Thermal preparation of conducting polyaniline/polypropylene composites and investigation of their structure and specific electrical conductivity

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In recent years many works have been devoted to conducting systems obtained from composites of polymers with a conjugated system of double bonds and classical thermoplastic polymers. Conduction in these systems is described using the theory of transport in heterogeneous media (ref. 1). Methods frequently employed for producing such materials are electropolymerisation, chemical polymerisation of monomers dissolved in a polymer matrix, and production of conducting blends by processing from solutions. The above methods have been described quite extensively in the literature with reference to polyaniline (refs. 2–5), but few works have been published concerning the problem of obtaining composites of polyaniline with thermoplastic polymers based on moulding from the molten phase (ref. 6).

To fill this gap we undertook studies with the aim of developing a thermal method for preparation of conducting composites based on polymer blends containing polyaniline.

In view of the specific nature of heat treatment, the main criterion for selecting the components of these blends was the condition of heat resistance at the processing temperature.

EXPERIMENTAL SECTION

Materials

Using the methods of thermal analysis, we identified substances that are able to provide the dielectric matrix, the conducting phase and a compatibiliser of the blends produced. Based on the results of preliminary studies, among the many variants that were considered, a series of polymer composites with the following composition was selected for further study:

- matrix: polypropylene (PP), unstabilised powder, Young’s modulus 1100 MPa, mass flow rate MFR (at 230°C/2.1 N), 3.5 g/10 min;
- conducting phase: polyaniline, synthesised by chemical oxidation (ref. 7) in collaboration with the Institute of Physical Chemistry and Polymer Technology of the Silesian Polytechnic, doped with phenylphosphonic acid (PPA);
- compatibiliser: lauryl gallate (LG), Aldrich.

Moulding of isotropic composites

The appropriate quantities of polyaniline and PPA were weighed, these components were carefully triturated, then the powdered PP and, if required, LG were added. Then the whole was homogenised thoroughly by hand and pelletised in a hydraulic press (pellet diameter 12.7 mm = 0.5 inch). The pellets were heat treated (at 180°C) at a pressure of 50 MPa. The processing temperature was established on the basis of previous thermal studies by DSC, carried out using the ‘TA Instruments – DuPont 2100’ system (Fig. 1).

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Characterisation of the composites

The specific conductivity was measured by Van der Pauw’s method (ref. 8), using a picoameter (Kithley type 487), in collaboration with the Department of Physics of the Condensed Phase of the Mining and Metallurgy Academy in Kraków. The morphology of the composites was characterised with the aid of a Polam P-113 polarising microscope fitted with a digital image analyser. The structure of the composites was investigated by X-ray studies (WAXS) using the URD 6 diffractometer from the Seifert company.

RESULTS AND DISCUSSION

Tables 1 and 2 give the compositions of the composites, without and with compatibiliser (LG) respectively.

Before the heat treatment, the homogenised compositions are friable, greenish-white in colour, and under the microscope it can be seen that there is good mixing of the components. After melting they assume a uniform, dark blue colour, they have a smooth surface and they become elastic.

Micrographs obtained in reflected light show good dispersion of the polyaniline, whereas in polarised light it is possible to observe the development of differences in the degree of crystallinity of the polypropylene. This is confirmed by analysis of the WAXS diffractograms (Fig. 2), carried out by the Hindeleh-Johnson method as modified by Rabiej and Wlochowicz (ref. 9); this indicates a degree of crystallinity varying in the range 27–35%. The so-called ‘conducting channels’, formed in the matrix as a result of heat treatment, are also clearly visible (Fig. 3, connected dark areas).
It follows from the measurements of conductivity that as the polyaniline/PPA molar ratio increases in the range from 0.25 to 0.77, the conductivity of the samples increases (from 7.13·10^{-11} to 5.11·10^{-6} S/cm), but it decreases somewhat (to 1.03·10^{-6} S/cm) when this ratio has a value of 1.04 (Fig. 4). The chemical structure of polyaniline (in the form of polyemeraldine) determines the maximum possible degree of protonation that can be attained: 0.5 (regardless of the initial molar ratio of polyaniline to PPA). This corresponds to conductivity of just 7.07·10^{-8} S/cm, therefore the maximum conductivity observed for polyaniline/PPA molar ratio of 0.77 confirms the view that doping in the molten phase is a process that is difficult and not very effective, therefore it is necessary to use a large excess of protonating agent, though beyond a certain content of this protonating agent, further increase in the amount of the latter does not lead to an increase in conductivity.

The experimentally determined values of specific electrical conductivity of the composites as a function of compatibiliser content (averaged within each series with different LG content) vary over a wide range, from 2.6·10^{-6} (series II in Table 3) to 2.1·10^{-10} S/cm (series V in Table 2) (Fig. 5). In comparison with composites that do not contain a homogenising additive (series I in Table 2, conductivity 7.07·10^{-8} S/cm) we observe a considerable increase in conductivity in the case of samples containing 10.3% LG (series II). Further increase in compatibiliser content then causes a regular and pronounced drop in specific conductivity to 2.13·10^{-10} S/cm (series V in Table 2, 35.2% LG).

The improvement in the degree of homogenisation of the composites with increase in the proportion of homogenising additive, confirmed on the basis of examination of the micrographs, is a feature that opposes specific conductivity. For practical purposes, composites containing 35.2% LG are dielectrics.

We attempted to explain the essential nature of the changes in specific conductivity of the composites as a function of the content of compatibiliser on the basis of the results of WAXS studies (Table 3). A analysis of the structural parameters indicates

<table>
<thead>
<tr>
<th>LG content, wt.%</th>
<th>Average size of PP crystallite, nm</th>
<th>Degree of crystallinity, %</th>
<th>Position of reflection of (110) plane</th>
<th>Specific conductivity, S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.8</td>
<td>35.3</td>
<td>13.95°</td>
<td>7.07·10^{-8}</td>
</tr>
<tr>
<td>21.2</td>
<td>18.4</td>
<td>29.7</td>
<td>14.10°</td>
<td>1.76·10^{-6}</td>
</tr>
<tr>
<td>28.8</td>
<td>15.0</td>
<td>29.8</td>
<td>14.30°</td>
<td>1.16·10^{-6}</td>
</tr>
<tr>
<td>35.2</td>
<td>14.8</td>
<td>35.6</td>
<td>14.45°</td>
<td>2.13·10^{-10}</td>
</tr>
</tbody>
</table>

Table 3 WAXS structural data for polyaniline/PP composites with different compatibiliser contents (series from Table 2)
that the conductivity values of the composites are somehow related to the average size of the crystallites formed in the polypropylene matrix. This dimension was determined normally to the series of (110) lattice planes. Increase in crystallite size generally tends to increase the conductivity of PP/polyaniline composites.

Taking into account that production of thermoplastic conducting blends based on PP and polyaniline is possible and gives interesting results, we undertook further work concerning the possibility of practical application of the composites obtained in the course of the research described in the present article.

CONCLUSIONS

We obtained, and conducted preliminary studies on isotropic, conducting polymeric composites containing doped polyaniline. A noteworthy point is that the reaction of protonation of the systems under investigation was carried out in the solid phase and in the molten phase (previously, doping has mainly been effected in solutions). It should be emphasised that our results confirm that it is possible to obtain polymeric systems with relatively high specific conductivity by means of thermal treatment. In the case of composites based on PP and heterogeneously doped polyaniline, we observed an improvement in the spatial configuration of the conducting phase, probably occurring as a result of increased separation of the components in the volume of the matrix with increase in average size of the PP crystallites that formed in the matrix.

It should be concluded, on the basis of the results and observations described here, that proposed future research should be in the following directions:

- improvement of the actual doping process and research into more effective protonating agents,
- modification of the matrix with the aim of improving the physical miscibility of the polymers,
- better rheological properties of the composites during processing.

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