Migration of a phenolic antioxidant from aluminium oxide-poly(ethylene-*co*-butyl acrylate) nanocomposites in aqueous media

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ABSTRACT

The migration of a phenolic antioxidant (Irganox 1010) from nanocomposites based on aluminium oxide (2–12 wt.%; uncoated or coated with aminopropyltriethoxysilane or octyltriethoxysilane) and poly (ethylene-*co*-butyl acrylate) (EBA) with 13 wt.% butyl acrylate nanocomposites in aqueous media (liquid water or air with 100%RH) at 90 °C was studied. The concentration of effective antioxidant in the composites was assessed by the oxidation induction time (OIT) measured by DSC. The flat OIT-profiles through the materials showed that the migration was controlled by the boundary conditions. The boundary antioxidant loss rates to the different media were (in relative units): 1 (dry air; data reported earlier), 1.5–3 (humid air) and 4–10 (liquid water). OIT-profiles for two-layer sandwich samples (a pristine EBA layer and a nanocomposite layer containing 0.2 wt.% Irganox 1010) showed that the antioxidant diffusivity was lowest in the composites containing uncoated nanoparticles (which had the highest surface concentration of hydroxyl groups of all the studied nanoparticles). The presence of water in the composites had only a small effect on the diffusivity; it was 10–50% greater than in the dry systems.

1. Introduction

Polymer nanocomposites are emerging materials for use in electrical insulation and other electrical applications [1–4]. Oxides of silicon, aluminium and titanium have attracted attention as in certain polymer matrices they provide a package of attractive thermal, mechanical and dielectric properties [5–7]. The control of particle dispersion in polymer nanocomposites in electrical insulations is vital, because agglomerates reduce the electrical breakdown strength. The high concentration of hydroxyl groups on the aluminium oxide nanoparticle surfaces (see e.g. McCafferty and Wightman [8]) provides a driving force for particle agglomeration. In addition, hydroxyl groups attract water molecules and lead to a significant water uptake in polymer composites containing uncoated aluminium oxide nanoparticles [9]. These two effects can be reduced by a surface treatment to reduce the hydroxyl group concentration and introduce suitable organophilic groups onto the aluminium oxide nanoparticle surfaces [9,10]. Reactions between the hydroxyl groups on the nanoparticle surfaces and organic

silanes (a wide range of different compounds are commercially available; Refs. [11–13] present a general background on these compounds and how they react with metal oxides) provide an avenue of possibilities to tailor the particle surfaces to achieve nanocomposites with a uniform particle distribution, a low water uptake and other useful functionalities.

Reliability and a long lifetime are essential for all polymeric materials used in electrical insulations. The long-term performance of polymer nanocomposites has not yet been studied to the same extent as that of the traditional materials used in electrical insulations. The interaction between antioxidants and a series of aluminium oxide nanofillers in poly(ethylene-*co*-butyl acrylate) (EBA) was recently studied [14]. Uncoated nanoparticles adsorbed a substantial fraction of the phenolic antioxidant (Irganox 1010) added to the EBA composites, whereas the composites containing octyltriethoxysilane- or aminopropyltriethoxysilane-coated nanoparticles showed a different behaviour: a low antioxidant adsorption on the particle surfaces, and a greater initial stability of one of the systems, as revealed by oxidation induction time data. It was also found that the adsorbed antioxidant molecules were slowly released during dry air ageing [14]. The present paper presents a further study of the same group of materials but with a new focus. Polymer insulators are in many instances in contact with moisture. Even in hydrophobic polymers such as polyethylene, moisture may have an

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impact on the lifetime, e.g. by water treeing that may be followed by electrical treeing and breakdown [15]. The current paper presents results from the ageing in aqueous media of composites containing aluminium oxide nanoparticles (uncoated and coated with octyltriethoxysilane or aminopropyltriethoxysilane) and EBA stabilized with 0.2 wt.% Irganox 1010. One of the media used, liquid water, saturates the polymer and also the available sites on the nanoparticles with moisture [9]. In addition, water was expected to have an effect on the boundary conditions by modifying the rate of loss of antioxidant at the boundary with respect to that towards a gas phase. Air at 100%RH should have exactly the same effect on the internal structure and processes, because the chemical potentials of water in the two media are exactly the same. We have found no scientific papers that present studies on the interactions between water, antioxidant and nanoparticles in polymer nanocomposites, despite their obvious practical relevance.

2. Experimental

2.1. Materials

Poly(ethylene-co-butyl acrylate) with 13 wt.% butyl acrylate (EBA) was supplied by Borealis, Stenungsund, Sweden. The density of the EBA was 924 kg m^{-3}. The melt flow index was 1.1 g (10 min)$^{-1}$ according to ISO 1133 (190 °C, 2.16 kg weight). Nanodur (ND) nanoparticles, supplied by Nanophase Inc., Romeoville, Illinois, USA, had the following characteristics: γ-phase Al$_2$O$_3$, spherical particle shape, average diameter = 45 μm, specific surface area = 40–45 m^2 g^{-1} according to nitrogen adsorption [10,14]. The nanoparticles were either used as received (uncoated) or after being coated with aminopropyltriethoxysilane or octyltriethoxysilane. Full details of the coating procedures have been presented in earlier papers [10,14]. The silane coverages of the aluminium oxide nanoparticles were 0.7 μmol silane m^{-2} (octyltriethoxysilane) and 2.2 μmol silane m^{-2} (aminopropyltriethoxysilane) [10]. The conversion from molar to molecular units is as follows: 1 μmol silane m^{-2} ≈ 0.60 silane molecule (nm)$^{-2}$. Surface energies calculated for uncoated, aminopropyltriethoxysilane-coated and octyltriethoxysilane-coated Al$_2$O$_3$ were 67, 38 and 35 mJ m^{-2} respectively, according to contact angle measurements (CAM 200, KSV Instruments Ltd., Helsinki, Finland) using water and diiodomethane. Irganox 1010 (CAS Number 6683-19-8; pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)) was provided by Ciba Specialty Chemicals Inc., Switzerland. EBA nanocomposites containing 0.2 wt.% Irganox 1010 and different mass fractions of nanoparticles (2, 6 and 12 wt.%) were prepared. The details of the procedures used are presented in papers by Gedde et al. [10,14]. The dispersion of the nanoparticles in the EBA matrix was generally good. The average numbers of nanoparticles in small agglomerates were: 1.7–2.3 (uncoated ND composites), 1.6–2.5 (aminopropyltriethoxysilane-coated ND composites) and 1.3–1.7 (octyltriethoxysilane-coated ND composites) [10]. The composites contained only a few large agglomerates; fewer than 5% of the nanoparticles were present in such agglomerates [10].

The extruded tape samples used in this study were 1 ± 0.2 mm thick and 60 ± 3 mm wide. Differential scanning calorimetry showed that the polymer crystallinity was 43 ± 2 wt.% and that the peak melting temperature was 104.5 ± 0.5 °C [10]. Sandwich samples with a total thickness of 3 mm consisting of a 1.5 mm layer of unstabilised EBA and a 1.5 mm layer of a compound containing 6 wt.% nanofiller particles (uncoated ND and ND coated with octyltriethoxysilane or aminopropyltriethoxysilane) and 0.2 wt. % Irganox 1010 were prepared. Dried pristine EBA–13 powders was compression-moulded into 1.5 mm thick sheets in a TP400 Fontijne Press (Netherlands) at 170 °C by applying a compressive load of

300 kN for 5 min and then cooling the material at a rate of 10 °C min^{-1} to room temperature while maintaining the compressive load. The nanocomposite layers were obtained by compression moulding of extruded tape materials in the aforementioned press. The sandwich samples were finally prepared by compression moulding at 170 °C for 5 min followed by a 10 °C min^{-1} cooling to room temperature while maintaining the compressive load.

2.2. Ageing of nanocomposite samples

The tape samples (thickness = 1 ± 0.2 mm) were aged in a ULE-699 ventilated oven (Memmert, Germany) at 90 ± 1 °C in two different media: (i) air at 100%RH and (ii) liquid water. The sandwich samples were aged at the same temperature in dry air (<5%RH) and in air at 100%RH.

2.3. Differential scanning calorimetry

A temperature- and energy-calibrated Mettler Toledo DSC-820 differential scanning calorimeter was used to assess the oxidation induction time (OIT). Samples weighing 20–26 mg were placed in 100 μL aluminium pans and sealed with a lid perforated with three 1 mm holes to allow gas transport to the sample. The samples were heated from 25 to 200 °C (rate = 10 °C min^{-1}) in nitrogen (flow rate = 50 mL min^{-1}), and kept at this temperature for 5 min while maintaining the nitrogen flow, after which the purge gas was switched to oxygen (flow rate = 50 mL min^{-1}). The OIT was obtained as the time between the oxygen switch and the intersection with the isothermal base line of the tangent to the curve at the point which deviated exothermally by 0.2 W g^{-1} from the base line. Each data point presented is the average of two independent measurements. The scatter in OIT for all the materials was typically less than 2 min.

3. Results and discussion

The concentration of effective antioxidant was assessed by determining the oxidation induction time (OIT); the latter being proportional to the concentration of effective phenolic antioxidant [16,17]. Alternative methods for assessing antioxidant concentration, particularly extraction followed by liquid chromatography, do not discriminate between effective and inactive (e.g. adsorbed or precipitated) antioxidant. The OIT measurements were all conducted on samples containing the entire cross-section. Figs. 1, 2 present a comparison between OIT data obtained after ageing in the aqueous media and data earlier reported for samples aged in dry air [14]. Data are presented in a subsequent part of this paper that shows that the antioxidant migration to the surrounding media was controlled by the boundary conditions. One of the most reasonable boundary loss equations (Eq. (1)) predicts that the logarithm of the normalised OIT should be proportional to time. This is the reason for the choice of abscissa and ordinate in the plots displayed in Figs. 1–3.

The composites containing 2 wt.% nanofiller showed a faster decrease in OIT with increasing exposure time on exposure to liquid water than on exposure to dry air or air at 100%RH; the factorial difference between the slopes in Fig. 1a and b was 5–6 between the water and dry air exposure data. The decrease in OIT was moderately faster (increased by ca. 50%) on exposure to humid air than to dry air (Fig. 1a and b). About 40% of the initial OIT remained after 700 h of exposure to liquid water, whereas more than 80% remained after exposure to humid or dry air.

The composite samples containing 6 wt.% nanofiller showed a similar behaviour; the fastest reduction in OIT occurred for the composites aged in water and the slowest decrease occurred for the