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Preliminary Test of Electroconductive Polyolefine Fibres Modified with Polyaniline

Abstract
Initial research into methods for obtaining anti-static fibres is presented. We used mixtures of polypropylene, serving as a polymer matrix, as well as polyaniline (PANI) as a conductive polymer and alkylobenzenesulphone acid (ABSA) and a protonating agent. The concentration of PANI used in our research varied from 0 to 10%, and that of alkylobenzenesulphone acid from 0 up to 30%. Polypropylene was added to complete the mixture up to 100%. DSC and WAXS tests were carried out, as were electrical resistance measurements by the four-conductor connection technique. The results showed that in general, the melt mixtures were fibre-grade, and of breaking strength partly even 60 MPa. Electroconductivity values of the order of 10^{-4} S/cm allowed the fibres obtained to be applied in fabrics with anti-static properties.

Key words: *electroconductive fibres, polyaniline, polypropylene, melting-spun process.*

Introduction

In the production and utilisation of textile products, a common problem is that they become statically charged very easily. Even natural fibres in dry conditions, devoid of moisture, accumulate large amount of static charges. This feature is predominant in synthetic fibres such as polypropylene or polyester fibres. This creates serious problems while processing fibres into products, and later during the use of products with such fibres as they can constitute a fire or explosion hazard. The fibres' electrostatic properties, the fact that they become charged easily, may result in serious damage to sensitive electronic equipment when using textile materials made of these fibres.

For these reasons, efforts have been made to reduce the influence of the unwanted electrostatic properties of fibres, especially of synthetic fibres. Anti-static end-use finishes have hitherto been the most basic and primary way of dealing with the problem. However, it should be noted that this solution, although quite inexpensive, is also of rather short duration - the antistatic surface obtained in processing is removed very quickly and easily, either by being rubbed or washed off.

Another way of improving the antistatic properties of a fabric is to weave some highly electrically conductive fibres into it: for example, metal (silver, copper or iron), carbon fibres, or fibres modified either with graphite or some ion compounds. Such fibres give very good results; however they are still not widely used, as production of them is very expensive, while their mechanical properties are rather poor.

More and more frequently, conductive polymers are used in modifying fibres. Polyaniline (PANI) seems the most interesting among many polymers of this type. It is a compound with a conjugated structure of dual bonds which may transfer static charges. An admixture, which may be some protonating substance (which in most cases is acid), causes a disturbance in the structure of the electrons of the compound. An increase in conductivity can also be observed. Among other interesting features of this compound, it should be noted that the monomer used in production of the polymer is very inexpensive. Polyaniline can also be very easily synthesised. Finally, it is highly chemically stable in its protonated state [1].

In this article we describe attempts to obtain PANI modified polypropylene (PP) fibres. Alkylobenzenesulphone acid was used as the protonating agent.

Experimental

Materials

- ELTEX P HY 001P polypropylene produced by SOLVAY.
- Polyaniline (PANI) synthesised by the authors [2].
- Alkylobenzenesulphone acid (CH_3-$(CH_2)_{10\text{-}14}$-C_6H_5-SO_3) (ABSA) made by Rokita S.A., Brzeg Dolny (Poland).
- Hydrochloric acid (HCl) - POCH Gliwice, Poland.
- Ammoniumpersulphate($(NH_4)_2S_2O_4$) - POCH Gliwice, Poland.
- Ammonium hydroxide (NH_4OH) - POCH Gliwice, Poland.

Component preparation

The polyaniline ()PANI) was synthesised in 1M HCl medium, at a temperature of -5°C and in the presence of $(NH_4)_2S_2O_4$. The polymer obtained was then neutralised with NH_4OH. After being completely neutralised, PANI was then washed in Soxlet apparatus for 48 hours [2].

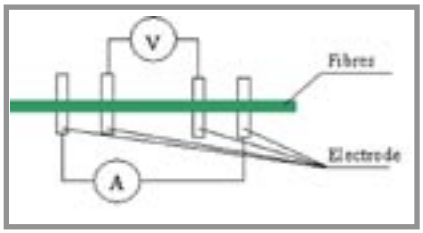

***Figure 1**. Schematic diagram of the electric resistance measurement circuit; the distance between the voltage electrodes was 1 cm.*

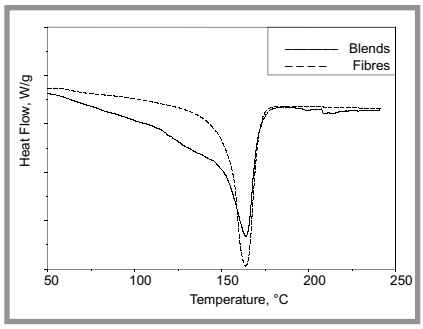

Figure 2. *DSC thermograms of blends and fibres PP/PANI.*

Composites preparation

The components were mixed in the following proportions: PANI 0, 1, 2.5, 5 and 10%, ABSA 0, 5, 10, 15, 20, 25 and 30%, by weight. Polypropylene was added, completing the mixture up to 100%. All the components were mechanically mixed together until they became fully homogenous. Next, the mixture obtained was thermally processed with the use of a Brabender extruder. The processing conditions were selected to obtain fibres for the chosen PANI and ABSA contents, to achieve the highest possible breaking strength of the fibres obtained. The detailed conditions are presented in [3]. In general, the temperature of the extruded melt was 190°C. The fibres were air-spun with a take-up velocity within the range from 50 m/min up to 1000 m/min, depending on the melt properties [3].

Measuring methods

Thermal analysis was carried out using an MDSC TA 5100Instruments Analyser; the heating rate was 20°C/min.

Wide-angle X-ray scattering (WAXS) measurements were performed with the use of an HZG-4 HZG-Dresden apparatus.

Electrical resistance measurements were carried out using a 2410 1100V SourceMeter® Keithley apparatus by the four-conductor connection technique and with the use of gold electrodes (Figure 1). To ensure that the apparatus' indications for fibres with lowest conductivity fell within the measuring range, the number of filaments used in the tests were chosen for these conditions, and were then used for all other fibres. The measurements carried out were treated as preliminary, and therefore no accuracy analysis was performed, as the accuracy was well above that desired as the conductivity differed in some powers of S/cm between the individual measuring points.

Results and Discussion

Many kinds of fibres were obtained from mixture prepared in the experiments. Nearly all of these mixtures presented fibre-grade quality, and only mixtures with very high concentration of PANI (10% and above) and ABSA (above 25%) caused problems when spinning the fibres.

The fibres spun had a smooth surface and a green colour (varying from light to dark green), which proved that PANI had been well mixed and protonated in the mixture. No defects could be noticed in the cross-sections of the fibres.

The thermal properties of polymer mixtures with polyaniline are well known from literature [4-12]. In general, these fibres are medially or highly thermally stable. The investigations we carried out confirmed this feature, which means that the electroconductive fibres obtained can also be highly thermally stable. Figure 2 shows some example thermograms of the mixture and the fibre consisting of 2.5% PANI, 20% ABSA and 77.5% PP.

It is noteworthy that until the mixture reaches the PP melting temperature, i.e. 163°C, a series of thermal reactions takes place in the substance. These are probably small-molecule solvents and water evaporation reactions. The PANI protonation reaction may also take place at this stage. Heating the mixture above the PP melting temperature causes no further reactions. The mixture is stable up to the temperature of 240°C.

The thermogram of the fibre shows no thermal reactions either below the temperature of 163°C or above it. The thermal effect of the melting process, which is more significant in the fibre than in the mixture, may imply higher crystallinity of the fibre. The lack of any other thermal reactions proves that the fibres are highly thermally stable.

Some examination and measurements of wide-angle X-ray scattering (WAXS) (Figure 3) carried out on a series of samples prove that the fibres obtained are highly crystalline. Pure PP, being most crystalline, serves as the reference sample.

The increase in concentration of PANI, from 0 to 5%, corresponds with a decrease in the degree of crystallinity of the fibre. This is caused by the larger amount of PANI, and also in the PANI and ABSA agglomerates which are formed, and which preclude PP crystallisation.

The breaking strength of the fibres obtained was determined and presented in Figure 4. As can be seen from the diagrams, the highest breaking strength was obtained for fibres with a PANI content of 5%. An increase in the ABSA content also causes an increase in the fibres' breaking strength. At a content of 15% and higher of ABSA, this influence is already small or even negative. A good opportunity is that this range of PANI and ABSA contents also includes those fibres with the highest conductivity. Measurements of electrical conductivity of the fibres allow us to determine its anti-static properties.

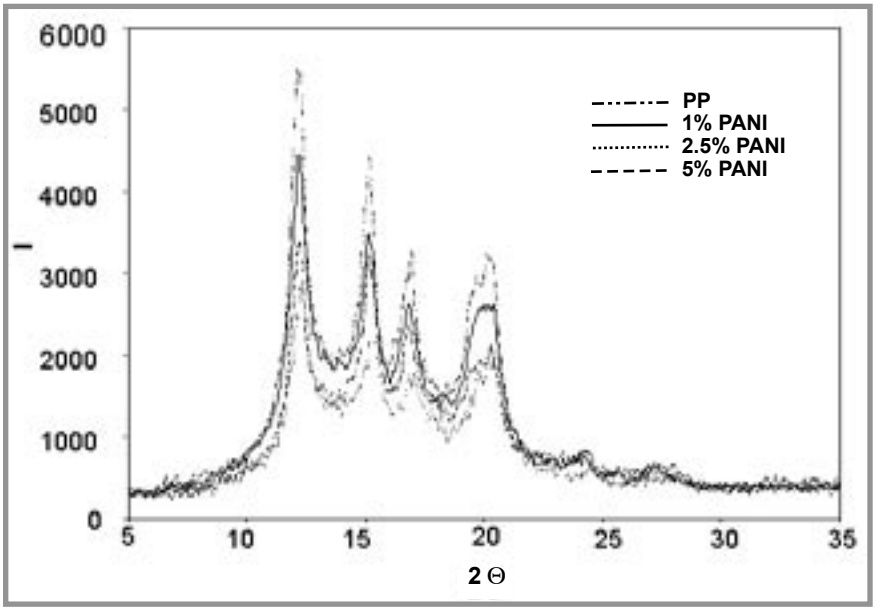

Figure 3. *WAXS patterns of PP/PANI/ABSA for different PANI content (ABSA - 20%).*

Figure 5 shows the relationship between conductivity of a series of samples with a constant ABSA concentration of 20% and a varying concentration of PANI, from 0 to 10%. A significant increase in conductivity can be noted until the polyaniline concentration reaches 5%. A further increase in concentration of this polymer results in a very small increase in the conductivity of the fibres or even a small decrease. A probable reason for this phenomenon is the low degree of protonation of PANI. No further conductivity paths are formed, simultaneously, poor dispersion of the polymer in the fibre is noted.

Figure 6 illustrates the dependence of conductivity of a series of samples (with constant (5%) concentration of PANI) on the change in concentration of ABSA (0 to 30%). An increase in conductivity can be observed until the acid reaches the concentration of 20%. A further increase in concentration of the acid results in a decrease in conductivity. This can be explained by the high degree of protonation of PANI, as well as the formation of new conductive paths. Adding further acid only results in an increase in the fibre's homogeneity; however no further conductive paths are formed, due to insufficient concentration of PANI.

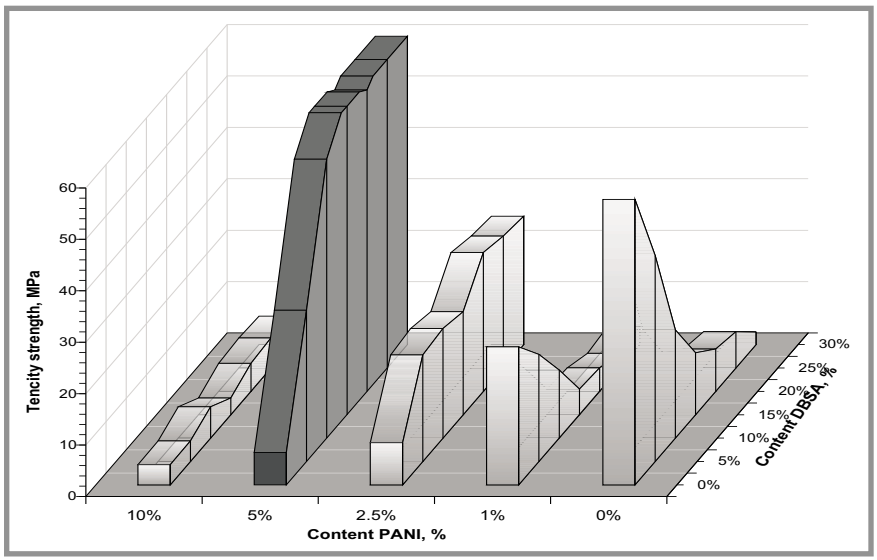

Figure 4. *Dependence of the fibres' breaking strength on the PANI and ABSA content. The fibres with the highest conductivities obtained are marked dark grey.*

Conclusions

- It is possible to obtain fibre-grade melts from PP-PANI mixtures with ABSA used as the protonating agent.
- An increase in conductivity from 10^{-15} S/cm for pure PP, up to 10^{-4} S/cm for the fibres containing protonated PANI with optimised PANI and ABSA contents, proves that the latter can be included in a group of anti-static products.
- The research described gives hope that it will be possible to create an industrial technology for manufacturing inexpensive and durable fibres, which can be used in anti-static products.

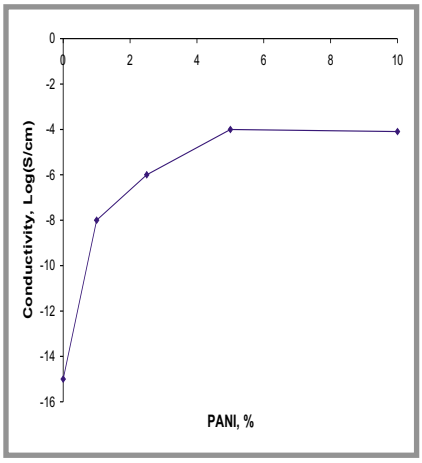

Figure 5*. Dependence of conductivity of PP/PANI fibres on the content of PANI (ABSA constant - 20%).*

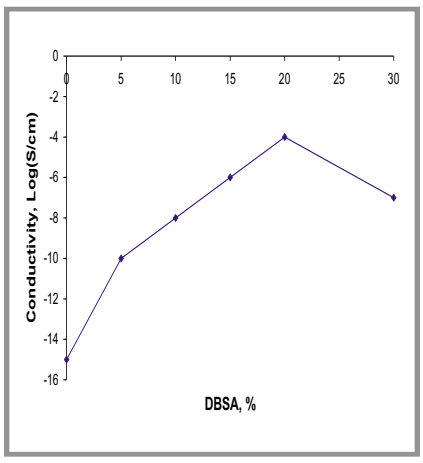

Figure 6. *Dependence of conductivity of PP/PANI fibres of 5% PANI on the content of ABSA.*

Acknowledgements

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