only weak forces are involved between phosphazenes and the inorganic network when hybrid materials are prepared. For others genuine chemical bonds are formed among them. In both cases relevant improvements for the applicability properties of phosphazene substrates are observed together with the onset of new features.

## INTRODUCTION

New materials possessing interesting applicative characteristics are nowadays accessible by synthesis at the interfaces between ceramics, metals and polymers<sup>1</sup>.

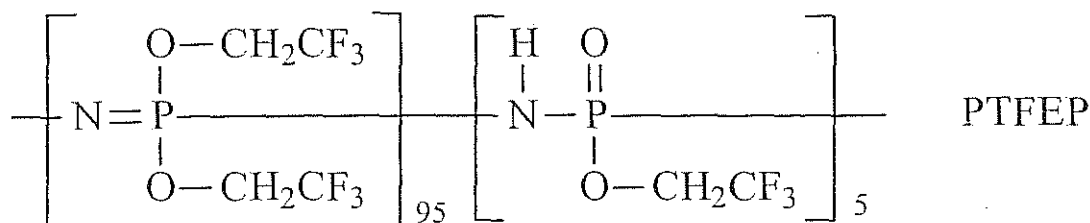
Very interesting perspectives, in fact, are provided by hybrid materials prepared through sol-gel technique<sup>2</sup> in which an organic part combined with an inorganic matrix. Properties of these new substrates inherently due to the organic component may be of interest for nonlinear optics<sup>3-5</sup>, light emission<sup>6,7</sup>, photochromism<sup>8</sup>, elasticity, chemical reactivity, molecular recognition, etc., while the inorganic support may be selected depending on its refractive index, dimensional stability, mechanical properties, and thermal and flame resistance.

From the synthetic point of view two main classes of compounds are accessible by sol-gel technique. In the first one, no chemical bonds are formed between the organic and the inorganic partners of the hybrids, and the only interaction existing between these substrates being relatively weak are based on Van der Waals forces, hydrogen bonding or electrostatic attractions. In the second class, on the contrary, true covalent linkages are generated between the organic and the inorganic phases in the hybrids producing monophased materials, e.g. ORMOSIL (Organically Modified Silicates)<sup>9</sup>, ORMOCERS (Organically Modified Ceramics)<sup>10</sup> or CERAMERS (Ceramics Polymers)<sup>11</sup>.

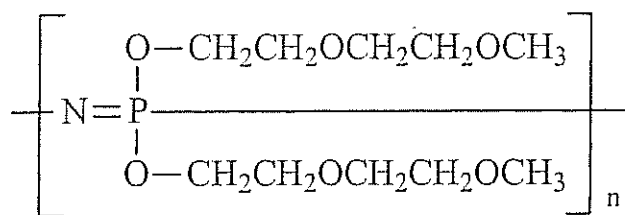
In the case of phosphazene substrates the preparation of hybrid materials combined with silica, titania, zirconia or alumina networks is a relatively recent research field<sup>12-14</sup>.

Four research groups are basically responsible for the advances obtained in this domain:

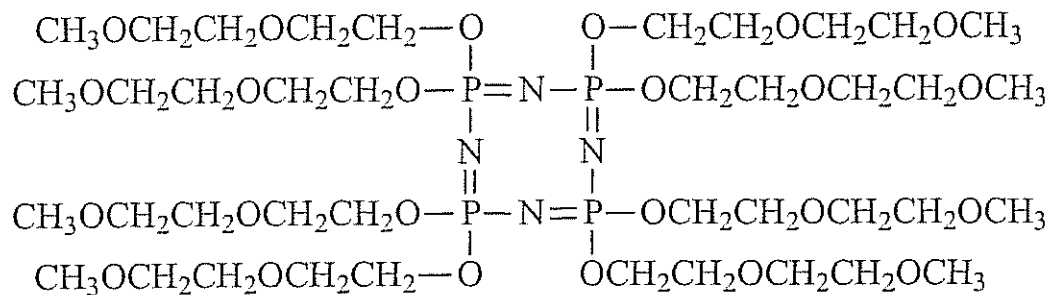
- (a) the Eastman Kodak team in USA<sup>15-23</sup> mostly investigated the utilization of poly[bis(2,2',2''-trifluoroethoxy)phosphazene], PTFEP, containing a small percentage of hydrolyzed units,



poly[bis(methoxyethoxyethoxy)phosphazene], MEEP, and octakis(methoxyethoxyethoxy)cyclotetra phosphazenes, MEEP Tetramer to prepare new hybrids in which no chemical bonds are formed between the phosphazene materials and the silica network. The good mechanical properties of these substrates are guaranteed by Van der Waals type interactions.

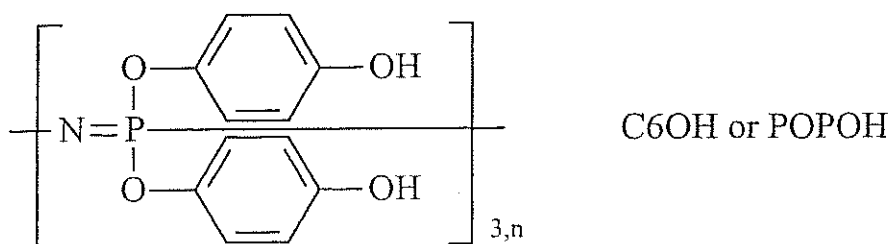


MEEP

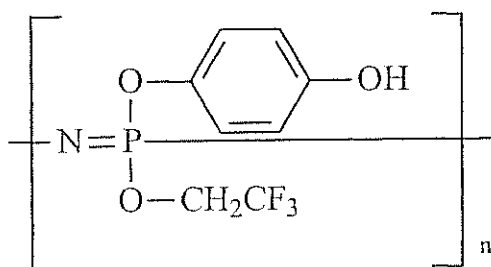


MEEP Tetramer

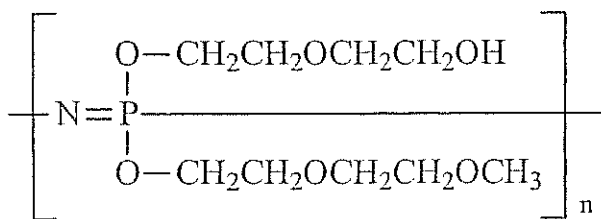
- (b) our group in Italy<sup>12-14,24-35</sup> has exploited hydroxylated phosphazenes starting from hexakis(4-hydroxyphenoxy)cyclophosphazene, C6OH, poly[bis(4-hydroxyphenoxy)phosphazene], POP-OH,



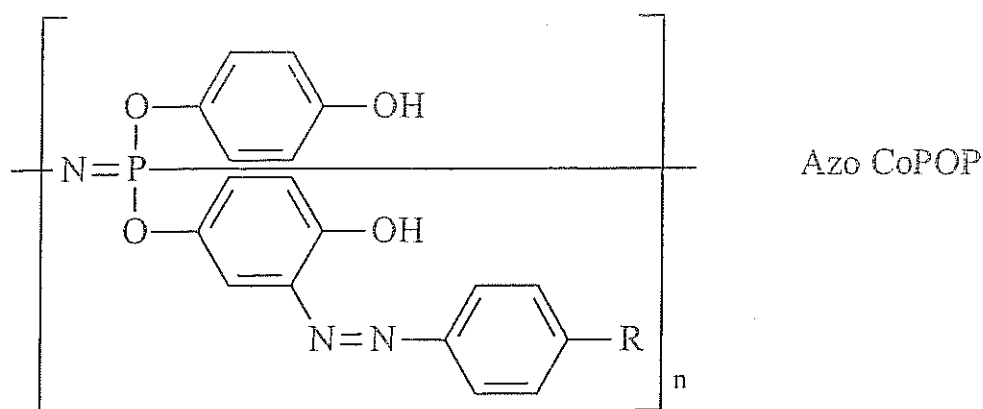
and other hydroxylated phosphazene copolymers such as



PhOH/TFE CoPOP

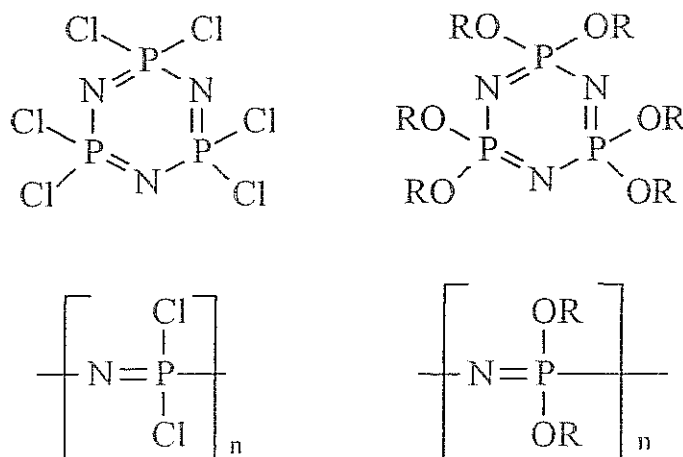


MEEPOH



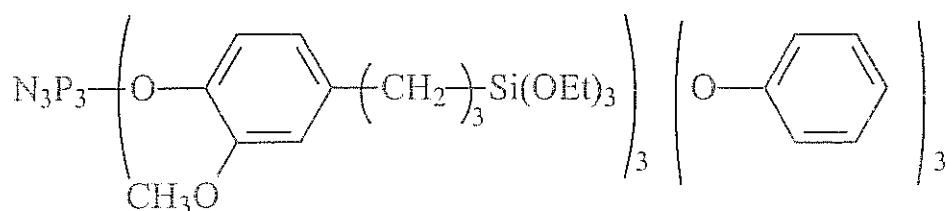
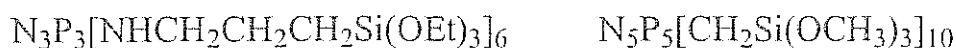
in order to guarantee the formation of genuine chemical bonds between the phosphazene materials and the inorganic matrix.

- (c) the group at the University of Montpellier (France)<sup>36-39</sup> in which hexachlorocyclophosphazene, polydichlorophosphazene, and cyclo- or polyphosphazenes substituted with alkoxy groups,



where R may be CH<sub>3</sub>, iso-C<sub>3</sub>C<sub>7</sub> or CH<sub>2</sub>CF<sub>3</sub> were used for the preparation of hybrid materials using a non-hydrolytic condensation process.

- (d) the group of Würzburg (Germany), which used cyclic phosphazenes derivatives containing free -Si(OR)<sub>3</sub> moieties<sup>10</sup> having the following structures



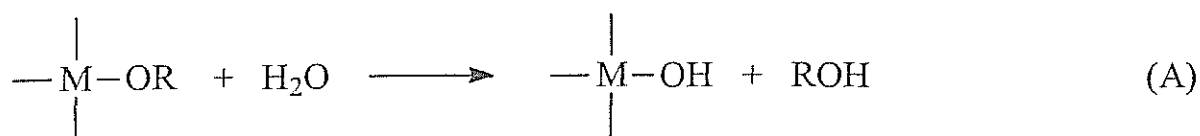
for the synthesis of sol-gel hybrid materials.

Few other strategies for obtaining new phosphazene/metal oxide hybrids through sol-gel have been explored<sup>40,41</sup> or have only been announced<sup>42</sup> without additional publication.

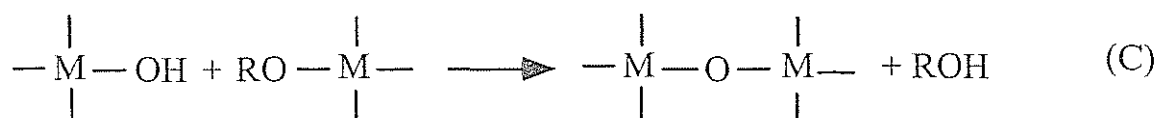
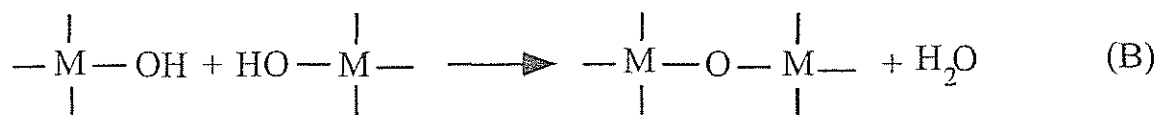
In this paper we would like to highlight the work carried out on phosphazene-based hybrids, with particular emphasis dedicated to possible practical utilization of these materials.

## SHORT INTRODUCTION TO THE SOL-GEL TECHNIQUE

The sol-gel process can be defined as a gentle chemical route to prepare a variety of inorganic materials through a very broad range of different procedures<sup>2,43</sup>. According to the more general approach, the sol-gel process is based on the formation of inorganic networks starting from solutions of molecular precursors, the *sol*, followed by its gelation to form a continuous solid network in a continuous liquid phase, the *gel*. Among precursors, metal alkoxides are most popular as they can undergo inorganic polymerization by hydrolysis-condensation reactions. The hydrolysis reaction (A) through the addition of water replaces alkoxide groups with hydroxyl groups



suitable for condensation (B,C) leading to the formation of oxo-bridges and the elimination of water or alcohol by-products, respectively:



Depending on the choice of precursors and synthetic conditions, the features of the gel network can be modulated in order to obtain different structures and functionalities in the final materials. This aspect has been extensively exploited not only to produce multi-component inorganic oxides but also to prepare the so-called organic/inorganic hybrid materials, where organic groups are dispersed within the inorganic network, on a scale from the sub-micronic range down to the nanometer level<sup>43</sup>.

The sol-to-gel transition can be exploited with the aim of producing coatings, fibers, powders and monoliths and this accounts for the large potentiality of the sol-gel technique. The applications of sol-gel processes have found outstanding success in the field of functional coatings, ceramic fibers, advanced fine-grains ceramics and ordered mesoporous materials and are still in expansion<sup>44</sup>.

Thanks to the wide potentialities of organic chemistry, the main development of sol-gel process is foreseen in the field of hybrid organic/inorganic materials, where organic and

inorganic components can give a synergistic effect in tailoring new materials. The introduction of non-polymerizable organic groups as well as of reactive organic functionalities allows the production of new interesting materials particularly for the development of optical devices; the control of phase interaction in hybrids prepared from organic polymers and inorganic oxo-clusters leads to the production of materials with modulated mechanical properties<sup>45,46</sup>. The almost unlimited availability of organic and organometallic compounds and polymers gives the opportunity to design, by the sol-gel process, new and successful materials for the century to come.

## SYNTHESIS OF CYCLO- AND POLY-PHOSPHAZENES

The cyclo (CPs) and poly (POPs) phosphazenes used in the preparation of hybrid materials through the sol-gel technique were synthesized according to standard procedures<sup>47-49</sup> based on the reaction of hexachlorocyclotriphosphazene, octachlorocyclotetraphosphazene or polydichlorophosphazene with the appropriate sodium salts of alkoxy or aryloxy derivatives, or with -NH<sub>2</sub>-functionalized organic compounds. When necessary suitable copolymerization<sup>50</sup> and/or functionalization<sup>51</sup> reactions have been exploited.

In particular:

- (a) Poly[bis(methoxyethoxyethoxy)phosphazene], MEEP, and octakis-(methoxyethoxyethoxy)cyclophosphazene (MEEP Tetramer) were prepared according to the procedure reported by Allcock<sup>52,53</sup> and Coltrain<sup>15,16,18,19,54</sup>. MEEP is an amorphous polymer<sup>52</sup>, with a very low T<sub>g</sub> value (-75°C)<sup>53</sup> which was selected for the preparation of hybrid materials using the sol-gel technique because of its remarkable importance as a water soluble material<sup>55,56</sup>, biologically important macromolecule<sup>57,58</sup>, ionic conductor when doped with Li<sup>+</sup> or Ag<sup>+</sup> salts<sup>52,53,59</sup>, and phase transfer catalyst<sup>60</sup>.
- (b) Hydroxylated poly[bis(methoxyethoxyethoxy)phosphazene], MEEP-OH was prepared by De Jaeger<sup>61,62</sup> by reacting MEEP with trimethylsilyl iodide<sup>63</sup> to deplete CH<sub>3</sub> end groups of the oligoethyleneoxide moieties in this polymer, thus forming a novel functionalized polyphosphazene bearing free hydroxyl groups;
- (c) poly[bis(2,2',2''-trifluoroethoxy)phosphazene], PTFEP, was prepared according to the synthetic procedure established by Ferrar<sup>64</sup>. This polymer is one of the most important phosphazene synthesized because of its good film forming capability<sup>65</sup>, micro-crystallinity<sup>66</sup>, high thermal stability<sup>67,68</sup>, good self-extinguishibility<sup>69</sup>, remarkable flame retardant characteristics<sup>70,71</sup>, noticeable mechanical properties<sup>72,73</sup>, great hydrolytic stability<sup>74</sup> and very high inertness towards chemicals<sup>65</sup>, biological agents<sup>57,75</sup>, atomic oxygen<sup>76</sup>, and light<sup>77,78</sup> or  $\gamma$ -rays<sup>79</sup> irradiation. Performances of this polymer as membrane were also evaluated<sup>80</sup>.
- (d) poly[bis(4-hydroxyphenoxy)phosphazene], POPOH, was prepared following the procedure established by Medici<sup>81</sup>, by reaction of poly[bis(4-methoxyphenoxy)phosphazene]<sup>82</sup> with BBr<sub>3</sub> under hydrolytic conditions. This functionalization leads to the removal of the methyl groups in the para position of the aromatic ring and the formation of free hydroxyl functions. The same procedure was adopted to prepare the corresponding phosphazene trimer hexakis(4-

- hydroxyphenoxy)cyclophosphazene,  $C_6OH^{81}$ , and  $PhOH/TFECoPOP^{12-14}$ , a phosphazene copolymer containing trifluoroethoxy groups and free hydroxyl functionalities;
- (e) AzoCoPOP was prepared by coupling POPOH with diazotized aromatic amines to obtain a deeply colored phosphazene copolymer bearing azo dyes substituents on the phosphorus atoms of the phosphazene chain<sup>26,83</sup>;
  - (f) in the recent work carried out by Leclercq<sup>36-39</sup>, neat hexachlorocyclophosphazene and polydichlorophosphazene together with alkoxy-substituted phosphazene derivatives were exploited using a non-hydrolytic approach to the synthesis of phosphazene metal oxide hybrid derivatives;
  - (g) finally, the synthesis of cyclophosphazenes substituted with trialkoxysilane moieties have been reported by Rose<sup>10</sup> starting from  $N_3P_3Cl_6$  and  $\gamma$ -aminopropyltriethoxysilane, cyclophosphazenes substituted with eugenol and hydrosilylation reaction with triethoxysilane  $HSi(OC_2H_5)_3$ , or, eventually from  $N_5P_5(CH_3)_{10}$  by lithiation with lithium n-butyl of the methyl groups followed by reaction with chlorotrimethylsilane

## SYNTHESIS OF PHOSPHAZENE/INORGANIC MATRIX HYBRID MATERIALS

Starting from the above described cyclo- and poly-phosphazenes, research has been carried out to obtain new hybrid derivatives formed by POPs and inorganic matrices of  $SiO_2$ ,  $TiO_2$ ,  $ZrO_2$  or  $Al_2O_3$ , respectively.

Thus Coltrain<sup>17,21</sup> first prepared MEEP/ $SiO_2$  composites by dissolving MEEP (average molecular weight about  $3 \times 10^6$   $g \cdot mol^{-1}$ ) in a 1:1 mixture of THF/methanol, adding tetraethoxysilane (TEOS) (50 % w/w respect to MEEP, resulting in composite film containing 23 % w/w of  $SiO_2$ ) and HCl. After stirring 15 min and heating at 60 °C for 30 min the solution was poured in a teflon dish obtaining a 75  $\mu m$  thick free standing film after 4 days. The resulting composite was a clear product, thus indicating a homogeneous dispersion of the polyphosphazene throughout the  $SiO_2$  matrix. Thicker samples (up to 0.5 cm) were prepared by a longer process for Shore A hardness measurements. An analogous procedure has been adopted when MEEP/ $TiO_2$ , MEEP/ $ZrO_2$  and MEEP/ $Al_2O_3$  hybrids have been prepared<sup>22,23</sup>.

Similarly, PTFEP/ $SiO_2$  composites have been obtained<sup>17,21</sup> using PTFEP (molecular weight of  $2 \times 10^5$   $g \cdot mol^{-1}$ ), TEOS and alkaline hydrolysis of the system by heating at 60°C for 30 min, storage at room temperature for 14 days and eventual heating at 50°C in vacuum for 10 days.

POPOH/ $SiO_2$  composites were prepared following two methods. In the first approach tetraethoxysilane (TEOS), the silica precursor exploited for these experiments, was dissolved in ethanol solutions, treated with water and HCl (TEOS/ $H_2O$ /HCl = 1/2/0.01), pre-hydrolyzed for 3, 6, 9, 12 h and eventually reacted with POPOH for an additional hour<sup>24,25</sup>. Following this procedure the hybrids obtained were often opaque materials frequently showing evident phase separation phenomena<sup>28</sup>. This method was successively improved by eliminating the pre-hydrolysis step, and simultaneously reacting POPOH, TEOS, water and HCl in ethanol for 6 h under inert atmosphere, and aging the resulting mixture for 24 h at room

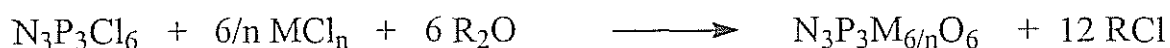


temperature<sup>28</sup>. Samples obtained in this case were transparent films or bulky materials showing no evident phase separation.

The second approach was also used for the preparation of MEEPOH/SiO<sub>2</sub><sup>27,31,84</sup>, PhOH/TFECoPOP/SiO<sub>2</sub><sup>13,14</sup> and Azo CoPOP/SiO<sub>2</sub><sup>26</sup> hybrids.

When TiO<sub>2</sub> and ZrO<sub>2</sub> composites were prepared<sup>25</sup>, acetylacetone was used to depress the chemical reactivity of the system.

New hybrid materials have been recently prepared by Leclercq<sup>36-39</sup> using chlorinated and alkoxy (ethoxy, isopropoxy and trifluoroethoxy) substituted cyclo- and poly-phosphazenes in combination with metal alkoxides, metal chlorides or metal chlorides in the presence of aliphatic ethers at 110°C in sealed ampoules. The three main types of reactions involved in this approach for cyclophosphazene derivatives are reported below:



where M = Si or Ti

It is important to stress that in these processes metal alkoxide functionalities may be present in the phosphazene substrate, in the metal alkoxide or may be generated *in situ* by the presence of an ether compound.

Finally the acid-catalyzed hydrolysis of the trialkoxysilane-containing cyclophosphazenes in the presence of TEOS leads the preparation of bulky materials and coatings containing cyclophosphazene units inside the silica network<sup>10</sup>.

## PROPERTIES AND PRACTICAL APPLICATIONS OF PHOSPHAZENE/INORGANIC MATRIX HYBRID MATERIALS

Previous sections on the synthesis of cyclo- and polyphosphazenes and on the preparation of tri-dimensional inorganic matrices by sol-gel technique, evidenced that novel phosphazene-containing hybrid materials can be obtained in a rather simple way using mild experimental conditions, which show improved features with respect to the original substrates, and that are potentially useful for a large variety of practical applications.

### Thermally Stable Materials

Investigations on the thermal characteristics of neat PTFEP<sup>17,21</sup>, MEEP<sup>17,21</sup>, POP-OH<sup>12,21,28,34,35</sup>, and on the related SiO<sub>2</sub> hybrid materials were carried out using DSC, DTA and TGA analyses.

According to DSC investigations<sup>17,21</sup>, neat MEEP is a polymer in the flow regime of viscoelasticity at ambient temperature, due to its very low T<sub>g</sub> value. It also seems to possess a low degree of crystallinity as demonstrated by the existence of an endothermic peak at 20-

30°C in its thermogram. This material, furthermore, shows a thermal stability limit at about 100°C; above this temperature thermal decomposition of the macromolecule takes place.

Hybrid MEEP/SiO<sub>2</sub> substrates obtained by incorporating MEEP into silica networks by sol-gel technique show practically no changes both in the T<sub>g</sub> and T<sub>m</sub> values of this polymer, to indicate that the SiO<sub>2</sub> network does not influence the chain mobility of MEEP and that the crystallinity of the phosphazene material is not destroyed by the hybrid formation process. These facts; together with the spectroscopic evidence that the <sup>31</sup>P {<sup>1</sup>H}NMR chemical shifts are not modified both in neat polymer and in the polymer incorporated into silica networks, suggests that only weak interactions take place between the phosphazene substrate and the inorganic matrix during hybrid preparation without onset of covalent chemical bonds. For the MEEP/SiO<sub>2</sub> hybrid, however, thermal decomposition by DSC starts to occur at about 200°C, indicating that the formation of hybrid materials introduced a strong increase in the thermal stability of MEEP and a remarkable enlargement of the service temperature range for the polymer.

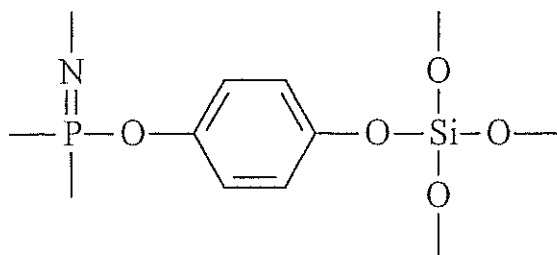
Similar results are obtained for PTFEP, whose T<sub>g</sub> is at -59°C, T(1) at 51°C and the thermal degradation starts at about 250°C<sup>17,21</sup>.

As far as POPOH is concerned, the polymer is a colorless material, fairly reactive toward oxygen (reticulation of the macromolecule takes place after prolonged air exposure<sup>28</sup>), diazotized aromatic amines<sup>26,83</sup>, formaldehyde<sup>83</sup>, and organic acid chlorides or anhydrides<sup>81</sup>. POPOH, therefore, needs to be manipulated almost immediately after preparation. By DSC measurements its T<sub>g</sub> was found to be +88°C<sup>28</sup>, possibly by formation of hydrogen bonding.

The presence of free hydroxy groups in this polymer provided the opportunity of preparing new hybrid materials by sol-gel technique in which the phosphazene polymer is chemically linked to the inorganic network of silica<sup>13,14,25,27-29,31-33,84</sup>.

This could be proved by considering:

- (a) a)DSC experiments carried out on POPOH/SiO<sub>2</sub> hybrids<sup>28</sup>, which evidenced the disappearance of the T<sub>g</sub> transition of POPOH in these materials, and selective extraction tests<sup>28</sup> of POPOH by acetone in which a very small amount of polymer was selectively extracted from the hybrids, while an almost quantitative extraction of POPOH took place when a physical mixture of the two components was considered;
- (b) spectroscopic (X-Ray, FTIR and NMR)<sup>32,34,35</sup> and thermal (DTA-TG)<sup>32,34,35</sup> data obtained by analyzing C6OH/SiO<sub>2</sub> hybrids of different compositions which unequivocally demonstrated the presence of C-O-Si- bonds in the structure of these materials.



The thermal stability of POPOH/SiO<sub>2</sub> composites was investigated by IR spectroscopy by heating POPOH/SiO<sub>2</sub> monoliths and following the disappearance of the band at 1500 cm<sup>-1</sup> (ν

C-C of the aromatic rings), and  $960\text{ cm}^{-1}$  ( $\nu$  P-O-Ph of the phosphazene system). These investigations evidenced that the bands are observable until  $400\text{C}^\circ$ , thus confirming that even in the case of POPOH the incorporation of the polymer in a hybrid structure results in the thermal stabilization of the macromolecule.

As far as the thermal stability of C6OH/SiO<sub>2</sub> hybrid materials is concerned, investigations have been carried out by TGA analysis and compared with the thermal behavior of the corresponding neat hydroxylated trimer<sup>32,34,35</sup>. From these researches it resulted that C6OH is completely degraded at temperatures at about  $950\text{C}^\circ$ , while the corresponding hybrid shows only a weight loss close to 20% w/w at comparable temperatures.

Similar results have been reported by Leclercq concerning the thermal stability of substituted cyclophosphazene/SiO<sub>2</sub> or TiO<sub>2</sub> hybrid derivatives<sup>36,39</sup>.

An improved thermal stability of cyclophosphazene-containing SiO<sub>2</sub> composites with respect to that of the original substrates was observed also by Rose<sup>10</sup> for bulky materials prepared starting from cyclophosphazenes functionalized with -Si(OR)<sub>3</sub> residues. From these investigations it was concluded that the discriminating factor on the thermal stability of the final composite was the type of P-Substituent bond present in the cyclophosphazenes. In fact the thermal stability of the hybrids prepared increased from  $220\text{C}^\circ$  to  $320\text{C}^\circ$  and eventually to  $430\text{C}^\circ$  depending on the presence of P-NH, P-O or P-C bonds, respectively, in the phosphazene substrates. This is not surprising in view of the particular thermal stability of the phosphorus carbon bonds with respect to phosphorus-oxygen and especially phosphorus-nitrogen linkage<sup>85</sup>.

## Phosphazene/Silica Hybrids with Improved Mechanical Properties

In an analogous way the mechanical properties of the above described phosphazene/SiO<sub>2</sub> composites were investigated using DMTA and Stress-Strain techniques, together with surface hardness measurements.

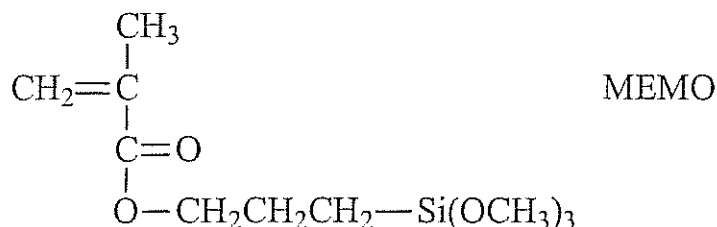
It was found that MEEP/TEOS 50/50 composites cured at room temperatures were free-standing films with remarkable dimensional stability throughout the range of temperatures selected for measurement. The storage modulus of the hybrids started from about  $10^{11}$  dynes/cm<sup>2</sup>, decreased during glass transition of the polymer component, leveling at about  $10^8$  dynes/cm<sup>2</sup> and further increased with the increase in temperature up to  $10^9$  dynes/cm<sup>2</sup>. The improvement in the mechanical properties of MEEP/SiO<sub>2</sub> composite was attributed to pseudo crosslinking phenomena between the SiO<sub>2</sub> network and the oligoethyleneoxide phosphazene substituent<sup>17,21</sup>. Flexible phosphazene coatings resisting to scratch and abrasion<sup>15,16,18</sup> or fibers<sup>19,20</sup> were also prepared starting from MEEP/SiO<sub>2</sub> composites to evidence the great flexibility of materials obtained starting from an unique MEEP chemical substrate.

Similar results were observed when MEEP/TiO<sub>2</sub>, MEEP/ZrO<sub>2</sub> and MEEP/Al<sub>2</sub>O<sub>3</sub> composites were exploited<sup>22,23</sup> as evidenced by Stress-Strain tests carried out on these materials. These tests showed the great influence on the final mechanical properties of the composite of the nature of the metal alkoxide exploited to prepare composites. The materials exhibited mostly a ductile behavior, especially for MEEP/SiO<sub>2</sub> and MEEP/ZrO<sub>2</sub> hybrids, sometimes (as in the cases of Al and Si oxides hybrids) with appearance of yield points, with

tensile modulus ranging between 30-200 MPa, to indicate that the alkoxide has a significant effect in the reinforcement of MEEP polymer.

A Shore A Hardness of 82.5 on average was measured for MEEP/SiO<sub>2</sub> hybrid composites<sup>17,21</sup>.

A significant improvement of surface hardness was observed also for coatings obtained by co-condensation processes of N<sub>3</sub>P<sub>3</sub>[O(CH<sub>2</sub>)<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> and methacryloyl-propyl triethoxysilane (MEMO)



and hybrid formation with hydrolyzed TEOS (256 N/mm<sup>2</sup>) with respect to that formed by condensing MEMO alone with TEOS (208 N/mm<sup>2</sup>) which was attributed to the presence of the cyclophosphazene residue in the composite<sup>10</sup>.

### Polyphosphazene Hybrids as Ionic Conductors

The ionic conductivity of sol-gel hybrid materials doped with Ag<sup>+</sup> or Li<sup>+</sup> salts was first investigated by Ferrar<sup>22,23</sup>, who reported the addition of up to 17% (w/w) of low lattice energy salts to the MEEP/inorganic oxide composite. Thanks to the retainment of the low glass transition characteristics of MEEP polymer due to the lack of chemical linkages between MEEP and the silica matrix (*vide supra*), authors claimed that the composite should display similar charge carrying properties as MEEP solid electrolytes. The addition of potassium triflate to the MEEP/alkoxide solution does not result in remarkable differences in the formation process of the composite. The presence of this salt induces ionic conductivity phenomena with values in the range of 10<sup>-5</sup> S/cm, similarly to what observed for MEEP homopolymer system<sup>52,59</sup>. Impedance measurements were carried out under ambient conditions and without an environmental control, to compare samples with and without salt addition. Although the general shape of the curves did not change, the conductivity of the composites containing salts were several orders of magnitude higher than those without salts. In the case of MEEP/TiO<sub>2</sub> composite a conductivity of 10<sup>-8.7</sup> and 10<sup>-5.0</sup> (ohm cm)<sup>-1</sup> was measured without and with salt, respectively<sup>22,23</sup>.

These findings were recently confirmed by Kim<sup>41</sup> who investigated the ionic conductivity of MEEP/TEOS composites as a function of the lithium triflate concentration in the hybrid, TEOS percentage, and temperature.

It was found that the ionic conductivity of the above mentioned hybrids initially increases with the increase in the salt concentration up to 10-15% w/w of CF<sub>3</sub>SO<sub>3</sub>Li, to decrease successively by further addition of the salt. These facts were explained by considering that the initial increase in the number of charge carriers, which enhances conductivity until 15% w/w of Li<sup>+</sup> concentration (maximum conductivity), is followed by a progressive reduction in the

segmental motions of the polymer host due to the formation of ion-pairs or larger agglomerates, which depress the ion transportation process (decreased conductivity).

The influence of the TEOS concentration on the ionic conductivity of MEEP/SiO<sub>2</sub> composites results in a decrease in this parameter by increasing TEOS during the synthesis. This fact was accounted for by assuming a lengthening of the conduction pathway due to phase separation between MEEP and TEOS.

The maximum ionic conductivity for MEEP/SiO<sub>2</sub> compositions was  $4.6 \times 10^{-5}$  S/cm, observed at 10% w/w TEOS and 15% w/w lithium triflate.

Finally, it was noted that higher conductivity phenomena are generated with increasing temperature. Most samples showed an Arrhenius type behavior, thus suggesting that ion diffusion is the main source of conductivity in these materials.

As reported above, the Glass Transition Temperature values of hybrid electrolytes were not significantly influenced by varying the amount of TEOS in the hybrid, thus confirming that only feeble interactions take place between MEEP polymer and the SiO<sub>2</sub> network and no true covalent linkages are produced between them.

The lack of chemical interactions between MEEP and the inorganic matrix was recently overcome by Brusatin<sup>27,28</sup>, who used a MEEP derivative functionalized with free hydroxy groups, MEEP-OH<sup>61,62</sup>. These functions, in fact, are expected to induce the formation of chemical bonds by reaction with condensed silica matrices, as previously demonstrated for C6OH<sup>32,34,35</sup>.

The results of the conductivity measurements carried out on various samples of these materials as a function of lithium content, thickness and thermal treatment gave values in the order of  $10^{-6}$  S/cm for lithium-containing samples and of about two order of magnitude lower for lithium-free samples. A diffusion coefficient  $D=1.2 \times 10^{-8}$  cm<sup>2</sup>s<sup>-1</sup> of the mobile charge carriers was also calculated.

An additional interesting application of MEEP/SiO<sub>2</sub> composites doped with inorganic salts was the possibility of obtaining antistatic coatings and fibers.

Antistatic coatings were prepared by Coltrain<sup>15,16,18</sup> by dissolving an etheric phosphazene material, typically MEEP or MEEP Tetramer, in ethanol while stirring, by adding a metal alkoxide precursor (e.g. TEOS) and hydrolyzing the material by addition of aqueous hydrochloric acid. CF<sub>3</sub>SO<sub>3</sub>K was eventually added to this mixture. The final solution was then spin coated at 2000 rpm for 30 sec and the coated sample cured at 250°C for 30 min. The final coating showed a surface resistivity of log 9 Ohm/sq at ambient conditions. Small differences in the experimental conditions were adopted when titanium isopropoxide was exploited as a metal alkoxide precursor.

The preparation of conductive fibers was claimed by Landry<sup>19,20,54</sup> by blending MEEP with metal alkoxide (ZrO<sub>2</sub> and TiO<sub>2</sub>) and salts (CF<sub>3</sub>SO<sub>3</sub>K) under sol-gel conditions. The synthetic approach used to obtain these materials was similar to that used for the preparation of antistatic coatings, but in this case the final solutions were formed into fibers by extrusion processes under appropriate experimental conditions.

## PHOSPHAZENE POLYMERS AS COLORED COATINGS

The synthesis of AzoCoPOP-containing hybrid materials was exploited using a polyphosphazene containing 15 % by mole of azo dyes attached to the inorganic -P=N- chain,

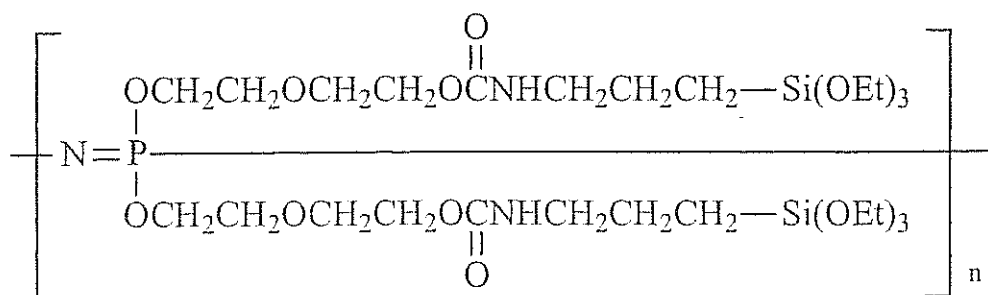
the residual 85 % of possible functionalities in the polymer being free hydroxyl groups. In this way the reaction of an ethanol solution of AzoCoPOP, with a mixture of TEOS/H<sub>2</sub>O/HCl = 1/4/0.01 on soda lime led to transparent colored films of hybrid materials showing considerably different UV visible spectroscopic features with respect to those of the original POPOH. In fact, the maximum in the UV absorption spectrum of POPOH, originally located at about 280 nm, was shifted towards the visible in a way which is respective of the possibility of electron delocalization along the azo dye/phosphazene structure, which in turn depends on the type of diazotized aromatic amine exploited for the coupling reaction with POPOH. In this way a relevant shift of the absorption spectrum of the pristine compound to form deeply colored materials could be observed.

### POPOH/SiO<sub>2</sub> HYBRID MATERIALS UNDER HIGH ENERGY IRRADIATION

Irradiation experiments using C or Au ions were performed on poly[bis(4-hydroxyphenoxy)phosphazene]/silicon oxides hybrid by J.C. Pivin<sup>29,30</sup>. The hybrid were obtained by dissolving POPOH in a solution of TEOS and ethanol, with different molar ratios between phosphazene and silica. After hydrolysis, films were deposited on silicon substrates. The analysis of the composition of films after irradiation showed that all parts of the polymeric chains are progressively destroyed, with increasing fluences of implanted ions. Carbonaceous clusters were formed by the decomposition of the phenyl rings which have an optical absorption spectrum typical of semiconductors. At higher irradiation fluences -P=N- and P-O- bonds were broken and, as a consequence, isolated silica clusters were formed. The demixing of SiO<sub>4</sub> groups from the phosphazene was detected by means of optical spectroscopy for a critical amount of energy deposited to each atom of the order of 100 eV, when most of polymer bonds was broken. In this way the structure was hardened by the carbonaceous component. Submicroscopic indentation tests showed that the films obtained were five times harder than the original samples.

### PHOSPHAZENE HYBRIDS FOR BIOMEDICAL APPLICATIONS

Phosphazene polymers for biomedical applications have been explored by Park<sup>40</sup> using a phosphazene macromolecule containing free triethoxysilane groups having the following chemical structure



to form a phosphazene/silicate network susceptible of reacting with hexamethylene diisocyanate through the urethane functionalities of the hybrid surface, eventually linking heparin residues on the surface of the phosphazene composite. The surface was fully characterized by ATR-IR spectroscopy and the final concentration of heparin groups determined by standard techniques. The biological activity of the immobilized heparin was evaluated to be 4 % that of the free heparin.

## PHOSPHAZENE HYBRID MATERIALS AS GAS SEPARATION MEMBRANES

POPOH/SiO<sub>2</sub> hybrid substrates have been exploited for the preparation of membranes for the selective separation of gas mixtures<sup>33</sup>. The general goal for this study was to obtain hybrid phosphazene-based membranes capable of performing separation processes under experimental conditions that are hardly afforded by purely polymeric membranes, i.e. high temperatures (above 100°C) and in the presence of aggressive chemicals. It has been thought, in fact, that the presence of phosphazene macromolecules in the silica hybrids should be able to improve the toughness of the ceramic network, while the stiffness of the phosphazene phase should be largely improved by the presence of the silica matrix. As a consequence, the overall mechanical and thermal properties of the composite are expected to be greatly enhanced with respect to the features of the single hybrid constituents<sup>29</sup>.

The membrane preparation process has been carried out in two steps. In the first step POPOH was dissolved in ethanol together with a TEOS solution hydrolyzed at pH = 2 (HCl). Then the reaction mixture was poured into tubular  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports (pore size 4 nm) for membrane deposition. The morphology of the deposited membrane layer was successively analyzed in dependence on the aging time and contact time in the support, with the aim of determining the best experimental conditions to prepare phosphazene-based hybrid membranes. In the second step the composite support used for POPOH membrane preparation was changed to TiO<sub>2</sub> (pore size 10 nm) and the new series of membranes obtained were tested for the selective separation of He/N<sub>2</sub> and He/CO<sub>2</sub> mixtures.

It was found that the POPOH/TEOS hybrid material forms a layer on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support and that it infiltrates the pores of the TiO<sub>2</sub> material. The membranes show an improved selectivity for the He/N<sub>2</sub> mixture, probably due to the binding action of the phosphazene polymer that limits the formation of cracks during the drying step, with an ideal selectivity very close to that of the Knudsen limit (2.65). On the contrary, in the case of He/CO<sub>2</sub> mixtures, the separation factor is far from this limit (3.65) due to an increased contribution of the viscous flow to the overall transport process.

## CONCLUSION

In this chapter we highlighted the work carried out in the field of phosphazene hybrid materials as obtained by exploiting the sol-gel technique, with particular emphasis on the synthetic approaches used for the preparation of these substrates and on the new possible practical applications of the materials obtained. It is significant that a consistent improvement of both thermal stability and mechanical properties was obtained for the large majority of

materials prepared in this way, regardless of the type of phosphazene substrate and metal alkoxide used for the materials tested and the experimental conditions adopted to synthesize them. It is also of importance that new applications (e.g. scratch-resistant coatings) have become accessible for phosphazenes and that tested applications (e.g. membranes, biomedical utilization and ionic conductors) have already found remarkable extension of their potential.

The impression is that this topic is still in its infancy and that its potential is very high for the production of new substrates for innovative applications in electro-optical, biomedical, and catalytic fields.

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