



Interactions between a phenolic antioxidant, moisture, peroxide and crosslinking by-products with metal oxide nanoparticles in branched polyethylene



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ABSTRACT

Polyethylene composites based on metal oxide nanoparticles are emerging materials for use in the insulation of extruded HVDC cables. The short-term electrical performance of these materials is adequate, but their stability for extended service needs to be assessed. This study is focussed on the capacity of the nanoparticles to adsorb polar species (water, dicumyl peroxide and byproducts from peroxide-vulcanisation, acetophenone and cumyl alcohol) that have an impact on the electrical conductivity of nanocomposites, the oxidative stability by adsorption of phenolic antioxidants on the nanoparticles and the potential transfer of catalytic impurities from the nanoparticles to the polymer. The adsorption of water, dicumyl peroxide, acetophenone, cumyl alcohol and Irganox 1076 (phenolic antioxidant) on pristine and coated (hydrophobic silanes and poly(lauryl methacrylate)) Al₂O₃, MgO and ZnO particles ranging from 25 nm to 2 μm was assessed. Composites based on low-density polyethylene and the particles mentioned (≤12 wt.%) were prepared, the degree of adsorption of Irganox 1076 onto the particles was assessed by OIT measurements, and the release of volatile species at elevated temperature was assessed by TG. The concentration of moisture adsorbed on the particles at 25 °C increased linearly with both increasing hydroxyl group concentration on the particle surfaces and increasing relative humidity. Dicumyl peroxide showed no adsorption on any of the nanoparticles. Acetophenone and cumyl alcohol showed a linear increase in adsorption with increasing concentration of hydroxyl groups, but the quantities were much smaller than those of water. Irganox 1076 adsorbed only onto the uncoated nanoparticles. Uncoated ZnO nanoparticles that contained ionic species promoted radical formation and a lowering of the OIT. This study showed that carefully coated pure metal oxide nanoparticles are not likely to adsorb phenolic antioxidants or dicumyl peroxide, but that they have the capacity to adsorb moisture and polar byproducts from peroxide vulcanisation, and that they will not introduce destabilizing ionic species into the polymer matrix. Low contents of dry, equiaxed ZnO and MgO particles strongly retarded the release of volatile species at temperatures above 300 °C.

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1. Introduction

Polymer nanocomposites are emerging materials for use in applications where reliability and a long lifetime are important. One of the first large-volume polymer nanocomposites based on montmorillonite and polyamide-6 is used in automotive applications [1]. Polymer nanocomposites in electrical insulations

currently receive a growing interest [2–7]. The first paper on polymer nanodielectrics dates back to 1994 [7].

The large specific surface area of the nanoparticles is one reason for the interest in these hybrid materials. A large fraction of the polymer is thus in close contact with the nanoparticle surfaces even in composites with a low filler content. The polymer layer adjacent to the nanoparticles shows mechanical, thermal and electrical properties different from those of the pristine polymer [8–20].

The use of metal oxide nanoparticles in polyethylene in high-voltage direct current (HVDC) cable insulation has recently received considerable interest. A Scopus search using the key words

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HVDC, nanocomposite and polyethylene revealed 52 articles: 28 peer-reviewed articles in journals, 21 conference papers and 3 reviews. The publication rate shows a pronounced increase since 2012. Nanocomposites based on small additions of MgO with a favourably low electrical conductivity and a low build-up of space charges were first reported in 2005 [21], followed by other papers on the same class of nanocomposites [22–25]. Similar data have been presented for ZnO nanocomposites [26,27]. Polyethylene/Al₂O₃ nanocomposites have received less attention [28]. The fact that the electrical conductivity of the nanocomposites is lower than for that of pristine low-density polyethylene is crucial for HVDC cables; the percentage loss of energy over a given distance of transmission decreases with increasing voltage. In order to move forward from today's maximum voltage for extruded HVDC cables (525 kV) to 1 MV, an almost ten-fold decrease in electrical conductivity is required [29].

Although an approach based on polyethylene nanocomposites is feasible, the effect of ageing, i.e. oxidation, the migration of polar or even ionic species from the surrounding materials, and the effects of impurities in the insulation need to be studied before the long-term functionality of these novel insulation materials can be guaranteed. The presence of low molar mass polar species, such as the peroxide-crosslinking by-products acetophenone (1-phenylethanone) and cumyl alcohol (2-phenyl-2-propanol), increases the electrical conductivity [29]. A low-level oxidation of polyethylene has a moderate depressing effect on the electrical conductivity [30]. These findings indicate that low molar mass polar species with a high mobility increase the electrical conductivity, whereas moderately polar polymer species act as traps for low molar mass species and thus tend to decrease the electrical conductivity. One of the potentially important effects of nanoparticles is their ability to trap polar and ionic species, especially in a hydrophobic polymer like polyethylene. The large specific surface area of the nanoparticles means that the nanoparticles are able to adsorb a substantial amount of low molar mass species. Many hydroxyl groups are present on the metal oxide nanoparticles [31–33], and these attract polar species, especially those that can form hydrogen bonds. However, it is essential that the particles are uniformly dispersed in the polymer, minimizing agglomeration of the nanoparticles, in order to avoid early electrical breakdown by treeing [34]. This can be achieved by surface treatment of the nanoparticles with a coating chemically compatible with the matrix polymer. The metal oxide nanoparticles thus need to be coated with a hydrophobic compound to be suitable for use in polyethylene. The question then is how the coating layer will influence the capacity of the nanoparticles to adsorb mobile polar species. Although polyethylene/metal oxide composites have shown suitable electrical properties compared with neat polyethylene, their durability has been questioned due to the interactions between active particle surfaces and antioxidants in the composites. Allen et al. [35] reported that the TiO₂ nanoparticles induced more degradation of polyethylene during processing and thermal ageing than micrometre-sized TiO₂ particles. Allen et al. [36] also found that the adsorption of antioxidants on SiO₂ nanoparticles made the composite more prone to oxidation than an unfilled pristine polymer with the same amount of antioxidant. Wong et al. [37] reported that organo-modified clay can increase the formation of free radicals and accelerate the depletion of antioxidant in composites. Morlat–Therias et al. [38] reported that the stability of PE/montmorillonite nanocomposites was lower than that of unfilled PE, which was attributed both to the adsorption of antioxidants on particles and to the catalytic effect of metal ions on polymer degradation.

The present study has used a standard method (oxidation

induction time (OIT) measurements by DSC) to reveal the adsorption of a phenolic antioxidant (Irganox 1076) onto a range of pristine and coated metal oxide (Al₂O₃, MgO and ZnO) particles ranging in average size from 25 nm to 2 μm. The particles have been coated with a hydrophobic silane (octyltriethoxysilane or octadecyltrimethoxysilane) and with a hydrophobic polymethacrylate (poly(lauryl methacrylate)) using atom transfer radical polymerisation. The concentration of phenolic antioxidant was deliberately kept low in order to avoid internal precipitation of the antioxidant [39]. Standard methods used to determine the antioxidant concentration in polymers, such as extraction followed by liquid chromatography fail to discriminate between efficient (soluble in the polymer matrix) and less efficient (adsorbed onto particles or internally precipitated) antioxidants. The OIT method, on the other hand, is sensitive to this difference in state of the antioxidants, and thus makes possibility to determine the fraction of adsorbed antioxidant [40,41]. The results obtained by OIT-DSC were further substantiated by assessing the amount of adsorbed antioxidant on the nanoparticles in *n*-heptane (a low molar mass analogue of polyethylene) using UV–Vis spectroscopy. The same approach was used to study the adsorption of crosslinking by-products (acetophenone and cumyl alcohol), because it is almost impossible to assess the adsorption of these compounds on the nanoparticles housed in polyethylene.

The particles studied were characterized with regard to size, specific surface area, hydroxyl group concentration and surface coating structure. The degrees of dispersion of the particles in the composites were assessed using electron microscopy. The adsorption of water, dicumyl peroxide, crosslinking by-products (acetophenone and cumyl alcohol) and a phenolic antioxidant on metal oxide particles was studied in *n*-heptane and polyethylene. An unexpected thermal stability of the polymer nanocomposites at high temperatures was noticed.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O, ≥ 98%), zinc acetate dihydrate (Zn(CH₃COO)₂ · 2H₂O, ≥ 99 wt.%), magnesium chloride (MgCl₂ · 6H₂O, ACS Reagent), sodium hydroxide (≥98%), ammonia hydroxide (aq. 25 wt.%), *n*-heptane (≥99.5%), octyltriethoxysilane (CAS number 2943–75–1, referred to as C8, ≥98%, 276.5 Da), octadecyltrimethoxysilane (CAS number 3069–42–9, referred to as C18, ≥90%, technical grade, 374.7 Da) and 3-aminopropyl (diethoxy)methylsilane (CAS number 3179–76–8; 97%) were purchased from Sigma Aldrich and used as received. 2-Bromoisobutyl bromide (CAS number 20769–85–1; 98%), copper(I) bromide (CAS number 7787–70–4; CuBr, 98%), copper(II) bromide (CAS number 7789–45–9; CuBr₂, 99%), 4-(dimethylamino)pyridine (CAS number 1122–58–3; 99%), triethylamine (CAS number 121–44–8; 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (CAS number 3083–10–1; 97%) and lauryl methacrylate (CAS number 142–90–5; 96%) were obtained from Sigma–Aldrich. Lauryl methacrylate was destabilized prior to use by passing it through a column of Al₂O₃ (neutral). 2-Propanol (≥98%) and ethanol (≥96 wt.%) were supplied by VWR. High resistivity Milli-Q water (18.2 MΩcm at 25 °C) was used in all the reactions. Tetrahydrofuran (THF; analytical grade), dichloromethane (analytical grade), methanol (HPLC-grade), diethyl ether (HPLC-grade) and toluene (HPLC-grade) were obtained from Sigma–Aldrich and used without further purification. A phenolic antioxidant, Irganox 1076 (octadecyl-3-(3,5-di-tert butyl-4-hydroxy phenyl)-propionate; CAS number 2082–79–3, *M* = 531 Da, melting point = 50–55 °C), was purchased from Ciba Speciality Chemicals, Switzerland. Dicumyl

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