CHARACTERISATION OF AN ELECTRICALLY CONDUCTIVE POLYMER COMPLEX

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ABSTRACT.

Polyaniline (PANI) is at present one of the most promising conductive polymers due to a number of important reasons including its chemical stability combined with high levels of electrical conductivity. Additionally, we have found that, following an in-situ deformation process, this polymer is suitable for the production of composites exhibiting a phase separated morphology with continuous fibrils of PANI in an insulating matrix. Nowadays, this type of material has potential applications in static dissipative packaging and industrial textiles. Accordingly, we report on the characterisation techniques performed to evaluate the suitability of three different samples of a PANI complex (PANIPOL^{TM}) for the production of this type of composite, following an in-situ process.

The characterisation techniques included thermogravimetry, differential scanning calorimetry and rheometry. Additionally, techniques such as X-ray diffraction, gravimetry, infrared spectroscopy, conductivity measurements, and optical and scanning electron microscopy were used to fully characterise the samples. The thermal limitations and stability of the samples were established and the flow properties of the materials in their molten state under different levels of shear rate were also analysed. The experimental results suggested low levels of crystallinity in the samples, aided in the identification of the samples' components, and revealed that the PANI particles were 7 μm in diameter or of a smaller size.

INTRODUCTION.

PANI is one of the most promising conductive polymers due to its excellent chemical stability combined with relatively high levels of conductivity [1,2]. The electrically conductive form of PANI (emeraldine salt, ES), obtained when the neat polymer is doped with a specific functionalized protonic acid, can be used to prepare melt processable blends with low percolation limits [3,4-6]. Recently, we have established the feasibility of processing this type of blend, following an in-situ deformation process, to produce extrudates exhibiting a morphology of continuous PANI fibres embedded in an insulating polymer matrix [7]. This type of composite could have potential applications as antistatic materials in the textile, carpet and packaging industries. In an in-situ process, the fibres are generated during the actual forming of the component. This has been the subject of extensive investigation [5,8-12] and it has been shown that under appropriate conditions, the dispersed phase can deform during processing to produce elongated structures, for example ellipsoids or even short fibres. Accordingly, in this paper we report on the characterisation techniques performed to evaluate the suitability of three different samples of a PANI complex (PANIPOL^{TM}) for the production of this type of composite following an in-situ deformation process.

Theoretical and experimental studies indicate that the morphology of a polymer blend is determined by parameters such as interfacial tension, viscosities of the materials, composition and processing conditions including temperature, residence time,

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flow patterns and shear rate levels [9,13,14]. However, among these parameters, the ratio of the viscosity of the dispersed phase to that of the matrix (That is, the viscosity ratio, p), can be used initially to suggest the size and, what is more relevant in this case, the shape of the dispersed phase. For example, it has been shown experimentally that when p is less than or near unity, the dispersed phase easily deforms into elongated structures [9]. On the other hand, when p is greater than one, the deformability is reduced. The theories developed to describe the deformability of the dispersed phase in a binary blend are mostly concerned with Newtonian systems [13]. However, these can be used as general guides to describe the deformability in pseudoplastic systems. For instance, the lower the viscosity ratio the lower the stability of the elongated domains (the higher the probability to break up into small droplets) [13]. This can be used as a general principle, when experimenting with different materials, to select the system most likely to exhibit a final morphology of fibres embedded in a continuos phase.

Great effort was put in the characterisation of the three samples of PANIPOL^{TM} as it was important to have more detailed information on their inherent limitations, especially those related with their thermal processing. In respect of this, the company supplying the samples provided some information. However, as we shall see later, differences in the thermal behaviour and stability were found. Moreover, we found that their rheology was also different. Therefore, we needed to find those distinctive characteristics that, eventually, would aid in selecting the most suitable sample to be in-situ deformed into fibres. At the same time, through these analyses we were able to establish the basis for selecting the processing conditions. The chemistry of the samples was elucidated by means of a combination of analysis techniques including infrared spectroscopy, X-ray diffraction and gravimetry. The morphology was also analysed by using optical and scanning electron microscopy techniques. This was correlated with the chemistry of the samples and, eventually, assisted in the interpretation of the morphology observed in the extrudates. Finally, the level of electrical conductivity in the samples was also evaluated.

MATERIALS.

The PANI complexes (PANIPOL^{TM} CX) were provided by NESTE Oy Chemicals. They are identified as PANIPOL 1 (code CX100X23), PANIPOL 2 (code CX100X03) and PANIPOL 3 (code CX300X33). The samples were supplied in the form of dark-green-coloured cylindrical compressed pellets. Their approximate composition was 25 weight % (wt.%) of ES and 75 wt.% of an organometallic zinc compound. The basic chemistry is the same in all the samples. The typical density, volume conductivity and maximum recommended processing temperature are, respectively, 1100 kg/m^3, 1 x 10^{-4} S/cm and 230°C. The samples are hygroscopic and the processing temperatures range from 100 to 225°C.

CHARACTERISATION TECHNIQUES.

X-ray diffraction.

Wide-angle X-ray diffraction experiments were performed on the three PANIPOL samples with a Philips 1050 Goniometer X-ray diffractometer using nickel-filtered copper-$K\alpha$ radiation with a wavelength of 1.5406 Å. The diffractometer was operated at 36 kV and 26 mA. For the experiments, a few of the as-received PANIPOL pellets were powdered with a pestle and mortar. The diffraction pattern was obtained by scanning the

powder in an interval of 2θ = 6 to 80 degrees at a rate of 0.02 degree/s. Experiments were also carried out on the pyrolysed pellets. About 25 gr. of the pellets were placed in a crucible and the pyrolysis was performed in a furnace (Lenton) at 850°C for 2 hrs. Afterwards, the crucible containing the pyrolysis product was cooled down in a desiccator where it was kept to await further analysis.

Gravimetry.

As the basic chemistry is the same in all the samples, the analysis was concentrated on one of the samples (PANIPOL 2). The main purpose of the analysis was to confirm the amount of ES in the as-received pellets. In addition, a first insight on the identity of the doping agent used was also provided. Four suspensions of the powdered pellets (ca. 2 gr.) in an excess (ca. 12 ml) of acetone (C_3H_6O, 99 % purity, from Aldrich) were sonicated in an ultrasonic bath (Kerry's LTD) for 15 min. Afterwards they were centrifuged (MSE centrifuge) for 15 min at 3000 rpm. The resultant solutions were decanted and a sample was collected for further examination. An excess of clean acetone was further added to the remaining sediments and the suspensions so obtained were subjected to the same sonication, centrifugation and decanting processes. This was carried out several times until the decanted solution was clean and transparent, suggesting that the process of dissolution in acetone of any additives susceptible to dissolution, and originally present in the sample had been completed. After the conclusion of seven dissolution cycles, the remaining sediments were placed in a Gallenkamp vacuum oven at 40°C where they were kept overnight to evaporate any possible remains of acetone. After cooling down in a desiccator the remaining sediments were weighed and the wt.% in each sample was calculated.

Infrared spectroscopy.

Fourier transform infrared (FTIR) spectroscopy experiments were performed on the three as-received samples. Similarly, the same analysis was performed on the decanted solutions obtained from each of the seven dissolution cycles in acetone. The samples are identified as solutions 1 to 7, where solution 1 is the sample collected after the first dissolution cycle, and solution 7 the sample collected after the last cycle. The FTIR spectrum of the PANIPOL complexes and solutions 1 to 7 was measured at room temperature with a Nicolet 710 FT-IR spectrometer in a spectral range of 4000 to 400 cm^{-1}. The PANIPOL specimens were prepared by grinding the powered pellets with potassium bromide (KBr) powder and then pressing the mixture into a tablet. The solutions were analysed by placing them, with the help of disposable micropipettes, between already prepared KBr discs.

Thermal analysis.

The thermal stability of the PANI complexes within the temperature range from 40 to 750°C was investigated using a Perkin-Elmer TGS-2 thermogravimetric analyser (TGA). The powdered pellets were analysed at a heating rate of 10°C/min. The thermal behaviour of the complexes over the range of temperature from 325 to 680°K (51.85 to 406.85^{o}C) was initially investigated using a Perkin-Elmer DSC-2C Differential Scanning Calorimeter (DSC). For each complex, the powdered pellets were analysed at a rate of 10°K/min. The thermal behaviour of the complexes during exposure to a heating-cooling-heating cycle was also analysed. For this, the analysis was performed in

a Perkin-Elmer DSC-7 Differential Scanning Calorimeter. The powdered complexes were heated at rate of 10°C/min from 35 to 110°C. The samples were kept for 10 min at the maximum temperature, after which they were cooled down to 35°C at a rate of 5°C/min. The samples were kept at this temperature for 0.5 min and afterwards they were heated up again to the maximum temperature at a rate of 10°C /min. All the experiments were performed in duplicate under a nitrogen atmosphere using samples with a weight of about 5 mg.

Rheometry.

The rheological behaviour of the three PANI complexes was investigated using a Davenport extrusion rheometer. The Poiseuille Law for capillary flow was used to calculate apparent viscosity-apparent wall shear rate relationships at different temperatures for each material. No end pressure drop correction was performed for the calculations. For the experiments, the materials were extruded using a capillary die with a length and radius of 35 and 0.8 mm, respectively. The rheological behaviour was analysed at 80, 100, 120 and 150°C.

Conductivity measurements.

The volume conductivity was evaluated at room temperature on the as-received pellets of a selected complex (PANIPOL 2). A Keithley 614 electrometer was used for measuring the electrical resistance of the samples. Mercury was used as electrical probes. The electrical resistance readings were taken after 5 min of sample electrification. The volume conductivity was evaluated on five specimens in accordance with Ohm's law assuming that the resistance readings were performed in an ohmic regime and that the specimens were perfect cylinders.

Morphological analysis.

The analysis was performed on one selected complex (PANIPOL 2). A small amount of the powdered pellets was mounted on a glass slide and the analysis was performed with a Reichert Microstar 110 optical microscope using incident light. Scanning electron microscopy (SEM) analysis was also performed on the powder. The analyses were performed with a JEOL JXA-840-A electron probe microanalyzer at 10 kV. For the analysis, the sample was previously gold coated for 4 min in an E5000 (Polaron Equipment Limited) SEM coating unit.

RESULTS AND DISCUSSION.

The X-ray diffraction patterns of the complexes were similar with slight differences among them. This suggested some differences in the composition of the samples. For simplicity, only the diffraction pattern of PANIPOL 2 is presented (Fig. 1a). As can be seen, the level of crystallinity detected is relatively low. From the reflections presented only a few can be clearly associated with crystalline regions (2θ = 8.96, 17.47 and 46.89^{o}). The X-ray diffractograms of a yellow powder collected from each of the pyrolysis products of the three PANIPOL samples were identical. A selected diffractogram is presented in Figure 1b. The relative intensities of the main reflections are in good agreement with those reported for zinc oxide (ZnO). This confirms the

presence of the element zinc in the pellets, originally forming part of the organometallic zinc compound.

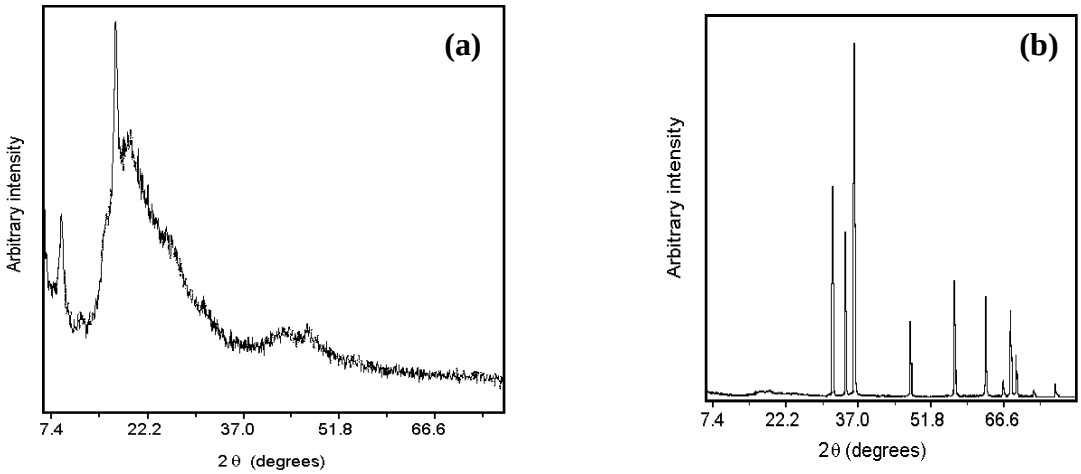

Figure 1. X-ray diffraction patterns of PANIPOL 2 (a) and the pyrolysis product (b).

With respect to the gravimetric analysis, it was noticed that after a few minutes of being collected, the decanted solutions from the first dissolution cycles in acetone showed a whitish precipitated solid. This colour is reported by Kärnä et al. [15,16] as characteristic of the reaction product of the mixture of ZnO with dodecyl-benzene sulphonic acid (DBSA). It is thus believed that the precipitate may be a Zn salt of DBSA, that is, $Zn(DBS)_2$ (the organometallic zinc compound, Zn dodecyl-benzene sulphonate). It was also noticed that these solutions became frothy when they were put in contact with water, which is characteristic of surfactants, for example DBSA or its derived salts [17,18]. Therefore it is very likely that the solutions decanted consist of acetone and ions of Zn and DBS in solution. The average wt.% corresponding to the final sediment in the samples after the conclusion of the dissolution cycles was 24.31. As doped polyaniline does not dissolve in acetone, it is believed that this corresponds to the wt.% composition of the ES in the original powdered PANIPOL samples. On the other hand, the weight loss, that is the 75.69 %, mainly corresponds to $Zn(DBS)_2$. As the powdered pellets were not previously dried for the analysis, then it is possible that the weight loss also includes some residual water initially absorbed from the environment because of the hygroscopic nature of the DBS salt. These results are in good agreement with the information provided by the supplier regarding the composition of the samples.

Regarding the FTIR experiments, it was found that the three PANIPOL samples presented a very similar spectrum. For simplicity, only a selected spectrum (PANIPOL 2) is presented in Fig. 2. The intensities of the main absorption peaks are assigned as follow: C-H bending for para-substituted benzene rings at 1011 cm^{-1}. The absorption peaks at 1184, 1130, and 1040 cm^{-1} can be considered as characteristic absorptions of the doping band since these peaks are characteristic of $–SO_2$- stretching in sulphonic acids or their derived salts. The absorption at 1299 cm^{-1} is assigned to C-N stretching vibration. The deformation of benzene and quinone rings are assigned at 1465 and 1612 cm^{-1}, respectively. The absorption peaks at 2853 and 2924 cm^{-1} correspond to $–CH_2$-stretching vibration whereas the absorption at 2956 cm^{-1} is assigned to CH_3- stretching vibrations. The OH band at 3564 cm^{-1} exists because of residual water absorbed from the environment. This results suggest that the doping agent is a para-substituted benzene sulphonic acid or its derived salt. The presence of saturated aliphatic hydrocarbons chains in the samples suggests that these may be the substituent group in the benzene

ring p-positions. Despite the fact that the FTIR technique cannot yield a conclusive estimate about the size and isomeric structure of the hydrocarbons chain, all these results in conjunction with the results obtained from gravimetric analysis, reinforce the concept about the use of DBSA as the doping agent. The FTIR results presented are in good agreement with those presented by Levon et al. [19] and Hsu et al. [20] for polyaniline doped with DBSA.

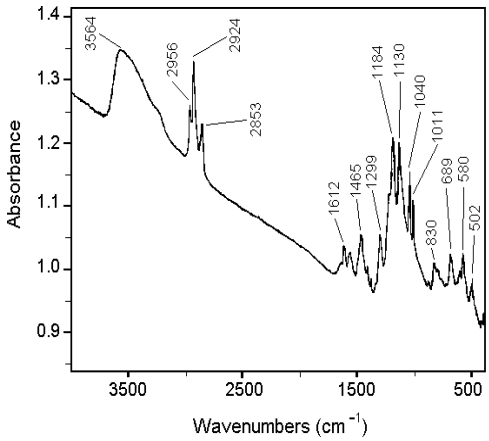

Figure 2. The FTIR spectrum of PANIPOL.

The FTIR spectrum of the solution 1 is presented in Figure 3a. To facilitate the interpretation of the spectrum, a sample of clean acetone was also analysed by FTIR. The two FTIR spectra are overlapped in Figure 3a to indicate better the identity of the chemical species extracted from PANIPOL by the solvent. The absorption peaks at 2999, 1710, 1417, 1363, 1222, 1095, 903 and 532 cm^{-1} are the characteristic ones for acetone, whereas the characteristic absorption peaks corresponding to the DBSA and its derived salt, also found in the spectrum of PANIPOL, are represented by the rest of the peaks, thus indicating the extraction of these compounds from the original sample.

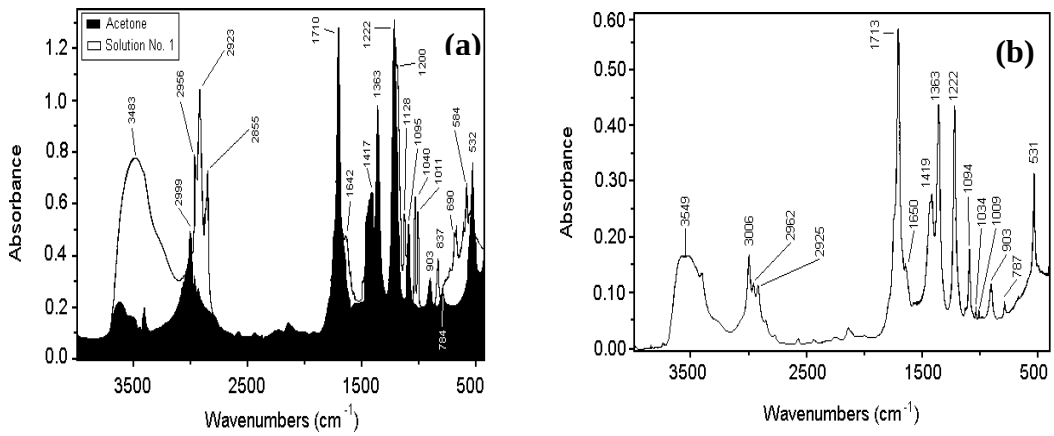

Figure 3. The FTIR spectra of solution 1 and acetone (a) and solution 7 (b).

The relative intensity of the majority of the absorption peaks corresponding to the DBSA and/or its derived salt decreased as the number of dissolution cycles in acetone was increased, indicating that the ES in the original PANIPOL sample was gradually being freed of the initially present DBS salt. For simplicity, only the FTIR spectrum corresponding to solution 7 (Fig. 3b) is presented to exemplify this process. As can be seen, Figure 3b also shows the characteristic peaks for the salt of DBS, indicating that the sample was not totally free of this, thus suggesting an incomplete extraction process.

However as can be observed, the absorption peaks corresponding to the acetone are more predominant. The peaks at around 3500 cm^{-1} (OH) appear as a result of residual water absorbed from the environment.

With respect to the thermal analysis, the TGA thermograms of the complexes were similar with slight differences among them. Again, this suggested some differences in the composition of the samples. For simplicity, only a selected thermogram (PANIPOL 2) is presented in Fig. 4a. The thermogram shows that there is a small weight loss (ca. 2.8 %) below 250°C corresponding to loss of water and low molecular weight oligomers. Between ca. 250 and 540°C an abrupt weight loss is observed (68.89 %) attributed to dopant loss and degradation of the polyaniline and $Zn(DBS)_2$, in that order. Above 540°C only about the 28.33 % of the original weight of the sample is left, corresponding to decomposition products, mainly containing Zn and carbon atoms. In general, these results, suggest that the complexes could be safely processed up to a maximum temperature of about 250°C without exposing them to severe degradation and loss of their electrically conductive characteristics. All the samples analysed by DSC over the range of temperatures from 51.85 to 406.85^{o}C also presented a very similar thermal behaviour. For simplicity, only a selected DSC thermogram (PANIPOL 2) is presented in Figure 4b. This Figure shows a broad endotherm between about 75 and 110°C, mainly attributed to the evaporation of water absorbed from the environment. An exothermic range is observed between about 140 and 150°C (characteristic of polyaniline doped with DBSA) due to a homogeneous phase transition occurring in the doped complex [15,19]. A group of endotherms is observed between about 150 and 250°C, possibly attributed to transitions in the internal structure of additives present in the sample. As in the TGA analysis, it is possible that loss of low molecular weight oligomers also occurs in this interval. Above ca. 250°C, a constant rising endotherm is observed which is attributed to the loss of the doping agent and degradation of the polyaniline and $Zn(DBS)_2$. These results are in good agreement with those obtained from the TGA experiments. None of the endotherms are associated with the melting of polyaniline as this polymer only soften and then decomposes at about 320°C. The presented TGA and DSC thermograms compare well with the observations reported by Zilberman et al. [21] on the thermal behaviour of polyaniline doped with DBSA.

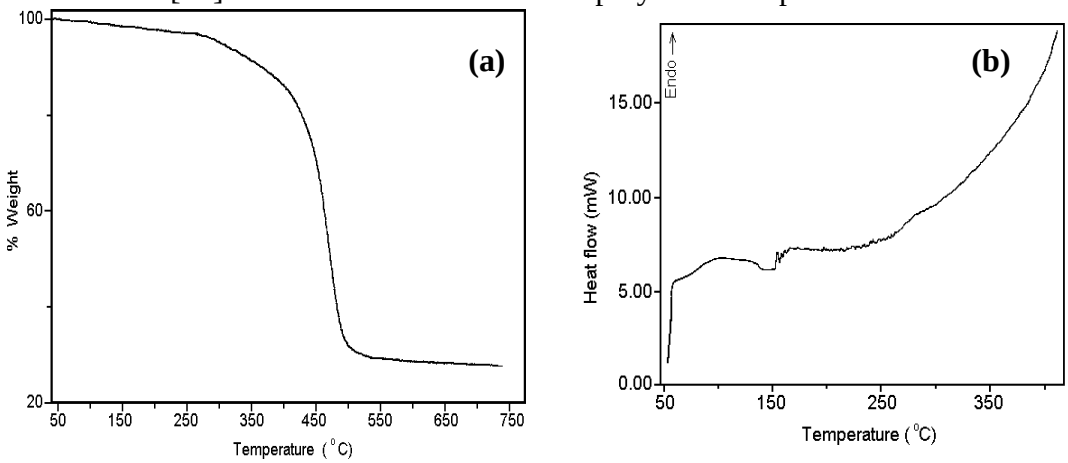

Figure 4. The TGA (a) and DSC (b) thermograms of PANIPOL 2.

The resultant thermal behaviour of the three PANIPOL complexes exposed to the heating-cooling-heating cycle is presented in Fig. 5. From this Figure, it can be observed that the thermal behaviour of the samples showed some differences. For example, the first heating scan in the thermogram of PANIPOL 1 shows what seems to be a melting peak at about 87.7^{o}C. This is confirmed by the crystallisation peak at about

70°C in the cooling scan and further reappearance of the melting peak at about the same temperature (87.7°C) in the second heating scan. In contrast, the thermograms of PANIPOL 2 and 3 do not indicate these thermal transitions in the samples during the same analysed interval of temperature. Moreover, the thermograms of PANIPOL 2 and 3 show some similarities, that is, two almost imperceptible endothermic regions at about 80 and 100°C. These endotherms, as also observed in Fig. 4b, may be associated with moisture and possible loss of low molecular weight oligomers. We believe that the endotherms observed in the thermogram of PANIPOL 1 (Fig. 5a) represent the melting point of a certain additive present in the sample, not used in the preparation of the samples 2 and 3.

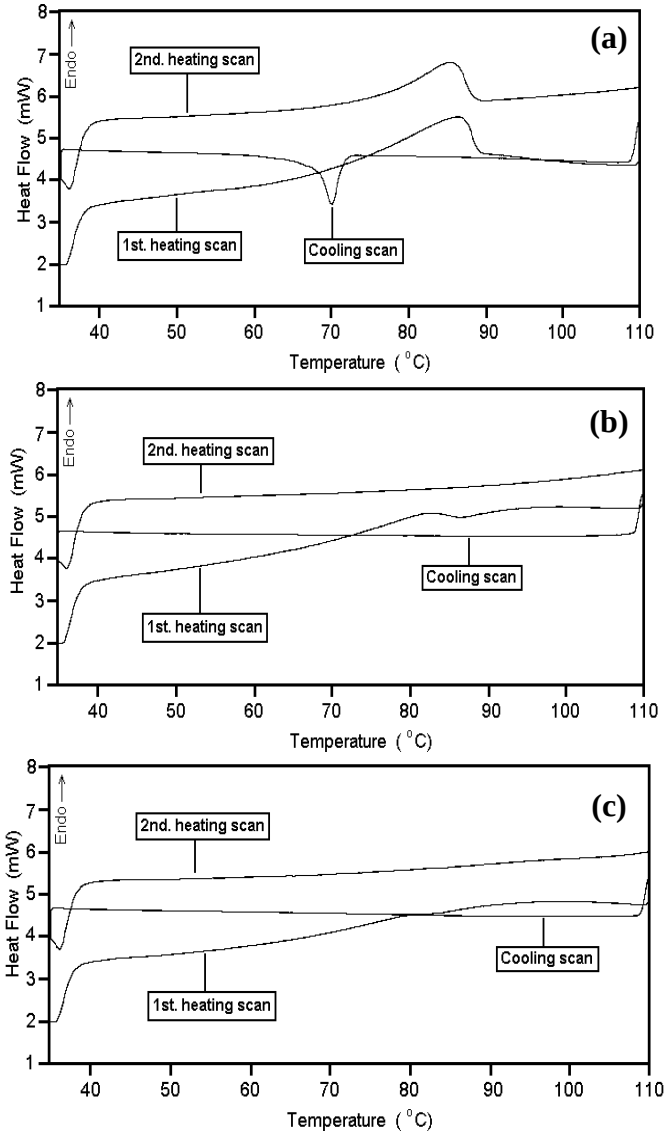

Figure 5. The heating-cooling-heating DSC thermograms of PANIPOL 1 (a), 2 (b) and 3 (c).

Concerning the rheological analysis, the extrusion of PANIPOL 2 and 3 at 80°C was not possible even at the lowest piston drive speed. It was initially anticipated that this could happen as the recommended processing temperature ranges from 100 to 225°C. However, we performed experiments at this temperature because the recommended processing range could vary depending on the equipment used. Regarding PANIPOL 1, the extrusion was accomplished at all the planned temperatures. This initially indicated

that this sample was less viscous than the other two samples. As we shall see later, this was the case at all comparable extrusion conditions. Apparent viscosity-apparent wall shear rate relationships for the three complexes at 100, 120 and 150°C are presented in Figure 6. The results suggest that the samples behave like a material obeying the power law (which is commonly proposed to describe pseudoplastic behaviour) in the shear rate interval from 3.59 to 717.00 s^{-1}.

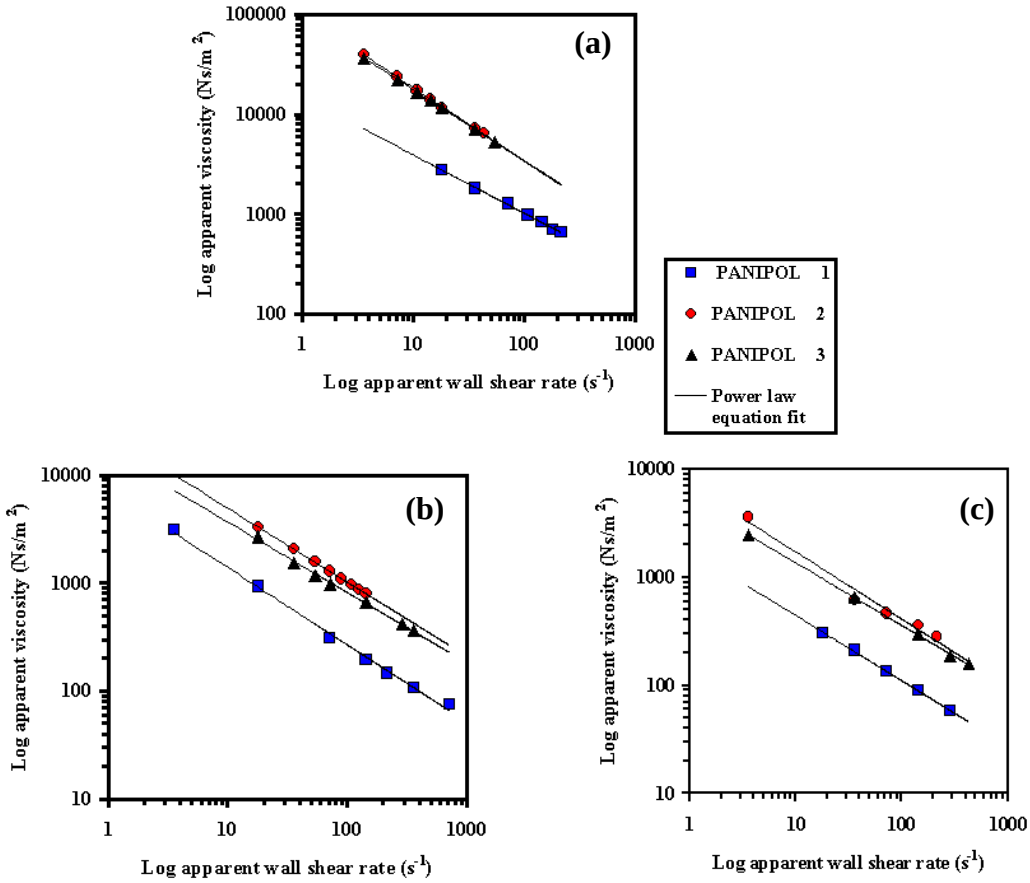

Figure 6. Apparent viscosity-apparent wall shear rate relationships for the PANIPOL complexes at 100 (a), 120 (b) and 150°C (c).

In general, the results indicate that PANIPOL 2 and 3 exhibit similar levels of viscosity at all comparable extrusion conditions. However, PANIPOL 2 proved to be the most viscous of the three samples. We believe that the three samples could be deformed into fibres following an in-situ deformation process, especially if the viscosity of the polymer matrix is higher than that of the complexes. However, the fact that PANIPOL 2 is the most viscous, suggests that the elongated domains of this sample would be the most stable and likely to maintain the desired morphology.

The evaluated average volume conductivity was 2.57 x 10^{-3} S/cm and this compares with the value of 1 x 10^{-4} S/cm reported by the company supplying the materials.

With respect to the morphological analysis, Figure 7a presents the morphology found in a granule of the powder pellets analysed under the optical microscope. It can be observed that some areas of the photograph are blurred indicating that those sections in the granule were out of focus during the analysis. This is the result of irregular thickness as no special technique was followed in the preparation of the sample other than mere pulverisation of the pellets. However, form the micrograph, spherical features can be seen dispersed all over the bulk of the granule. For example, note the features

reflecting the light in the encircled area. The observed morphology seems to suggests that the globular features are bound together by a different material, thus indicating that the morphology of the samples consists of at least two different phases, one in the form of spherical particles and another one serving as a dispersing medium. Through this analysis it was not possible to have a clear estimate about the size of the particles as the photograph was taken at insufficient magnification. This is shown better in the SEM micrograph (Fig. 7b) which indicates that the particles are about 7 μm in diameter or of a smaller size. Figure 7b also reveal that the analysed granule is composed of densely packed particles. The morphology presented in Fig. 7 resembles the morphology observed by some researchers for conducting polyaniline prepared by different routes such as conventional chemical [22,23] and dispersion [24-26] polymerisation, respectively. It is however worth pointing out that the diameters reported for the polyaniline particles in the above works were all within a nanometric scale, which differ considerable with the size of the particles observed in our samples. However, as is also mentioned in the references cited above, the size of the conducting domains depends on the synthesis route of the polymer, and what is more, diameters of about 20-50 μm have also been reported [27,28]. Consequently, we believe that the observed spherical features in our sample correspond to the conducting polyaniline particles dispersed in a continuous phase.

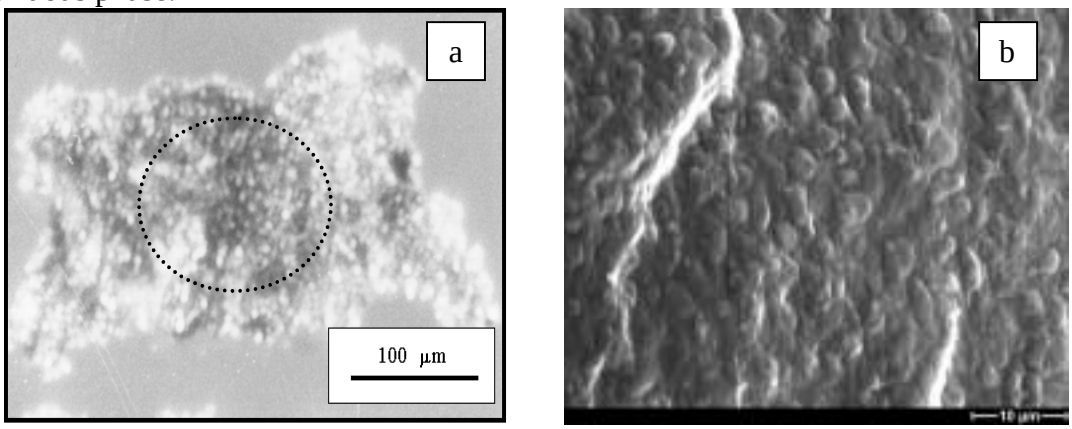

Figure 7. Optical (a) and SEM (b) micrographs of a granule of PANIPOL 2 powder.

CONCLUSIONS.

The results from the X-ray diffraction experiments revealed that the level of crystallinity detected in the PANIPOL complexes was relatively low. The presence of the element Zn in the pellets was also confirmed through this analysis. The gravimetric analysis confirmed the amount of the conducting polyaniline salt in the pellets (that is, ca. 25 wt.%). This analysis also aided in establishing an initial hypothesis about the use of DBSA and a Zn salt of DBS in the manufacture of the pellets. The concept about the use of DBSA and a Zn salt of DBS as the doping and organometallic compounds, respectively, was reinforced by the results yielded from the FTIR analysis.

The thermal limitations of the PANIPOL samples were established through TGA and DSC analyses. These analyses confirmed that the samples could be safely processed up to a maximum temperature of about 250°C without exposure to severe degradation and loss of the electrically conductive characteristics. The rheometry analysis showed that PANIPOL 2 was the most viscous of the three samples. This suggests that, when blended with a highly viscous matrix, this sample would be most successfully deformed into uniform fibres by the carrying action of the matrix during the forming process.

The level of electrical conductivity measured in the samples was 2.57 x 10^{-3} S/cm comparing well with the value reported by the supplying company. The morphological analysis performed on the pellets showed the presence of spherical features surrounded by a continuous phase. These features, which are about 7 μm in diameter (or of a smaller size), are believed to be the particles of the conducting polyaniline.

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