"Measure what is measurable,
and make measurable what is not so".

***Galileo** (1564–1642), Italian scientist.*

CHAPTER 3

RAW MATERIALS SELECTION

3.1 INTRODUCTION.

This chapter deals with the description of the raw materials used. In this project experimentation with polyaniline (PANI) to serve as the conducting phase was performed. For this, three samples of electrically conductive PANIPOL™ complex were used. Their characteristics are described in section 3.2. The interest in using these materials was based on the fact that PANI is at present, one of the most promising conductive polymers. This is due to a number of important reasons including its chemical stability combined with high levels of electrical conductivity. Additionally, it is known that, when blended with conventional polymers, PANIPOL™ acts as a processing aid [71], that is, the melt viscosity and required processing temperatures are generally lower for the blends than for the matrix polymers, thus facilitating the blending process. Also, an additional advantage over other conventional conducting materials (e.g., metals or semiconductors) is that the PANI phase is more likely to be deformed into fibres by stress transfer from the polymer matrix. The work that Etches [146] carried out related to the production of extrudates composed of PANIPOL™ and a thermoplastic elastomer, namely polystyrene-polybutadiene-polystyrene block copolymer (SBS), evinced the possibility of deforming the PANI phase into fibres within the SBS matrix, following an in-situ deformation process. Despite the referred work rendered encouraging results, much of the process, however, needed to be improved. This, together with the reasons already pointed out, were determinant factors to justify the use of PANIPOL™ in the present project.

With respect to the insulating matrix, of primary importance is that the material selected should possess thermoplasticity and a high viscosity to induce the in-situ formation of the dispersed conducting phase into fibres. Accordingly, experimentation was carried out with the same grade of SBS used in the work of Etches. This particular grade of SBS is a viscous material that has also been successfully used as a matrix in self-reinforcing composite applications (see for example the work of Callister [147], Holloway [148] and Steadman [149]). In addition, as mentioned before, previous experimentation with this material [146] established its feasibility in the in-situ production of PANI fibres. Its characteristics are described in section 3.3.1.

Investigation of alternative systems was also performed. For this, low density polyethylene (LDPE) and polypropylene (PP) were, respectively, blended with PANIPOL^{TM}. These polymers were selected, taking into account that their processing flow viscosities are comparable, or greater than that of the SBS at suitable processing temperatures. As will be seen later (section 4.6), this was confirmed experimentally. Also, it was important that the polymers could be processed within a suitable processing temperature window, dictated by the allowed processing temperature of the dispersed PANIPOL^{TM} phase. Another factor that contributed to the selection of these polymers is the existing evidence about their use for inducing the production of PANI fibres following an in-situ process. For example, Virtanen et al. [28] and Passiniemi et al. [121] have reported on the production of PANIPOL^{TM}-PP filaments exhibiting a phase separated morphology with continuous fibrils of PANI in the PP matrix. On the other hand, Yang et al. [150] has given an account on the production of doped PANI-LDPE extrudates in which orientation of the conducting phase in the extrusion direction was observed. The characteristics of the LDPE and PP grades used in this project are summarised in sections 3.3.2 and 3.3.3 respectively.

3.2 ELECTRICALLY CONDUCTIVE PANIPOL^{TM} COMPLEXES.

The samples were provided by NESTE Oy Chemicals and they are identified as follow:

- PANIPOL^{TM} 1: PANIPOL^{TM} CX, code CX100X23, lot 6C0113/1.
- PANIPOL^{TM} 2: PANIPOL^{TM} CX, code CX100X03, lot 7C0002/2.
- PANIPOL^{TM} 3: PANIPOL^{TM} CX, code CX300X33, lot 6C0120/4.

The samples were supplied in the form of cylindrical compressed pellets and, as indicated by the supplying company [71], their composition is about 25 weight % (wt. %) of polyaniline salt and about 75 wt. % of a zinc compound. However, they differ in viscosity and plasticizing effect intended for different processing applications such as blown film (PANIPOL^{TM} 1), injection moulding (PANIPOL^{TM} 2) and fibre spinning (PANIPOL^{TM} 3) [151]. The viscosity is adjusted with the amount and type of plasticizer component. The basic chemistry, however, is the same in all the samples. However,

regarding their thermal behaviour and stability, respectively, slight differences might come from variation in batch quality [151]. The PANIPOL™ complexes typically contain some plasticiser and/or compatibility agents in addition to polyaniline and counter-ions. Generally, the electrical conductivity of the compressed pellets ranges from 10^{-3} to 30 S/cm [71]. However, the typical volume conductivity value, provided by the supplier, for the three samples is 1 x 10^{-4} S/cm. This information, together with other properties, is presented in Table 3.1.

Table 3.1. Typical properties of NESTE PANIPOL™ complexes[a] [71].

Colour	Dark green
Volume conductivity	1 x 10^{-4} S/cm
Volatile matter	< 5 wt. %
Density	1100 kg/m^3
Absorption of water	Hygroscopic
Maximum allowed processing temperature	230°C
Processing temperature range	100-225°C

[a]Typical values obtained by NESTE Oy Chemicals. Not to be regarded as specification.

3.3 MATRIX MATERIALS.

3.3.1 POLYSTYRENE-POLYBUTADIENE-POLYSTYRENE BLOCK COPOLYMER.

The material was provided by Shell Chemicals and is identified as KRATON™ D-1102CU (formerly Cariflex TR-1102). The polymer, supplied as porous pellets, is a linear three-block copolymer consisting of chains of the form polystyrene (PS)-polybutadiene (PB)-polystyrene (PS). Typical properties are presented in Table 3.2.

Table 3.2. Typical properties of KRATON™ D-1102CU [152].

Volatile matter	0.30 wt. %
Ash	0.10 wt. %
Melt flow rate (200°C/5 kg)	6 g/10min
Density	940 kg/m^3
Tensile strength	33 MPa
Modulus (300%)	2.9 MPa

The structure and properties of this particular copolymer have been extensively investigated in the past (for example Folkes et al. [153,154]) and it has been found that

the microstructure consists of a segregated phase of PS (25 wt. %) within a matrix of PB. The PS exists in the form of long cylinders, having a typical diameter of about 15 nm. These cylinders can be very regularly arranged so as to form a macrolattice with spacings of the order of 30 to 40 nm. For the particular case of a cylindrical morphology, the lattice is hexagonal, although in most specimens this ordering is usually only short range. If very special care is taken, the melt-processed specimens can be such that most, if not all, of the material exhibits a uniformly oriented macrolattice or "single-crystal". Specimens like this have been prepared using extrusion processes. The glass transition temperature of the PS phase is 373 K (100°C) [155], while that of the PB (cis-1,4-PB) ranges from 167 to 178 K (i.e., from -106 to -95°C) [155]. The volume conductivity value reported for the SBS is 1 x 10^{-14} S/cm [156].

3.3.2 LOW DENSITY POLYETHYLENE.

Low density polyethylene, Novex LD5320AA, was provided by BP Chemicals. The polymer was supplied as free-additive pellets, and its melt flow rate (190°C/2.16 kg) and density are 2.3 g/10 min and 921 kg/m^{3}, respectively [157]. The melting temperature of the material measured by us in a Perkin-Elmer DSC-7 differential scanning calorimeter is 111°C (experimental conditions similar to the ones described in section 4.5.2). The volume conductivity value reported for the LDPE is 1 x 10^{-16} S/cm [156].

3.3.3 POLYPROPYLENE.

Polypropylene, Novolen® 2300L, was provided in the form of pellets by BASF Chemicals. Typical properties are presented in Table 3.3.

Table 3.3. Typical properties of BASF Novolen® 2300L polypropylene [158].

Density	910 kg/m^{3}
Melt flow rate (230°C/2.16 kg)	8 g/10 min
Melting temperature	163°C
Volume conductivity	1 x 10^{-15} S/cm