polymer report

Curable electrically conductive resins with polyaniline fillers

Poopathy Kathirgamanathan
Unit for Speciality Electronic Polymers, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK
(Received 19 November 1992; revised 17 February 1993)

Polyaniline(s) based on conductive epoxy and poly(urethane–acrylate) systems have been formulated and characterized. The anomalous behaviour of polyaniline(s) in comparison to carbon- or metal-filled systems is attributed to 'molecular level dispersion'.

(Keywords: electrical conduction; resins; polyaniline; fillers)

INTRODUCTION

Conducting adhesives are extensively used in electronic applications[1–4]. Most of the adhesives currently available are based on either metals, doped metal oxides or carbon black. Metal loadings of 60–90% (w/w) are required to achieve optimum conductivity[5]. Doped metal oxides are prone to attack by atmospheric moisture, thereby reducing the conductivity of the adhesive or coating concerned. Carbon-black-based coatings do not offer the possibility of pigmentation nor do they have adequate stability, as far as the conductivity is concerned, on thermal cycling. Further, the intermediate conductivities required for charge dissipation are not readily achievable with carbon blacks[6].

This paper reports the use of inherently conducting polymers (ICPs) for the production of conductive adhesives providing superior properties to carbon black. Polyaniline(s) have been chosen because of their high thermal stability (up to 250°C as determined by thermogravimetric and gas chromatography–mass spectrometric analysis).

EXPERIMENTAL

Polyaniline–*p*-toluenesulfonate (PAPTS) was prepared by oxidizing aniline with potassium persulfate in the presence of *p*-toluenesulfonic acid, according to reference 7. The PAPTS was obtained as a dark-green powder; it had an average particle size of $1.0 \pm 0.2\ \mu m$, density of $1.41\ g\ cm^{-3}$, surface area of $5.4\ m^2\ g^{-1}$ and a conductivity of $9 \pm 3\ S\ cm^{-1}$ (compacted disc, four-probe).

Copoly(*o*-toluidine / *o*-ethylaniline)*p*-toluenesulfonate (POTOEPTS) was prepared according to reference 8. The dark-green powder had an average particle size of $1.5 \pm 0.5\ \mu m$, density of $1.40\ g\ cm^{-3}$, surface area of $10\ m^2\ g^{-1}$ and a conductivity of $1 \times 10^{-3}\ S\ cm^{-1}$.

The ICPs were dispersed in a polymer resin in a beaker or on glass plates and were mixed with other additives (e.g. hardeners, photoinitiators, binders etc.) if and when necessary. In some cases a Silverson high shear mixer was employed to assist the blending. The loaded resins were cured either thermally in an air circulating oven or photochemically using a u.v. lamp, commonly used in developing printing plates.

RESULTS AND DISCUSSION

Conducting epoxy adhesives

An epoxy system based on PAPTS was compared with a system loaded with carbon black (BP 2000, from CABOT) and a system loaded with silver-coated nickel flakes (from Novamet, conductivity $1 \times 10^4\ S\ cm^{-1}$ (compacted disc)). The epoxy system was based on Epikote 828 EL and Cardura E10 (10:1) (these are epoxy derivatized bisphenol A/bisphenol F systems, from Shell Chemicals), 1-butyl imidazole as an accelerator and *cis*-1,2,3,4-tetrahydrophthalic anhydride hardener (50 parts per hundred parts resin). The loaded epoxy/hardener system was applied as a coating 500 μm thick and heated at 120°C for 1 h. Polyaniline-based hardeners did not cure the epoxy system because of protonation by the protons from the dopant of polyaniline, nor did they make the system poorly conducting owing to abstraction of protons from the polyaniline, which is important for conduction as polyaniline is a proton conductor[9].

Figure 1 compares the volume conductivity (four-probe) of epoxy systems loaded with PAPTS, carbon and silver-coated nickel flakes. It is clear that carbon black percolates at a low volume loading of approximately 5% (v/v), PAPTS at about 10% (v/v) and silver-coated nickel flakes at about 26% (v/v). This is because carbon black is known to form chains when it is loaded into a polymeric system, and as the particle size of carbon black is 10–100 nm, the tunnelling conduction also takes place[10–14]. While the percolation curves (i.e. conductivity *versus* volume curves) for carbon black and silver-coated nickel flakes are steep, the percolation curve for PAPTS is very shallow and the transition is gradual. This may be explained on the basis of molecular level interaction of the organic PAPTS with the resin/hardener system. As a result of the gradual increase in conductivity with volume loading, conductivities in the range 10^{-8}–$10^{-3}\ S\ cm^{-1}$ can be produced. This range is required for controlled charge dissipation[15]. The maximum

0032-3861/93/132907-02

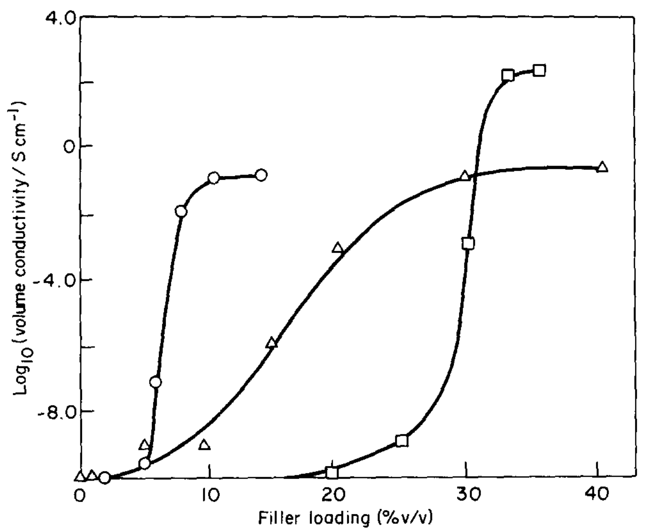

Figure 1 Volume conductivity *versus* volume loading for expoxy systems loaded with: △, PAPTS; ○, carbon black; □, silver-coated nickel

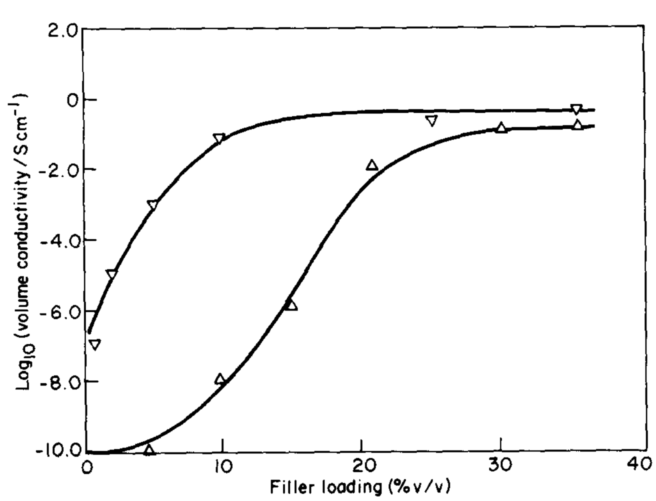

Figure 2 Volume conductivity *versus* volume loading for poly (urethane–acrylate) systems loaded with: △, PAPTS; ▽, POTOEPTS

conductivity of the epoxy system achieved in all cases is about 10- to 100-fold lower than the conductivities of the fillers, as expected.

Conducting poly(urethane–acrylate)

PAPTS and POTOEPTS systems were incorporated into a photocurable system consisting of poly(urethane–acrylate) resin (Ebercryl 4833), polyfunctional oligoester (Ubichem 4 00) and a triazine photoinitiator. Dimethylformamide (DMF) was used as a thinner. The resin system was loaded with PAPTS and POTOEPTS; a coating approximately 10 μm thick was made and cured for 30 s under a u.v. lamp. *Figure 2* illustrates the conductivity *versus* volume loading of PAPTS and POTOEPTS. The POTOEPTS shows dramatically different behaviour to PAPTS in that the percolation region is absent. This anomaly might be explained on the basis of the fact that POTOEPTS actually dissolves in DMF (PAPTS does not dissolve to an appreciable degree); the dispersion is thus uniform (i.e. the POTOEPTS is present on a molecular level throughout the matrix) and therefore the percolation behaviour usually observed in the case of filler–polymer matrices will not appear in a 'molecularly dispersed' system[16,17]. The other interesting feature is that the maximum conductivity achieved for the POTOEPTS system is 100-fold higher than that of the filler. This is again an anomalous behaviour that can only be explained on the basis of molecular orientation and consequent reticulation, as opposed to a 'filled' system which always has lower conductivity than the filler itself (see *Figure 1*).

It is therefore an example of a 'molecularly dispersed' system exhibiting superior properties to a 'filled' macroscopic system.

In conclusion, it has been shown that ICPs can be used to produce useful conductive adhesives and coatings. Conductivity *versus* temperature studies are being carried out to clarify the mechanism of conduction in these novel composites.

ACKNOWLEDGEMENT

The author thanks Mr A. Hart of Hart Coating Technology for the provision of samples of silver-coated nickel flakes, and Professor D. E. Williams for encouragement. Dr J. B. Jackson of Cookson Technology Centre is thanked for providing some starting materials.

REFERENCES

1 Braithwaite, N. and Weaver, G. 'Electronic Materials', Butterworths Scientific, London, 1990
2 Harper, A. C. *Electron. Packaging Prod.* 1984, 143
3 Tsukagoshi, I., Yamaguchi, Y. and Nakayama, T. European Patent 0140619, 1985
4 Skeist, I. (Ed.) 'Handbook of Adhesives' 3rd edn, van Nostrand Reinhold, New York, 1990
5 Bhattacharya, S. K. 'Metal-Filled Polymers', Marcel Dekker, New York, 1986
6 Kathirgamanathan, P. in 'High Value Polymers' (Ed. A. H. Fawcett), Royal Society of Chemistry, Cambridge, UK, 1991
7 Kathirgamanathan, P., Adams, P. N., Marsh, A. M. and Shah, D. European Patent 873 061337, 1987
8 Kathirgamanathan, P., Adams, P. N., Quill, K. and Underhill, A. E. *J. Mater. Chem.* 1992, **1**(1), 141
9 McDiarmid, A. G., Mu, S. L., Somasiri, N. L. D. and Wu, W. *Mol. Cryst. Liq Cryst.* 1985, **121**, 187
10 Sheng, P., Chel, D. S. and Giltleman, J. I. *Phys. Rev. Lett.* 1978, **40**, 1197
11 Wessling, B. W. *Kunst. German Plast.* 1986, **76**(10), 69
12 Degusa, Cheshire, Technical Bulletin Pigments No. 69, 1986
13 Cabot Corporation, Cheshire, Technical Report S. 39, 1987
14 Van Dumpt, J. D. *Plast. Compound.* 1988, 37
15 'Military Handbook', US Defence Department, 1980, p. 263
16 Wessling, B., Volk, H., Mathew, W. R. and Kulkarni, V. G. *Mol. Cryst. Liq. Cryst.* 1988, **160**, 205
17 Wessling, B. *Synth. Met.* 1988, **27**, A83