

The preparation and characterisation of a complex of copper with poly(acrylic acid) and an assessment of its suitability as an anti-static additive for polyethylene

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Abstract

The preparation and some properties of a complex formed between poly(acrylic acid) and copper carbonate are described. Spectral studies indicate that the copper ions are in an octahedral environment. The thermal behaviour of the copper complex has been studied by thermogravimetry and differential thermal analysis. The thermal decomposition study shows that the copper complex (which is hydrated) first loses water, followed by the organic ligand, to give copper oxide. The copper complex as well as poly(acrylic acid) were investigated as possible anti-static additives, but were found to be less effective than commercial additives. However, there is evidence that the copper complex may produce longer lasting anti-static properties.

INTRODUCTION

During moulding and extrusion processes, molten polyethylene is in contact with metal surfaces and the separation process which takes place can lead to high static charge. The accumulation of this static electricity on the surface of the polymer can give rise to dangerous situations such as fire and explosion hazards due to higher energy discharges in air. Further, surface soiling can occur, producing items of unacceptable appearance to the consumer. Anti-static agents such as fatty acid monoglycerides or diglycerides and ethoxylated fatty amines are used to overcome this static accumulation. This paper describes an investigation into the use of poly(acrylic acid) and a copper–poly(acrylic acid/acrylate) complex as possible anti-static agents for polyethylene. Spectral studies have been

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used to characterise the copper complex and to interpret the type of coordination which takes place to the metal ion. A thermal stability study of the copper complex has also been carried out.

EXPERIMENTAL

Preparation of the copper complex

The copper complex with poly(acrylic acid) was prepared by adding copper carbonate (0.01 mol) of poly(acrylic acid) (MW = 2000) (0.07 mol) dissolved in 100 cm³ of deionised water. The solution was stirred for 8 h and the residual carbonate was removed by filtration. The green copper complex was obtained by reducing the volume of solution by evaporation and finally drying in an oven at 60°C for 12 h.

Preparation of metal complex high density polyethylene (HDPE) blends

The metal complexes, (0.5 wt.%), poly(acrylic acid) ligand (0.5 wt.%) and commercial anti-static agent (0.5 wt.%) were each separately pre-blended with 36 g of HDPE. The preblends were added to a Brabender plasticorder and mixed at a temperature of 160°C using a rotor speed of 60 rev min⁻¹. After 5 min, the blends were removed and compression moulded at 180°C into small plaques (1 mm thick) and films (0.1 mm thick) for subsequent measurement of surface resistivity and charge decay respectively.

Apparatus and measurements

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses using a Carlo Erba elemental analyser.

The IR spectra were obtained using KBr discs (4000–600 cm⁻¹) and polyethylene discs (600–200 cm⁻¹) with a Perkin-Elmer model 598 IR spectrophotometer.

The electronic spectra were obtained using a Beckman Acta MIV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant.

The thermal analysis studies were carried out on a Stanton-Redcroft model STA 1500 thermobalance. The TG and DTA curves were obtained at a heating rate of $10^{\circ}\text{C min}^{-1}$. In all cases the $20\text{--}800^{\circ}\text{C}$ range was studied. Surface resistivity measurements were carried out to BS 2782, Part 2, 1976 using a Hewlett-Packard 1600 8A resistivity cell.

Charge decay measurements were carried out using equipment at BP Chemicals Ltd, Grangemouth Research and Development Department, which conformed to BS 2782 Part 2, method 250C, 1976.

RESULTS AND DISCUSSION

The experimental results from the analyses of the copper ion, carbon and hydrogen for the copper complex are: theory (wt.%) Cu 5.08, C 46.10, H 5.32; found (wt.%) Cu 4.75, C 46.19, H 5.41. The results give an empirical formula of $\text{Cu}(\text{C}_{48}\text{H}_{66}\text{O}_{34})$ for the complex and indicate a high level of purity.

A single broad absorption band in the electronic spectrum of the copper complex (with a maximum absorption at 14388 cm^{-1}) indicates that the copper ion is in an octahedral environment [1]. A magnetic moment of 1.89 BM was obtained for this complex, indicating no magnetic spin–spin interaction between the copper atoms in the compound.

The IR spectrum of the copper complex shows a strong broad absorption band in the region $3720\text{--}3280\text{ cm}^{-1}$, which indicates the presence of water of crystallisation [2]. A strong band at 1721 cm^{-1} attributed to the $\nu(\text{COOH})$ vibration is observed in the IR spectrum of the poly(acrylic acid). In the copper complex strong bands are observed at $1720, 1554, 1451$ and 1413 cm^{-1} . The band at 1720 cm^{-1} corresponds to the $\nu(\text{COOH})$ vibrations and indicates the presence of $-\text{COOH}$ groups in the copper complex, whereas the remaining bands correspond to the $\nu(\text{COO}^-)$ group which has complexed to the copper ion [2]. A band at 276 cm^{-1} , which has been assigned to the $\text{Cu}\text{--}\text{O}$ vibration, is indicative of the copper atom being in an octahedral environment [2].

The fact that the copper complex was isolated as a powder from aqueous solution means that information regarding the stereochemistry of the copper atom has been obtained from elemental analyses and spectral data. It is suggested that the copper atoms are bonded to carboxylate groups in the same polymer chain, or to carboxylate groups in different polymer chains, to give a planar four-coordinate environment for the copper atoms. A six-coordinate environment for each copper atom is obtained by the copper atom bonding to oxygen atoms of other poly(acrylate–acrylic acid) chains. The water molecules are attached by hydrogen bonding. The molecular formula for the complex is $\text{Cu}(\text{CH}_2\text{CHCOO})_2(\text{CH}_2\text{CHCOOH})_{14}2\text{H}_2\text{O}$.

The TG and DTA trace for the copper–poly(acrylic acid/acrylate)

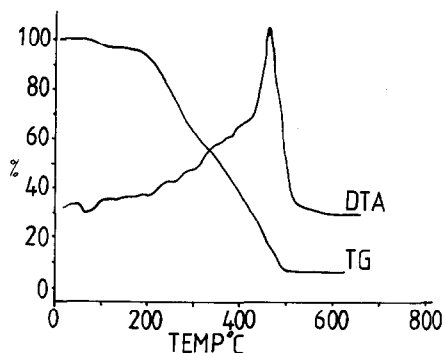
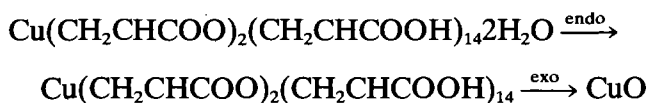


Fig. 1. TG and DTA traces for copper complex. Sample weight = 4.97 mg.

complex is shown in Fig. 1. The complex undergoes an endothermic reaction with loss of two molecules of water, followed by an exothermic reaction with loss of the organic ligand to give copper(II) oxide. The scheme of decomposition is



The HDPE samples containing the commercial anti-static additives have lower surface resistivities than pure HDPE, or the HDPE containing the copper-poly(acrylic acid/acrylate) complex, both initially and 336 h after moulding (Table 1). The copper complex does not reduce the surface resistivity as much as the commercial anti-static additive. The charge decay measurements (Table 1) provide no information about how quickly charge is dissipated from the surface of the HDPE containing the copper complex. The commercial additive has the same performance both 0 h and 336 h after moulding. An important property of an anti-static agent is its mobility within the polymer system, which enables it to migrate to the

TABLE 1

Electrical properties of HDPE blends

Compound	Surface resistivity (Ω)		Charge decay (S)	
	0 h after moulding	336 h after moulding	0 h after moulding	336 h after moulding
HDPE	1.50×10^{17}	9.40×10^{16}	>120	>120
Poly(acrylic acid)-HDPE	1.88×10^{17}	1.88×10^{17}	>120	>120
Commercial-additive-HDPE	1.32×10^{13}	7.52×10^{13}	1.0	1.0
Copper-complex-HDPE	5.45×10^{16}	5.64×10^{16}	>120	>120

polymer surface. The polymeric structure proposed for the copper complex will inhibit mobility within the HDPE, reducing its effectiveness as an anti-static agent. This is confirmed by the values obtained for the ligand poly(acrylic acid) shown in Table 1.

REFERENCES

- 1 J.R. Allan, N.D. Baird and A.L. Kassyk, *J. Therm. Anal.*, 16 (1979) 79.
- 2 J.R. Allan, H.J. Bowley, B.R. Carson and D.L. Gerrard, *Thermochim. Acta*, 144 (1989) 187.