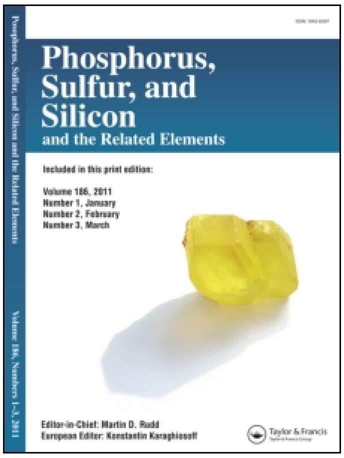

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Mazzah, Ahmed , Dez, Isabelle , Pemberton, Lydie and De Jaeger, Roger(1999) 'Organophosphazene Compounds as Modifiers of Organic Polymers: Syntheses and Characterization Aspects', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 209 — 212

To link to this Article: DOI: 10.1080/10426509908546219

URL: http://dx.doi.org/10.1080/10426509908546219

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 209-212
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Organophosphazene Compounds as Modifiers of Organic Polymers : Syntheses and Characterization Aspects

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The synthesis of new types of organic-inorganic polymers (urethane-phosphazene polymers) from cyclotriphosphazenes and the use of polyorganophosphazenes in the surface modification of organic polymers such as Poly(viny alcohol) (PVA) and poly(ethylene-co-vinyl alcohol) (EVOH) have been investigated.

In both cases, the goal of the studies was to combine the usual advantages of the organic polymers and some of the properties of phosphazenes, namely mechanical properties, thermal stability, light-heat and fire resistance by incorporating them into the carbon chain or by superficial grafting.

Keywords: Urethane phosphazene polymers, PVA, EVOH, Grafting

INTRODUCTION

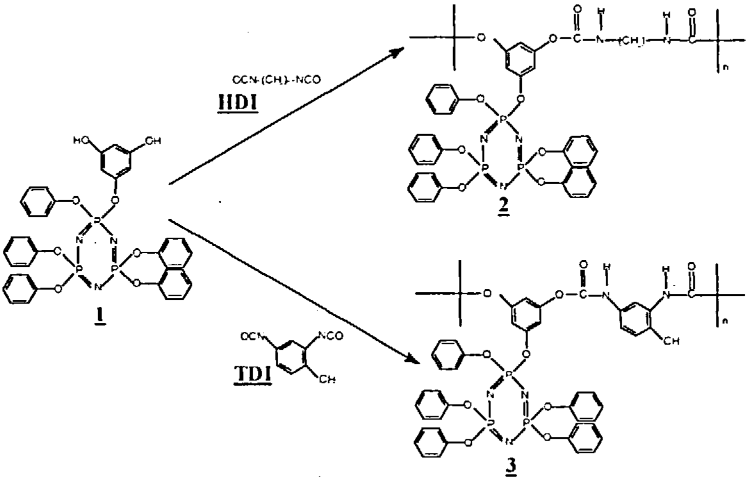
A continuous trend is observed towards the development of polymeric materials in order to improve their chemical and mechanical properties. This trend has led to the modification of polymeric materials, not only inducing important variations in their bulk properties, such as flame retardancy or thermal stability, but also modifying their surface properties.

In this paper we first report the preparation of organic-inorganic polymers from diisocyanates and cyclotriphosphazene containing two hydroxyl groups[1-2] and their characterization by thermal analysis. Then we describe different methods of grafting of a poly(organophosphazene) (POPZ) onto the surface of poly(vinyl alcohol) (PVA) and poly(ethylene-co-vinyl alcohol) (EVOH) films. The grafting process and the characterization by XPS analysis, ATR-I.R. spectroscopy and contact angle measurements of the ungrafted and grafted substrates are presented[1-4].

ORGANIC-INORGANIC HYBRID POLYMERS

The first type of modification is related to the structural modification of the chain. The phosphorus atom can be incorporated into the backbone of the resulting oligomers either by using the method previously described by Kajiwara[5], or by an alternative approach as proposed by Allen[6] for preparing a polymer in which the phosphazene is introduced as a pendant group.

In order to achieve this goal, several functional cyclotriphosphazenes were synthesized[1-2]. One of them 1 was used for the synthesis of hybrid phosphazene-urethane hybrid polymers 2 and 3 as described in the following scheme. In this case the phosphazene group was incorporated as a pendant group.



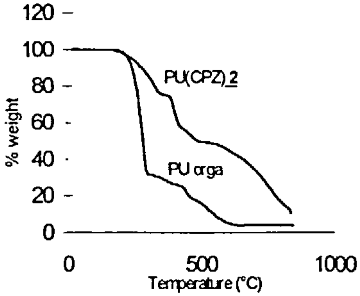
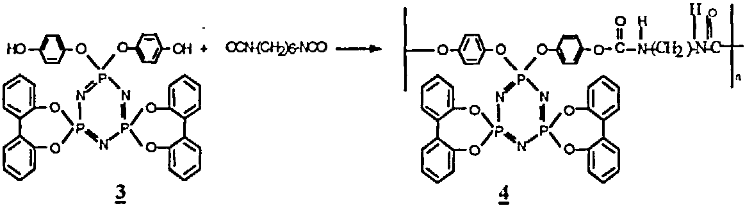


Fig. 1 : ATG of modified polymer 2 and organic polyurethane

The thermal stability and the degradation behavior of polymer 2 were investigated by thermogravimetric analysis in air. The corresponding thermogram, is compared with that of the corresponding free cyclophosphazene-urethane polymer (Figure.1). The result shows that the incorporation of the cyclophosphazene moiety increases the thermal stability of the polymer. Indeed, the temperature required for 10% weight loss (T_{10}) is 274 °C for 2 and 209 °C for the organic polymer. It is also a noteworthy feature that polymer 2 retains approximately 50% of its original weight at 500 °C, in sharp contrast with the complete decomposition of the organic polyurethane at the same temperature.

In a same way, the cyclolinear polyurethane 4 containing the phosphorus atom in the polymer backbone was obtained by reaction between HDI and 2,2-bis-

(4-hydroxyphenoxy) 4,4- 6-6-bis[spiro 2,2 dioxy,1 1 biphenyl) cyclotriphosphazene 3[2].

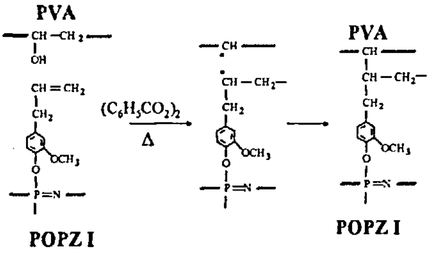


Its thermal stability was evaluated and compared with that of the organic polyurethane polymer synthesized from 3, 3'- (ethylenedioxy)diphenol and hexamethylene diisocyanate (HDI). The TGA curve exhibits the same characteristic features as the corresponding polymer with cyclophosphazene as a pendant group[1].

SURFACE MODIFICATION OF ORGANIC POLYMERS

The objective of this work was to obtain organic polymer film surfaces with some of the properties of the POPZ polymers, such as hydrophobicity, while preserving the bulk performances of the films. To achieve this goal, several strategies were explored.

First, a polyorganophosphazene bearing allylic functions (POPZI) was grafted onto the surface of a poly(vinyl alcohol) (PVA) film using the benzoyl peroxyde as a radical initiator (scheme 1).



Scheme 1

Another alternative to this process involved the reaction between a POPZ containing succinic anhydride groups with the hydroxylated film surface. In this case a comparison was made, with the use of XPS analysis, of the results obtained by changing the substrate (EVOH) or (PVA) or the concentration of the POPZ solution. This clearly demonstrated the influence of the hydroxyl group surface density and the concentration of succinic anhydride functions[4].

In both cases, ATR-IR, UV, XPS and X-ray fluorescence spectroscopies, and contact angle measurements were used to characterize the resultant surfaces. The presence of covalently bonded and cross-linked POPZ on the PVA surface conferred a hydrophobic character, which may be helpful for preserving oxygen barrier properties at high humidity level, and consequently, of great interest for packaging applications.

A third type of grafting was also used using triethoxysilane as coupling agent. In this case, three methods using this compound for the grafting of allylic functionalized polyorganophosphazenes onto the surface of PVA or EVOH copolymers films were studied.

It was shown that :

The first, based on the previous functionalization of POPZ with silane allowed us to obtain thick deposited layers. However, the substrate surface was not homogeneous.

The second, based on the previous functionalization of the hydroxylated polymers with silane, gave thin polyphosphazene grafted layers. The XPS analysis and contact angle measurements provided only slight changes in the surfaces.

Finaly, the third method which consisted of simultaneous functionalization and grafting reactions, improved the procedure, giving an intermediate thickness of the polyphosphazene layers.

In each case, this coating, conferred a hydrophobic character to the hydroxylated substrate.

CONCLUSION

The incorporation of cyclotriphosphazene either in the backbone or as a pendant group increases the thermal stability of the organic polymers. In the case of a superficial modification of PVA or EVOH with POPZ, it was shown that the grafting yield was higher when using the silylated POPZ.

This coating with polyorganophosphazenes conferred a hydrophobic character to the hydroxylated substrates. That could induce a greater resistance to the attack of moisture and consequently improve the preservation of their gas barrier properties in case of humidity exposure.

In addition, considering the large diversity of the potential structures of the POPZ polymers, it should be possible to infer many other properties, for example electrical conductibility, resistance to solvents and other chemicals, for any carbon backboned polymer bearing hydroxyl groups.

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