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SMART CONDUCTIVE INKS

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Abstract. A novel conductive ink, suitable for employment in a pressure-sensitive automatic system, was prepared and characterized *via* scanning electron microscopy, FTIR and differential scanning calorimetry. The ink was obtained as a composite by mixing a solution of ethyl acrylate-methyl acrylate (50/50 ratio) copolymer and carbon black and graphite into a solvent standard for acrylic polymers. The ink average electrical resistance ranges from 40 ohms/cm to 150 ohms/cm.

Key words: conductive ink, "smart materials", composite, copolymer, carbon black, graphite.

1. Introduction

The so-called "smart materials" have become a very attractive and actively developing area of research in the last few years [1-10] not only because of the intellectual beauty of the concept itself, but also because of the real possibility of producing devices which adapt themselves to the varying chemical and physical conditions of the environment [5, 6]. Composite materials have certainly a key role to play in this new area, since it has been demonstrated how a composite, provided it has a properly controlled microstructure, can represent the basis of a "smart" device [7, 8]. One specific field of great scientific and technological interest is that of sensors of various kinds, particularly "smart" pressure sensors.

On the other hand, inks constitute a very active area of R&D for they represent a very profitable market for different applications worldwide. In principle, electrically conductive pigments have been reported by using a number of different materials [7-13] and they could be employed by embedding them into a polymeric matrix to produce a "smart" device through a percolation phenomenon [14]. Conductive inks are typically produced by either embedding metallic particles (silver, copper or other metallic flakes) in a retaining matrix or by using carbon particles in a matrix. Although carbon phases (except some nanophases) are of the order of 100 times less conductive than metals their very low cost along with other technical characteristics (resistance to corrosion, *etc*.) make them attractive. Originally, the matrix of choice was ceramic, but nowadays polymer thick films (PTF) are replacing it extensively. The matrix is usually non conductive, thus, once the ink has been applied, the matrix requires to be reduced to achieve the conductance throughout the material via direct contact of the conductive particles with each other, which is achieved by curing. The whole process results in the need for a tough and expensive substrate. Moreover, different ink formulations imply that curing is just one factor determining the final bulk conductivity of the printed ink.

Another important technical limitation of the reported conductive inks is that they are not chemically compatible with most engineering polymers, which would provide the device with the mechanical endurance required for practical application at a reasonable performance/cost relationship. Accordingly, in this work the development of a new conductive ink, formed by carbon black particles suspended in a novel low cost (of the order of any commercial acrylic available) acrylic copolymer (ethyl acrylate/methyl acrylate = 50/50, %) [13], suitable to be mixed with commercial acrylics (PMMA, for instance), is reported.

2. Experimental

Ethyl acrylate (EA), methyl acrylate (MA), 2-mercaptoethanol (2-MEOH), 2'2'-azobisisobutyronitrile (AIBN), pyromellitic dianhydride (PMDA), neopentyl glycol (NPG), 1,4 butanediol (1-4 BD) and thymol blue were purchased from Aldrich. N'N-dimethyl formamide (DMF) and imidazole (IMDA) were obtained from Sigma.

The ink was obtained by mixing 100 phr of ethyl acrylate-methyl acrylate copolymer (50/50 composition, as described in [13]) and carbon black, 20 phr of standard thinner, 15 phr of black carbon, and 10 phr of 99.99 %

pure graphite. These substances were mixed for 4 h at 100 ppm. Ink viscosity was controlled by the added amount of standard thinner, which allowed a workable material. The ethyl acrylate-methy acrylate copolymer was prepared according to the technology originally developed in our group, which has been described previously [10, 11, 13].

Following the ASTM D3359-83, adhesion tests were performed by casting the ink onto a flat clean nylon surface through serigraphy, simulating the impressed circuits to be eventually used in the applications. Afterwards, an adhesive tape was applied to the surface in such a way that by pulling it one could see whether the ink was pulled out from the surface or not. Ten tests were performed. Moreover, the ink thickness was an important factor to be accounted for, so it was controlled to around 100 μm. The electrical resistivity was measured with a standard resistivity meter (Radio Shack). Scanning electron microscopy (SEM) was performed in a JEOL 5200 machine at 25 keV on as-casted specimens. The infrared spectrum (FTIR) was obtained from the dry ink by using the diffuse reflection technique in a Nicolet 900 bench. Due to the thickness and characteristics of the samples, standard absorbance IR measurements could not be employed. Differential scanning calorimetry (DSC) was carried out in a Perkin Elmer apparatus.

3. Results and Discussion

The copolymer employed was synthesized by first producing the acrylate precursors, according to the reaction scheme in Fig. 1, where the hydroxyl-terminated ethyl acrylate or methyl acrylate (HTEA or HTMA, respectively) are schematically shown. Reacted in a 50/50 (%) ratio, the hydroxyl groups favour the reaction with the carbon black and provide the adhesive and mechanical properties to these copolymers.

The copolymerization experiments were carried out in a previously flamed borosilicate reaction flask equipped with a magnetic stirring bar, using toluene as solvent. The initiator, monomer, and transfer agent were weighed and then added continuously during six minutes into the flask containing refluxing toluene in a nitrogen atmosphere. A relatively high concentration of initiator and of 2-MEOH was used for the purpose of guaranteeing a low molecular weight. The reaction temperature and time were chosen from a practical point of view since the acrylates have a very high reactivity. Polymerization reactions were run at constant temperature of 328 or 338 K in a thermostated oil bath.

The conductive ink had very good adhesive properties, since the copolymer utilized has chemical groups that allow it to act as "hot melt" adhesives [15], which is in fact part of the reason for the success of the present technology. Fig. 2 shows an FTIR spectra containing, among others [12], unsaturated amines (O), primary alcohol (A), nitrate (P), aromatic rings (Q), epoxy (R), aliphatic peroxide (S), and sulphide (U), which provide good adhesion properties and good mechanical performance.

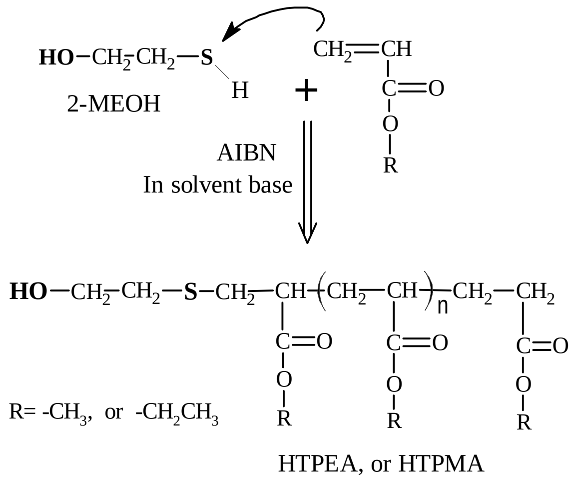

Fig. 1. Structures of the single hydroxyl-terminated ethyl acrylate-methyl acrylate

Tensile testing in an Instron machine showed failure at the load of 400 kg/cm^2, as an average of over 10 tests, which is a very good figure for these types of materials [9]. The maximum elongation attained was 273%, again as an average of more than 10 tests, which is also a very good mechanical behaviour.

One interesting property of the developed ink is its low T_g, of the order of 233 K, as observed in the DSC curve in Fig. 3 (the derivative of such curve shows the T_g precisely at that low temperature). That is, the ink, once dried, behaves like elastomer, which opens the possibility of producing flexible electrically-conducting circuits.

The microstructure of the final ink is very homogeneous, as can be observed in the SEM micrograph on Fig. 4, where the granular structure corresponds to the graphite-carbon black particles. No agglomeration of the carbon black particles was observed, indicating a good dispersion within the polymeric matrix. Also, the fracture surface (Fig. 4) did not show debonding of the carbon black, thus revealing a good interface, important for the mechanical performance of the material.

It is important to point out that both resistivity and adhesion behavior of the ink can be controlled through a careful control of copolymer-carbon black-graphite relationship, which enables to truly engineer the final properties of this composite material.

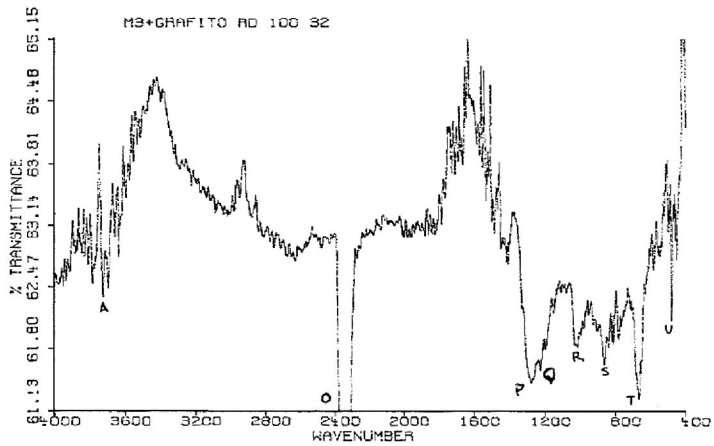

Fig. 2. Infrared spectrum of the conductive ink

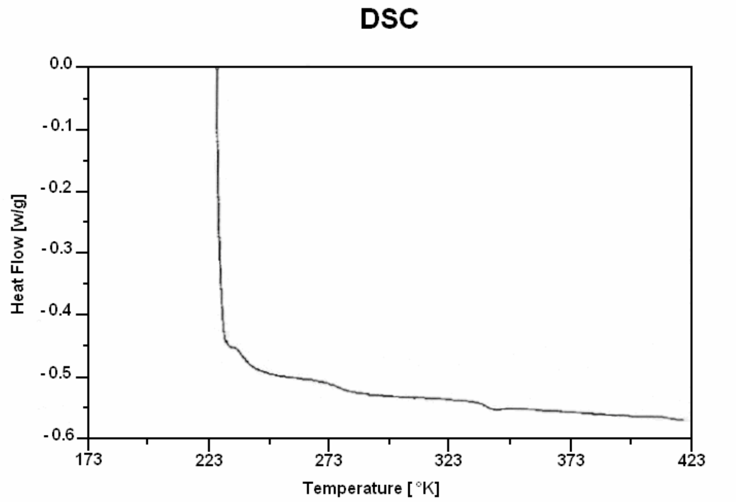

Fig. 3. DSC diagram of the conductive ink

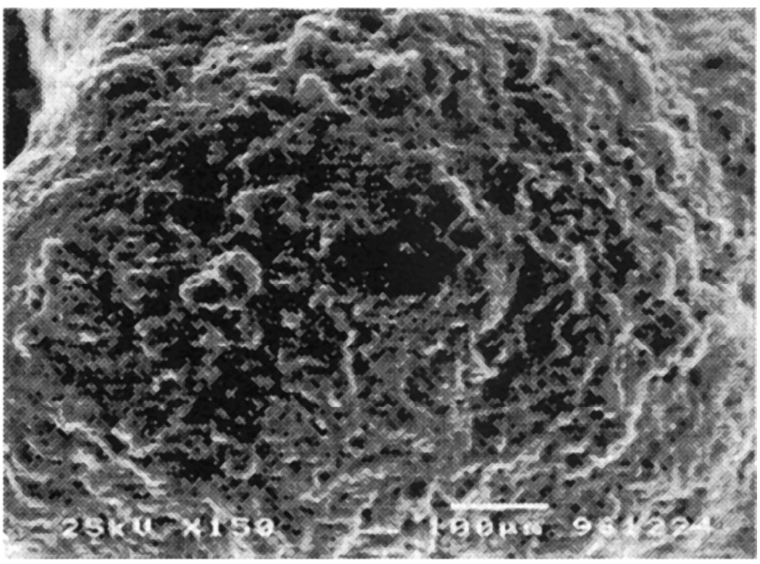

Fig. 4. SEM micrograph of the conductive ink

4. Conclusions

The described conductive ink can be used to produce flexible electrical circuits via simple printing techniques. Thus, one can develop measurement equipment for biomedical or other industrial applications. Among the uses of this ink, already developed in our group, "smart" pressure sensors[6], level sensors, digital adjustments for electronic circuits, oil pressure sensors in automobiles, glucose biosensors, MEMS (MicroElectroMechanical Systems), and other can be mentioned, which illustrates the wide variety of applications for "smart" composite materials.

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РОЗУМНІ ПРОВІДНІ ЧОРНИЛА

Анотація. *Розроблено нові провідні чорнила, придатні для автоматичних систем, чутливих до дії тиску. За допомогою скануючої електронної мікроскопії та диференційної скануючої калориметрії визначено їх характеристику. Чорнило одержане як композит змішуванням кополімеру етил- та метил-акрилату (співвідношення 50/50), технічного вуглецю і графіту у стандартному розчиннику для акрилових полімерів. Встановлено, що середній електричний опір чорнила від 40 до 150 Ом/с/см.*

Ключові слова: *провідні чорнила, розумні матеріали, композит, кополімер, технічний вуглець, графіт.*