Evaluation of Polyesterimide Nanocomposites Using Methods of Thermal Analysis

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Abstract. Polyesterimide resin applied for winding impregnation has been modified by incorporating the hydrophilic and hydrophobic nanosilica, montmorillonite and aluminium oxide. For assessment of the resins in liquid and cured states thermoanalytical methods TG/DSC were used. For pure and nanofilled resins the results of investigation of AFM topography, bond strength, dielectric strength and partial discharge resistance have been also presented. It was found that dielectric and mechanical properties of polyesterimide resin containing hydrophilic silica as well aluminium oxide were much improved as compared to pure resin. Based on our investigations we have found that the methods of thermal analysis may be very useful for evaluation of nanocomposites: DSC/TGA study of resins in the liquid state under dynamic conditions can be applied to pre-select nanocomposites; isothermal TG curves of cured resins can be utilized for thermal stability evaluation; in turn, TG study after thermal ageing of cured resins could confirm the barrier properties of nanocomposites.

1. Introduction
It is well known that polymer nanocomposites exhibit improved properties relative to unfilled polymers. For many nanocomposites have been noted an increase in thermal stability [1-6] and better mechanical [6] and dielectric properties [7-8]. One of the first developed nanodielectrics was “corona-resistant” enamel for winding wires [9-11]. In turn, the article presents the results of investigation of polyesterimide impregnating resin that was filled using various nanoparticles [12]. The aim of our studies was to show the possibilities of using thermal analysis methods for the assessment of nanocomposites. The mechanical and dielectric properties of nanofilled resins as well as surface topography were also presented.

2. Experimental
Four kinds of nanofillers, i.e.: aluminium oxide Alu C, hydrophobic nanosilica Aerosil R 202, hydrophilic nanosilica Aerosil 200 (all from Evonik) and montmorillonite MMT Rheospan AS (Nanocor) in an amount of 1.5wt% have been added to base polyesterimide resin (Polifarb CW) and was dispersed using a method described in our patent [13].

For all the pure and nanofilled resins it was performed: (i) the TG/DTG/DSC study for resins in a liquid state (temperature range 23 up to 800°C, a heating rate of 10K/min, air atmosphere) using a thermogravimetric analyser TGA/DSC1 (Mettler Toledo); (ii) the bond strength test acc. to IEC
60455-2; (iii) dielectric strength test acc. to IEC 60455-2; (iv) determining of partial discharge resistance (lifetime) under pulse voltage 1100V/20 kHz. Moreover, for two kind of cured PEI samples, both the pure and nanofilled with hydrophilic nanosilica resins the following results of investigation were presented: (i) surface topography by the atomic force microscopy (AFM) with a scanning size of 1 μm. Tested surface was prepared by breaking in order to obtain natural fracture; (ii) the TG curves under isothermal conditions, i.e. at 240°C, 260°C and 280°C; (iii) bond strength after various periods of thermal ageing at 250°C; (iv) the TG curves under dynamic conditions after thermal ageing at 210°C.

3. Results and discussion
The results of the investigation of bond strength, dielectric strength and partial discharge resistance under pulse voltage 1100V/20 kHz testing of pure and nanofilled resins are compared in Table 1.

Table 1. The results of testing of mechanical and dielectric properties of pure and nanofilled resins.

| Properties                              | Pure PEI resin | PEI resin + MMT | PEI resin + hydrophobic nanosilica | PEI resin + hydrophilic nanosilica | PEI resin + aluminium oxide |
|-----------------------------------------|----------------|-----------------|-------------------------------------|-------------------------------------|----------------------------|
| Bond strength at 23°C†                   | 184            | 169             | 144                                 | 230                                 | 205                        |
| Dielectric strength at 180°C‡ [kV/mm]   | 40.2           | 33.8            | 19.0                                | 72.8                                | 62.3                       |
| Partial discharge resistance (lifetime) under pulse voltage 1100V/20 kHz** [min] | 45             | 41              | 23                                  | 254                                 | 479                        |

† the average of 10 measurements
‡ the average of 5 measurements

It may be noted that the resins containing hydrophilic nanosilica and aluminum oxide show a marked improvement of the bond strength, dielectric strength and partial discharge resistance whereas the resins containing montmorillonite and hydrophobic nanosilica have the properties much worse than pure PEI resin. The TG/DTG/DSC thermograms of these resins in liquid state are presented in Fig. 1. The resins with hydrophilic nanosilica and aluminium oxide have showed unchanged the TG and DSC curves as compared to pure resin. On the other hand these resins whose properties deteriorated (i.e. with MMT and with hydrophobic nanosilica) show a clear distortion of the process of solvent evaporation and gelling up to 150°C (Fig. 1); the rate of solvent loss was reduced and therefore copolymerization process has been disturbed. So it can be concluded that the thermoanalytical studies of resins modified with nanofillers in the liquid state can be useful in pre-selection of nanofilled resins.

The AFM topography images of samples of pure and nanofilled with hydrophilic nanosilica PEI resins are compared in Fig. 2 and 3, respectively (scanning size: 1 μm). For pure sample, obtained results revealed usually the regular step-like structures at submicrometer level (Fig. 2). The topography of nanofilled sample is quite different; it shows densely packed array of similar objects (Fig. 3) with the grain size of about 10-30 nm. A weaker tendency of creating regular structures during cracking of nanocomposite could suggest better mechanical properties.

For two PEI resins in cured state: pure and modified with hydrophilic nanosilica the TG curves under isothermal conditions, i.e. at 240°C, 260°C and 280°C during period of 10 h, are presented on Fig. 4. It can be seen that mass loss of the nanofilled resin at all test temperatures is slower. It can prove that the thermal stability of nanofilled resin is better. In nanocomposite, due to the barrier effect of the nanofiller particles, on the one hand a mass transfer of degrading polymer to the vapour phase and on the other hand, oxygen transfer through polymer could be inhibited [14].
The improved thermal stability of the PEI resin modified with nanosilica was confirmed by investigation of the bond strength values after various periods during thermal ageing at 250ºC. After aging period of 1700 h the nanofilled resin showed the clearly higher level of bond strength (23.1 N) than pure one (11.2 N).

Figure 1. The TG/DTG/DSC curves of the pure and modified with 
\( \text{Al}_2\text{O}_3 \), hydrophobic and hydrophilic \( \text{SiO}_2 \), and MMT resins in liquid state

Figure 2. AFM image of the pure PEI resin.

Figure 3. AFM image of the PEI resin with hydrophilic nanosilica.

The TG curves of both pure and filled with hydrophilic nanosilica PEI resins have been determined after various ageing periods at raised temperatures. It was found that very high abnormal peaks appear always on the TG curves of the pure resin at about 420ºC. As example, the TG curves of the resins after period 840 h of thermal ageing at 210ºC are shown in Fig. 5. The cause of the occurrence of these peaks may be a violent releasing of gaseous products of thermal ageing. However this phenomenon does not appear in the case of nanofilled resin, probably because of the barrier properties of the nanocomposite (Fig. 5).
4. Conclusions
Polyesterimide resin filled with nanosilica, montmorillonite and aluminium oxide have been investigated. The significant improvement of dielectric and mechanical properties of resins comprising a hydrophilic nanosilica and aluminium oxide was obtained. It was found also that the thermal analysis methods can be very useful in assessment of nanocomposites, i.e.: (i) the TG/DTG/DSC study of resins in the liquid state can be used to preliminary assess nanofilled resins; (ii) TG study of cured resins at isothermal conditions can be applied to evaluate the comparative thermal stability of developed nanocomposites; (iii) TG study of pure and nanofilled PEI resins after thermal ageing may be the evidence of the barrier properties of nanocomposites.

5. References
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Acknowledgments
This work was supported by the WRC EIT+ NanoMat under grant “The Application of Nanotechnology in Advanced Materials” co-financed by the EU from the resources of EFRD.