# Organic-Inorganic Hybrid Fillers for The Controlled Release of Antioxidants

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**Summary:** the barrier provided by the inorganic domains of organic-inorganic hybrids towards the absorption of low molecular weight penetrants was used in this study as a basis for the development of systems capable of desorbing antioxidants at a slow rate. Polyethyleneoxide-silica hybrids, compatibilized with glycidoxylpropyltrimethoxysilane, were used as carriers of conventional stabilizers for polymers, respectively two phenolic antioxidants and one hindered aromatic diamine system. Ternary phase diagrams were produced in order to determine the "compatibile compositions" using DSC to measure changes in melting point and enthalpy of the antioxidant and polyethylene oxide (PEO). A compatible composition of PEO-silica-BHT (*tert.* butyl hydroxyl toluene) was used to produce a filler, which was pressed on the form of a fine powder between two polyamide-6 films and subsequently sandwiched with further seven layers of fresh films. The multiple-film stack was aged first in an air circulated oven at 60 °C for 360 days and then for further 475 days at ambient atmospheric conditions. The concentration of carbonyl groups in the aged films was monitored by ATR-IR spectroscopy. A sigmoidal increase was found for the amount of new carbonyl groups formed, starting from the inside layer nearest to the source of antioxidant. This confirms that the antioxidant has diffused from the filler into the surrounding polymer matrix and has reduced the rate of evolution of carbonyl groups resulting from oxidative degradation reactions.

**Keywords:** aging; antioxidant; filler; organic-inorganic hybrids; slow-release

## Introduction

The main feature of organic-inorganic (O-I) hybrid materials is their nanostructured morphology, consisting of co-continuous domains of the constituent components.[1–7] These materials have invariably been prepared by the sol-gel route, starting with a metal alkoxide and either a functionalised liquid oligomer or a high molecular weight polymer in solution.[8] The metal alkoxides that have been widely used for the preparation of O-I hybrids are tetraethoxysilane for the production of silica domains. Although hybrids based on titania have also been reported in the literature, it has not been possible to obtain co-continuous domains in these systems due to the high reactivity of the alkoxide precursors and the crystalline nature of the resulting oxide.

Antioxidants, often referred to as heat stabilisers, are incorporated into polymers to prevent the deterioration of properties, resulting from "thermal oxidation reactions".[9,10]

A major difficulty experienced in achieving the highest possible efficiency in the use of stabilisers arise from two contrasting requirements: The molecules of an anti-

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oxidant are expected to have a ‘‘high mobilty’’ so that they can interact with free radicals on the polymer chains. At the same time, they must have ‘‘non-migratory’’ characteristics, i.e. ‘‘low mobility’’, to prevent them from evaporating into the atmosphere during both processing and in service.[11]

The stabilisation efficiency of antioxidants added directly to polymers (normally in the form of fine powders which melt during compounding and processing operations), is often limited by their low level of miscibility in polymers (particularly the non-polar types) which causes them to bloom to the surface of the product. The small amounts of the remaing soluble antioxidant eventually become ‘‘extinct’’ after reacting with the free radical species produced by the thermal oxidation process. This marks the end of the useful life of the product as it is followed by a rapid deterioration of the properties.[12]

The scope of this study was to explore novel methods by which the service life of polymer products can be prolonged by increasing the stabilisation efficiency of existing stabilisers through controlled release from ‘‘purposely designed’’ functional fillers.

O-I hybrids can be considered to be useful ‘‘carriers of antioxidants’’ for the production of such fillers, owing to the large resistance to the diffusion of low molecular weight penetrants,[13] which results primarily from the high tortuosity of the pathways (the organic phase and the interphases).

The investigation was focused on two types of antioxidant systems, respectively hindered phenols and aromatic amines, which were introduced into an O-I hybrid based on compatibilized polyethylene oxide (PEO) – silica systems. The PEO component was a high molecular weight type in order to provide a favourable route for the controlled release of antioxidant from the filler into the polymer, owing to both its low melting point (66 °C) and its ability to swell in water without leaching out, as it is entrapped within the percolated silica- sol nanoparticles.

## Experimental Part

### Materials

(1) The alkoxysilanes precursor used in these reactions is tetraethoxysilane (TEOS), supplied by Fluka Chemie AG, 98% pure. This is a transparent liquid, with a relative density of 0.933 and boiling point in the range 163–167 °C. Knowing that the molecular weight of TEOS is 208.33 $g \cdot mol^{-1}$ and that of $SiO_2$ is 60.08 $g \cdot mol^{-1}$ it is possible to calculate the theoretical silica content that is expected in the final hybrid.

A functionalised alkoxysilane coupling agent, 3-glycidyloxypropyltrimethoxysilane (GOTMS), was used to increase the interactions between the organic and inorganic components and to achieve a nanostructured morphology for the resulting hybrid material.[14] GOTMS it is a transparent liquid with a boiling point of 260 °C, It was supplied by Fluka Chemie AG.

(2) The antioxidants used for the production of hybrids are:
(i) 3,5-di-tert-butyl-4-hydroxytoluene(BHT). This has a melting point of 73 °C. and was supplied as a fine powder by Aldrich.
(ii) Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate. This has a melting range of 49–54 °C and was supplied by Ciba Specialty Chemicals with the trade name of Irganox 1076 (I-1076).
(iii) N-isopropyl-N′-phenyl-p-phenylenediamine. This has melting point in the range 75–80 °C and was supplied by Flexsys N.V./S.A. under the trade name of IPPD with a purity >97%.

(3) The polymer used was poly(ethylene oxide) (PEO) supplied in form of fine white powder by Union Carbide Corporation under the trade name of Polyox resin WSRN-10. The number average molecular weight is in the region of 100,000 and the melting range is 63–69 °C. It was used as a 10%w/w in THF, supplied by Fisher Chemicals as analytical grade more than 99% pure.
(4) Ethanol was used to misciblize the alkoxysilane/water mixture. It was supplied

by Fisher Chemicals, as an analytical grade. The water used was deionised in the laboratory.

(5) In the production of alkoxysilane/water precursor solution hydrochloric acid (HCl) was used as catalyst for the hydrolysis/condensation reaction. It was supplied by Fluka Chemie AG as 32% w/w solution in water and was diluted to 2% w/w with demineralised water.

(6) Poly(caprolactam) (Polyamide 6 or Nylon 6) films of thickness 12 μm were supplied by SNIA S.p.a. Polyamides were chosen for the study as they are miscible with both phenolic and amine compounds (the chemical nature of stabilisers). At the same time they represent a class of engineering polymers with poor ageing characteristics and would, therefore, benefit from extended protection through the slow release of stabilisers.

## Preparation of Antioxidant-Silica Hybrids and Characterization

A closed cylindrical glass container (25 mm diameter) was used as the reaction vessel. A paraffin oil bath on a hot plate provided the temperature control and a magnetic stirrer provided for the homogeneity of the mixture. The silica precursor solution mixture, containing TEOS, GOTMS, EtOH, $H_2O$ and HCl, was stirred for 10 minutes before the antioxidant was added in the form of alcoholic solution at 20%w/w concentration. After the incorporation of the antioxidant and the PEO solutions, the mixture was stirred in a closed vessel for one hour or until the onset of gelation, which ever occurred first. The ratio $H_2O$/TEOS was always adjusted at 1 mole of $H_2O$ per mole of alkoxy group in the system, and the GOTMS content was kept constant at a 1:0.15 molar ratio with respect to TEOS (1:0.01 weight ratio). The solution mixture was stirred for 1 hour in a closed vessel at 60 °C. and then cast as a film and the solvent was evaporate over 48 hours at room temperature before being ground into a fine powder.

The techniques used to assess the compatibility of the components in the hybrid system were: a) Visual inspection to observe whether the cast films were opaque due to the presence of phase separated domains larger than about 0.4 μm. b) Stereoscan electron microscopy on samples broken after refrigeration in liquid nitrogen, using a Stereoscan 360 apparatus by Cambridge Instrument. c) Differential thermal analysis using Dupont Instruments 910 DSC over the temperature between −30 °C and 200 °C at 10 K/minute and with a nitrogen flow of 50 $cm^3$/minute.

## Preparation and Setup of Multiple-Film Stack for Ageing

A layer (about 1 mm thick) of powdered filler PEO/Silica/BHT with weight ratio 40/40/20 (i.e. a compatible formulation) was spread between two films of Nylon 6 and compressed in a hydraulics press at 160 °C under 9.5 MPa pressure for 10 minutes, using two protective foils of PET (200 μm). This step allows large amounts of antioxidants to diffuse into the Nylon film. Circular discs were cut out from the pressed filler-film sandwich were stacked (8 on each side) according the setup used by Roe et al. and placed between two PTFE sheets and secured between perforated aluminium plates.[15] These then placed in an air circulating oven at 60 °C and removed after 360 days and then aged in a dark environment (to minimise the extent of light induced degradation) at room temperature and atmospheric pressure for 520 days. The experimental setup was devised to minimize the oxygen diffusion from the atmosphere in the second stage of ageing process. During the first stage the films were separated at various intervals so that they were all subjected to the same duration of exposure to oxygen before being placed back into the ageing oven. In this way although the extent of oxidation is reduced the approach makes it possible to emphasise the effect of antioxidant diffusion under mild oxidation conditions.

To this end the first stage of the ageing programme was devised to allow the diffusion of the antioxidant from the filler into the vary film layers, via the first layer containing large amounts of pre-dissolved antioxidant. The second stage was to induce natural oxidative ageing of the films containing different levels of infused antioxidant.

At the end of the ageing period the single Nylon films were removed from the sandwich and characterized by ATR-IR spectroscopy. Spectra were collected, as the average of 128 scans with a resolution of 4 $cm^{-1}$ over the range 4000 to 650 $cm^{-1}$, using a Nexus Thermo Nicolet instrument equipped with an attenuated total reflection accessory using ZnSe crystal. Carbonyl stretching integration in the region 1680–1780 $cm^{-1}$ was performed using the Nicolet Omnic 5.2 software. The first film (in direct contact with the antioxidant-bearing filler) and the last film (in contact with the supporting sheet) were not analysed to avoid the influence of artefacts associated with preparation procedure and difference in environmental conditions from the inner films. The films were numbered in ascending order, starting from the inner film in contact with the filler.

## Results and Discussion

### Compatibility of Antioxidants in Silica Hybrids

The hybrid systems produced were deemed to ‘‘incompatible’’ if the melting transition of the antioxidant could be identified, even if it was different from that exhibited in its isolated state due to partial miscibility. The theoretical melting enthalpy of the antioxidant was calculated on the basis that it is directly proportional to the mass content. Any discrepancy was used as an estimate of the level of incompatibility, based on the % non-crystallised antioxidant in the system.

#### *a) Binary Combinations*

The silica-phenolic antioxidant (BHT and I-1076) binary combinations were’’incompatible (i.e. not fully miscible) at any concentration. This was indicated by their opaque appearance and confirmed in the DSC analysis, which revealed a melting endothermic peak at around the melting point of the antioxidant.

The DSC scans carried out on Silica-IPPD hybrids with different combinations, on the other hand, were deemed to be ‘‘compatible’’ up to about 30–40%, depending on the preparation procedure (see Figure 1 and data in Table 1).

Both types of antioxidants, on the other hand, were found to be ‘‘compatible’’ over a wide range of compositions. Furthermore the plot in Figure 2, for PEO/IPPD systems, shows that the depression of melting point takes place for both components, which indicates that their miscibility can be attributed primarily to the strong interaction between the antioxidant and the PEO molecules. For the case of PEO/I-1076 binary systems, on the other hand, an appreciable reduction in enthalpy, resulting from partial miscibility, is evident only at low antioxidant concentrations (see Table 2).

#### *b) PEO-$SiO_2$-Antioxidant Hybrids*

In Figure 3 are presented typical DSC thermograms for ternary compositions of PEO/silica hybrids containing BHT near the miscibility threshold. For many hybrids the melting point of the individual components was found to be appreciably different from the values of the same compounds in isolation, and often the melting transition of PEO and/or BHT were completely absent [see thermogram for hybrid PEO (50)/Silica (20)/BHT (30), which shows that the PEO melting point is depressed to 55 °C (from 65 °C for pure PEO) and the $T_m$ for BHT is not visible]. At higher BHT content (60%), on the other hand, is visible the $T_m$ of BHT while the $T_m$ of PEO is depressed to 51.5 °C.

The miscibility diagram for PEO-$SiO_2$-BHT hybrids is shown in Figure 4.

The black dots represent those compositions where a separate peak of melting of

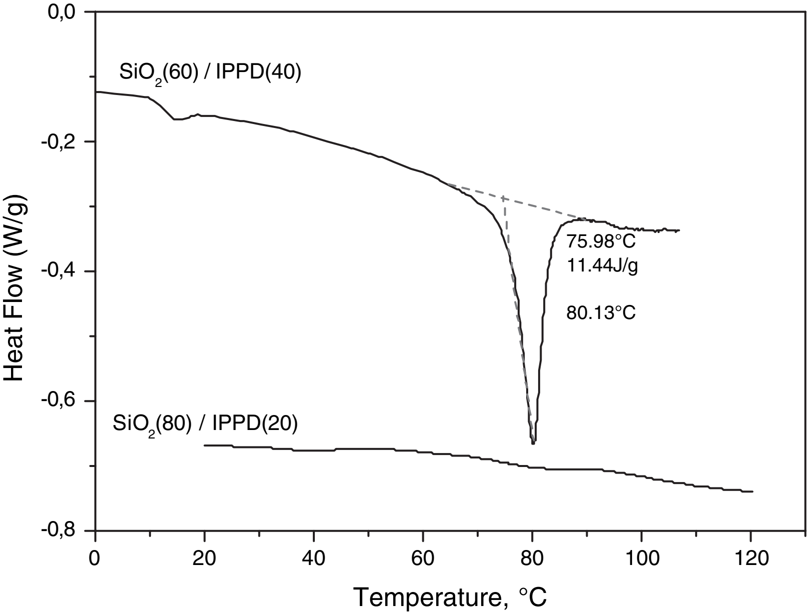

***Figure 1.***
DSC thermograms of binary Silica-IPPD hybrids of different compositions($SiO_2$(80)/IPPD(20) and ($SiO_2$(60)/IPPD(40).

BHT was clearly present, i.e. it was clearly distinguishable from the PEO melting transition at around 50 to 60 °C, even though the temperature was in some composition significantly lower than that of pure BHT crystals (see Figure 5 related to hybrid PEO (40)/Silica (10)/BHT (50). In this system: the melting transition of PEO at 55 °C is followed by a partially overlapping melting shoulder at 67 °C, which can be attributed to the co-crystallization of BHT with PEO.

Although a contour has been drawn to separate the two regions the dividing line is blurred in so far the precise location is affected by the preparation conditions and thermal history (see Figure 5)

The presence of two crystallisable components markedly complicates the situation, because in such cases the antioxidant can dissolve in the organic polymer, as well as being strongly adsorbed on the surface of the inorganic silica domains. At the same time there could be an overlap of melting

***Table 1.***
Melting enthalpy of binary Silica-IPPD antioxidant hybrids.

| Sample | $SiO_2$ | IPPD | $T_m$ | Measured $\Delta H_f$ | Theoretical $\Delta H_f$ (expected) | Discrepancy $\Delta H_f$ | % non-crystallised AO* |
|---|---|---|---|---|---|---|---|
| | % wt/wt | % wt/wt | °C | J/g (AO*+$SiO_2$) | J/g (AO*) | J/g (AO*) | |
| Pure $SiO_2$ | 1 | 0 | N/A | 0 | 0 | 0 | 0 |
| IPPD(20) | 80 | 20 | N/A | 0 | 24.6 | 24.6 | 100 |
| IPPD(30) | 70 | 30 | 75.4 | 2.6 | 36.9 | 34.3 | 93 |
| IPPD(40) | 60 | 40 | 80.1 | 11.4 | 49.2 | 37.8 | 77 |
| IPPD(60) | 40 | 60 | 79.1 | 46.1 | 73.9 | 27.8 | 38 |
| Pure IPPD | 0 | 100 | 81.8 | 123.1 | 123.1 | 0 | 0 |

* AO refers to Antioxidant.

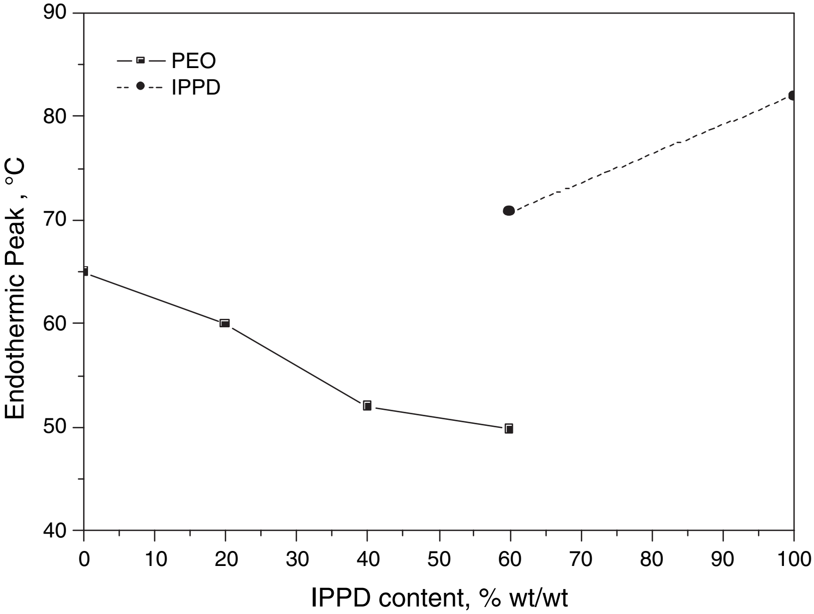

***Figure 2.***
Variation of melting transition in binary mixtures of PEO/IPPD.

transitions (particularly when the $T_m$'s of the two crystallisable components are close), even if these are present as separate phases. For compositions containing 10 %w/w I-1076 and PEO/silica ratio equal to 45/45, for instance, there is a clear phase separation (Figure 6 left) This means that the disappearance of the melting curve of the phenolic antioxidant I-1076 in some of the DSC thermograms could be an artefact caused by PEO obscuring the melting of the minor phase. This is confirmed by the observation that the melting transition of the I-1076 component at higher concentrations appears as shoulder in the PEO melting curve.

A close examination of the micrographs in Figure 6provides an insight into the importance of miscibilising the PEO/silica components and, preferably, also the PEO/antioxidant combination, in the ternary antioxidant hybrid. From a visual examination of these micrographs it is noted that PEO crystallises into large spherulites containing clusters of well separated fibrillar/lamellae domains, while the antioxidant precipitates as discrete particle miscible PEO/silica phase, which prevents it from shrinking unimpeded into a continuous and homogeneous structure. At the same time, it should be noted that if the silica component had precipitated it would have

***Table 2.***
Melting enthalpy of PEO/Irganox 1076 mixtures.

| Sample | PEO | Irganox 1076 | $T_m$ | Measured $\Delta H_f$ | Theoretical PEO $\Delta H_f$ | Discrepancy $\Delta H_f$ [measured - calculated PEO] |
|---|---|---|---|---|---|---|
| | % wt/wt | % wt/wt | °C | J/g | J/g | J/g |
| Pure PEO | 100 | 0 | 64.8 | 153.2 | | |
| PEO (90) -I1076 (10) | 90 | 10 | 60.4 | 111.3 | 137.9 | −26.6 |
| Pure I-1076 | 0 | 100 | 52.7 | 80.6 | – | – |

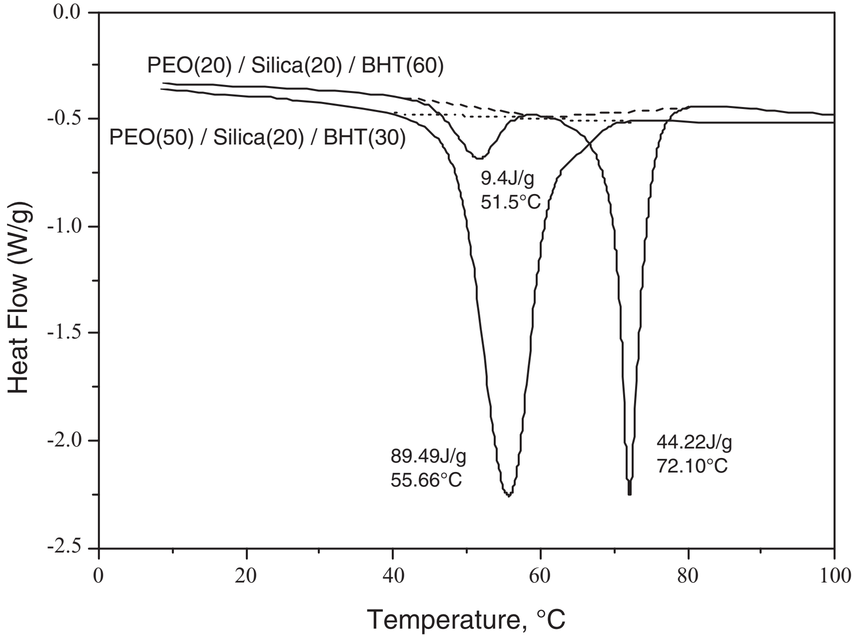

***Figure 3.***
DSC thermograms of ternary hybrids PEO/Silica/BHT[PEO(20)/Silica (20)/BHT(60) and PEO(50)/Silica(20)/BHT(30)].

appeared as uniform spherical nano-dimensioned particles, which would not have been subjected to the tridimensional constraints revealed by the morphology of the systems.

The lack of miscibility of PEO/I-1076, therefore, has to be held responsible for the incompatibility of PEO/silica/I-1076 ternary hybrids, as it allows the I-1076 to undergo a rapid crystallisation (see Figure 7–right). Its low level of solubility allows it to precipitate out at very low concentrations, i.e in the early stages of the ''preparation'' when the viscosity of the surrounding medium is still relatively low (Figure 6 – left).

Contrary to the above, in the case of PEO-$SiO_2$-IPPD hybrids the three components interact strongly so that complete compatibilisation is achieved even at relatively high IPPD concentrations (Figure 7 – left).

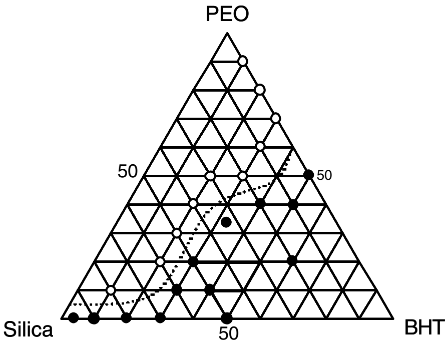

***Figure 4.***
Miscibility diagram for PEO/Silica/BHT hybrids.

## Diffusion of Antioxidant from Hybrid Silica Fillers

A ternary hybrids, selected from the regions of miscible compositions and both containing 20% BHT, 40% silica, and 40% PEO were used to assess the diffusion characteristics of the antioxidant from the filler and into the polyamide matrix.

### Spectra of Aged Films

It was not possible to discern the presence of BHT in the ATR-IR spectra of the aged Nylon 6 films due to the many overlapping

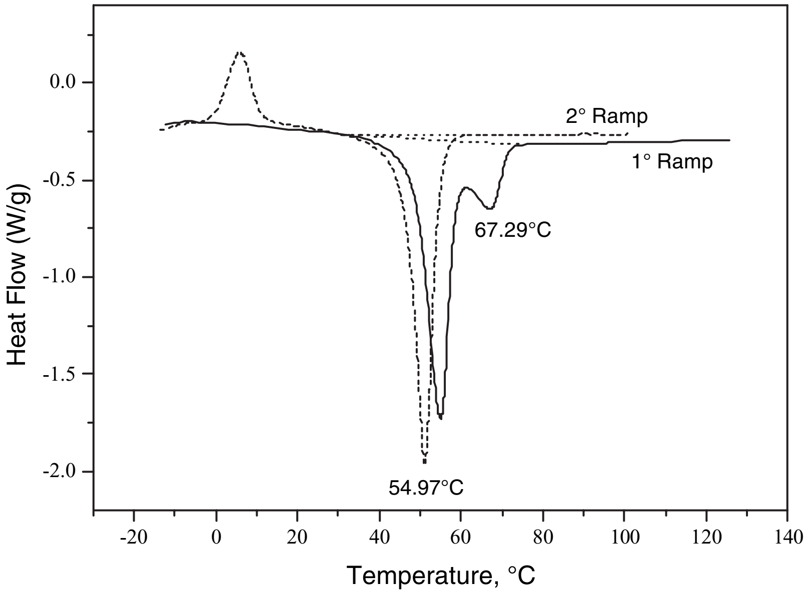

***Figure 5.***
Effect of thermal history on DSC thermograms of ternary hybrids [System PEO(40)/Silica(10)/BHT(50)].

absorptions bands. Some important features of the degradation reactions can be observed in the carbonyl region (1690–1780 $\text{cm}^{-}1$). In particular the Nylon 6 films subjected to prolonged ageing, as described in the experimental section, show an increase of absorption intensity in the region 1690–1780 $\text{cm}^{-1}$ due to the formation of different carbonyl groups.

Figure 8 shows the ATR spectra for the carbonyl region of individual Nylon 6 films within the stack after ageing. Each spectrum is identified with a number in ascending order, which denotes the position with respect to the PEO-Silica-BHT filler. The spectrum of Nylon 6 before ageing is also reported for comparison.

Unaged Nylon 6 exhibits only a small carbonyl absorbance band, which is ascribed to the presence of vary species formed during the processing of the neat polymer films.

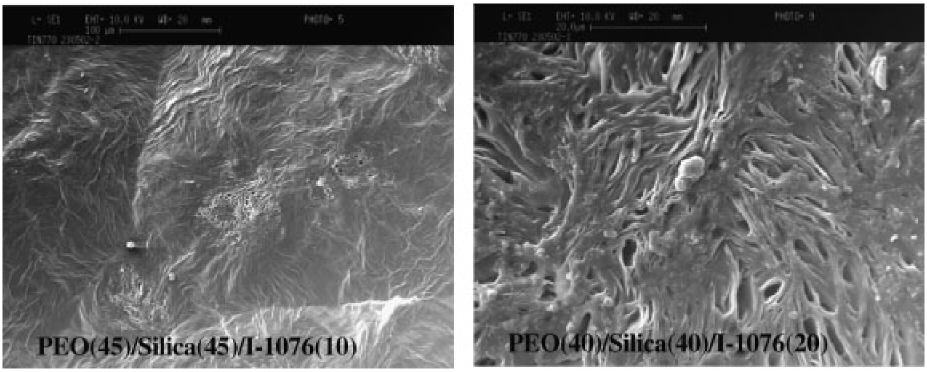

***Figure 6.***
SEM micrographs of ternary PEO/Silica/I-1076 hybrids. This morphology arises as a result of the constraints imposed by the surrounding.

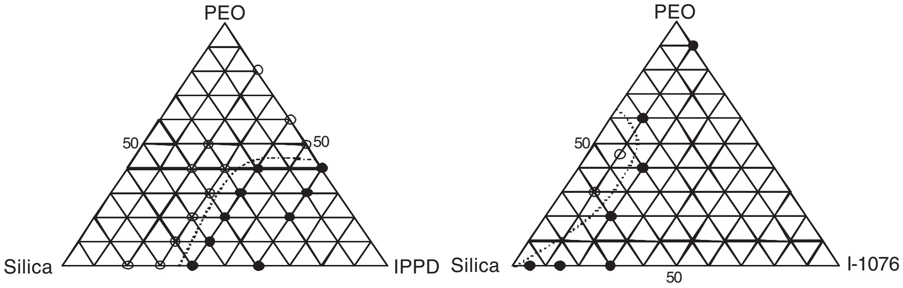

***Figure 7.***
Miscibility diagrams for PEO/Silica/IPPD and PEO/Silica/I-1076 systems.

The effect of prolonged ageing is evident from ATR spectra related to the several films present inside the stack. These spectra show that the films closer to the PEO-Silica-BHT filler exhibit a broad absorption band due to the overlapping of at least two absorption peaks at 1710 $cm^{-1}$ and 1725 $cm^{-1}$. Furthermore a shoulder can be detected at 1735–1740 $cm^{-1}$. On the other hand, those films further from the antioxidant source (the filler) show an absorption band with identifiable peaks at 1738, 1725 and 1710 $cm^{-1}$. A fourth peaks can be detected at 1690 $cm^{-1}$ through the second derivative of the spectrum. This peak is superimposed by the absorbance due to the primary amide groups at 1640 $cm^{-1}$ (not shown in the spectra) and it is less evident in the spectra of the films closer to the antioxidant reservoir. The identification and the assignment of the several absorbance bands was carried out according to the analysis by Cerruti et al.[16] The two peaks at 1735 and 1690 $cm^{-1}$ are

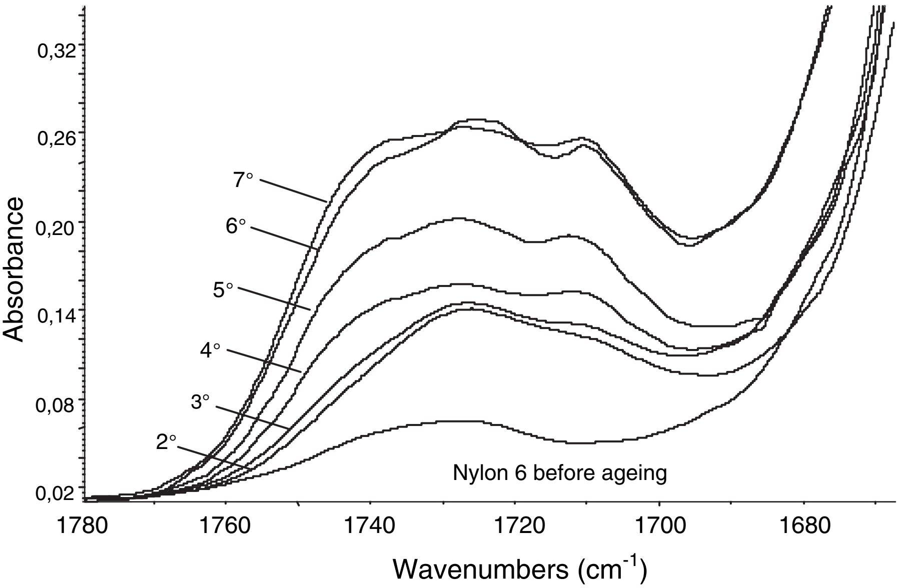

***Figure 8.***
Evolution of the carbonyl region of Nylon 6 films during ageing (The numbers on the curves denote to the position of the film in the stack: The smallest number, corresponds to the film closest to the filler. The largest number refers to the film furthest from the filler.)

associated with the presence of imide groups (–$CH_2CONHCOCH_2$–). The absorbance peak at 1710 $cm^{-1}$ is attributed to associated carboxylic acids, and the absorbance peak at 1725 $cm^{-1}$ is due to the presence of aldehyde groups. However the experimental results can be rationalised by taking into account the simplified photo-oxidation of polyamides proposed by Tang et al.[17] and the auto-oxidation process proposed by Shelton et al.[18]. The absorbance features due to the presence of imides groups (1738 and 1690 $cm^{-1}$) clearly increases with increasing the distance from the source of antioxidant (i.e.the film closest to the filler). In particular the peak at 1738 $cm^{-1}$ is very useful to describe the effect of the stabilization processes due to the antioxidant because its absorbance (intensity or area) does not depend on the contribution of carbonyls groups of Nylon 6 (primary amide) in the carbonyl region. The increase in amount of imide groups moving from the inner towards the external films can be correlated with the release of BHT from the PEO-Silica-BHT filler and its subsequent diffusion throughout the multiple-film stack. The films closer to the antioxidant carrier exhibits the lowest level of oxidation, indicated by the low concentration of imide groups, because the ability of BHT to diffuse and to trap a large amount of free radicals.

The films remote from the filler, on the other hand, contain a large amount of imide groups because of the lower amounts of BHT arriving from the reservoir and not available to delay the autocatalytic propagation reactions.

The presence of carboxylic acid groups (1710 $cm^{-1}$) and aldehydes (1725 $cm^{-1}$), which are observable in the spectra related to the films closer to the BHT source, on the other hand, could be due to the inefficiency of BHT for the trapping of all free radicals generated during the ageing period.

Further insights about the oxidative degradation of the Nylon 6 films can be obtained from the plot in Figure 9, showing the increase of the overall carbonyls in the range 1680–1780 $cm^{-1}$. In particular in Figure 9 is reported the change in the area under the carbonyl region for the different films in ascending order from the BHT source. The area was integrated with respect to a linear baseline whose end points were selected for each films in the region between 1780 and 1695 $cm^{-1}$ according to the IR spectrum shape.

The sigmoidal shape of trend line for the increase of absorbance in the carbonyl region with distance from the filler is

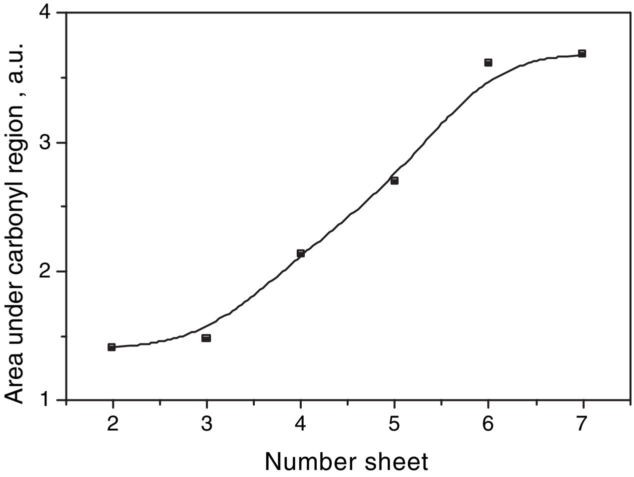

**Figure 9.**
Change of carbonyl absorption area in ATR-IR spectra of Nylon 6 films after ageing.

indicative of the slow diffusion of BHT that has taken place during ageing. The rapid increase in carbonyl groups from the third film onwards indicates that a significant amount of BHT is only just reaching these positions, while the constant and larger amounts of carbonyl groups in the 6th layer and above indicates that they are free of BHT.

## Conclusion

From the results of the work and the related discussion it can be concluded that it is possible to produce functional fillers containing large amounts of an antioxidant fully miscibilised with the polyethylene oxide and silica using a sol-gel preparation procedure.

It has been shown that amine based antioxidants can be compatibilised over a wider range of compositions than phenolic types. Furhermore the presence of a long aliphatic chain in a phenolic system drastically reduced the maximum amount of antioxidant can be incorporated into the filler.

From simulated ageing experiments on Nylon 6 films it has been shown that the antioxidant can diffuse into the surrounding polymer matrix and reduce the rate of evolution of carbonyl groups resulting from oxidative degradation reactions.

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