Barrier properties of impregnating varnishes with nanosilica

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Abstract. The result of investigation of impregnating electroinsulating varnishes modified with two types of nanosilica at loading from 0.5% to 5% w.t., using diverse method of dispersing are presented in the paper. All composites with nanosilica have shown a rise of temperature of thermal decomposition, an increased bonding strength, decreasing of water absorption and a significantly improved resistance to partial discharges. The polyesteimide varnish with nanosilica has a dramatic, above 20 times longer time life under partial discharges condition, than that for the standard varnish. Thus we have obtained a polymer nanocomposite with an unusual resistance to that exposure. That better resistance we can explain by barrier properties for development of discharges, that cause decreasing of erosion. However, the dramatic improving of the properties can be an evidence that the used method of composite preparing enabled us to obtain a nanocomposite.

1. Introduction
The development of nanotechnology provides the advantage of unique opportunities to create new materials with unusual, impossible so far to achieve properties. Polymer nanocomposites, i.e. polymers containing particles of fillers that have at least one dimension less than 100 nm, represent a radical alternative to conventional filled polymers [1]. Topologic similarities between polymer nanocomposites and other multiphase polymers like semicristal polymers or colloids can facilitate understanding the phenomena that occur and enable to control their properties. An addition of even a very little amount of nanofillers could cause changes due to physical or chemical interactions between nanoparticles and polymer matrix; nanoparticles can play a similar role like the other additives for plastics (e.g. catalyser). Microscopy images are often presented in literature as an evidence of obtaining a nanocomposite, although by necessity they relate to a very small part of material. The attribute of nanocomposites should be, first of all, a drastic improvement in the composite properties [3, 4]. In the paper the result of investigation of polyester and polyesterimide varnishes used for impregnation of electrical motors modified with two types of nanosilica are presented.

2. Experimental

2.1 Samples
Tree types of electroinsulating varnishes on the basis of polyester resin and two esterimide resins (named A and B) were modified with two kinds of nanosilica (named S1 and S2). S1 was high purity hydrophilic fumed nanosilica applied to rheology and thixotropy control of liquid systems, with a specific surface area of about 400 m$^2$/g, average grain size 7 nm and taped density approx. 50 l/g. S2 was highly porous precipitated silica applied as a matting agent, with the pore volume 1.8 ml/g, oil adsorption 300g/100 g, a specific surface area of about 40 m$^2$/g and 10% wax surface treatment.

2.2 Investigations
Comparative investigations of the viscosity, bonding strength and water absorption for pure and modified with nanosilica varnishes have been carried out according to the relevant EN 60455-2 standard.
Thermoanalytical testing TG/DTA/DTG was carried out in air atmosphere, at a heating rate of 10 K min$^{-1}$, in the temperature range 25-800°C with derrivatograph MOM. In addition, the resistance to partial discharges (which can appear in same cases in low voltage electrical motors) was determined under square bipolar pulse voltage with the amplitude of 1100 kV and frequency of 20 kHz.

3. Results and discussions

At the first, we performed checking of processing parameters: viscosity and gelling temperatures of nanofilled with nanosilica composites. We have ascertained that they did not change significantly, provided that silica loading was below 5%wt.

Thermograms of the liquid varnishes have shown that the range of temperatures of gelling and loss of volatile matter remained practically unchanged after adding of S1 and S2. The TG and DTG curves of the all cured varnishes showed a two-step degradation, i.e. the decomposition and then combustion above about 450°C. The DTA curves presented 3 exothermic peaks at a temperature range from aprox. 410 to 600°C. The TG curves for polyester standard and nanofilled with S1 varnishes were shown in Fig. 1.

![Fig. 1 The TG curves of the polyester standard and nanofilled with S1 varnishes](image)

Determined from thermoanalytical testing (TG curve) temperatures of the thermal decomposition of the all modified with nanosilica varnishes are higher than that for pure varnish (Table 1); polyester varnish has shown much increasing, by even 40°C. We can conclude that incorporated nanoparticles caused an additional cross-linking and in effect the better thermal resistance.

For all prepared nanocomposites the bonding strength was raised. The most increasing, by about 30-40%, is also for the polyester varnish (Fig. 2). We can see, that for nanosilica S1 with a higher specific area the improving effect can be obtained at lower loading than for nanosilica S2.
Table 1 Temperatures of the thermal decomposition of the standard and modified with nanosilica varnishes determined on the base of thermoanalytical testing

| Varnish + nanosilica | Temperatures of the thermal decomposition [°C] |
|----------------------|-----------------------------------------------|
| polyester            | 320                                           |
| polyester +3%S2      | 360                                           |
| polyester +1%S1      | 360                                           |
| polyesterimide A     | 355                                           |
| polyesterimide A+3%S2| 360                                           |
| polyesterimide A+1.5%S1| 360                                         |
| polyesterimide d B   | 340                                           |
| polyesterimide B+3%S2| 360                                           |
| polyesterimide B+5%S2| 350                                           |

Fig. 2 Comparison of bonding strength of polyester varnish with and without nanosilica type S1 and S2

Barrier properties for water of varnish composites with nanosilica were also enhanced. With regard to “labyrinth” effect, i.e. elongation of the water particles path, due to the presence of dispersed phase of nanofiller, decreasing of water absorption was gained (Fig. 3).
Two composition: polyesterimide A with 1.5%wt. nanosilica S1 and polyesterimide B with 5%wt. nanosilica S2 showed a drastic enhancement of resistance to partial discharges (20-40 times longer durability) (Fig. 4). We can suppose that nanosilica can improve the barrier properties for penetration of material by partial discharges.
The raised resistance to partial discharges, analogous as for barrier properties to water, can be related with an extension of their path to weak points (i.e. points containing only varnish) due to the presence of resistant to discharges nanosilica. 

The obtained polyesterimide A varnish with nanosilica S1 in liquid state is a colloidal suspension of silica nanoparticles in varnish. It has been stored in room temperature and after a half of year has not sedimented or gelled. 

The lack of big agglomerates or sedimentation and a dramatic improvement of barrier properties, all of this are the evidence that the developed method of nanosilica dispersing of nanocomposite has it made possible to obtain a nanocomposite.

4. Conclusions

Presented results of investigations showed, that incorporation of nanosilica to electroinsulating varnish allows to improve properties, especially the barrier ones. Using the method of preparing nano-filled varnish made it possible to obtain the polymer nanocomposite with an unusual resistance to partial discharges.

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References

[1] R. A. Vaia, H. D. Wagner, Framework for nanocomposites, Materials Today, Volume 7, Issue 11, November 2006, p. 32-37
[2] N. Guz, J. J. Rushchitsky, and I. A. Guz, Establishing fundamentals of the mechanics of nanocomposites, International Applied Mechanics, Vol. 43, No. 3, 2007, 247-271
[3] Hongyan Li, Gang Liu, Bin Liu, Wei Chen, Shoutian Chen, Dielectric properties of polyimide/Al2O3 hybrids synthesized by in-situ polymerization Materials Letters 61 (2007) 1507–1511,
[4] M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, C.W. Reed, R. Keefe and W. Zenger, Polymer Nanocomposite Dielectrics – The Role of Interface, IEEE Transactions on Dielectrics and Electrical Insulation Vol. 12, No. 4; August 2005, 629-643