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Varnishes modified with nanoparticles for use in electrical insulation

Summary — This paper presents the results of investigation of impregnating polyester varnish modified by incorporation of various nanoparticles: fumed nanosilica, nanosilica and titanium dioxide obtained *via* sol-gel process, zinc oxide or montmorillonite at loading 1—3 wt. %. The compositions have been formulated using various recipes and methods of preparation of nanoparticles. The processing, mechanical, electrical, barrier and thermal properties have been examined for both basic pure varnish and varnish with nanofillers. Improving of dielectric properties (electrical strength, resistance to pulse voltage) of insulating varnishes is possible by incorporation of nanoparticles. Nanofilled varnishes exhibit also the increased thermal endurance, bond strength and smaller susceptibility to water absorption.

Key words: insulating varnishes, polyester, nanofillers, dielectric properties.

MODYFIKOWANE NANOCZĄSTKAMI LAKIERY DO ZASTOSOWANIA W POWŁOKACH ELEKTROIZOLACYJNYCH

Streszczenie — Przedstawiono wyniki badań nasycającego poliestrowego lakieru modyfikowanego na drodze wprowadzenia (w ilościach 1—3 % mas.) nanocząstek różnych nanonapełniaczy: krzemionki płomieniowej, krzemionki oraz ditlenku tytanu otrzymanych metodą zol-żel, tlenku cynku albo montmorylonitu. Kompozycje zawierały ponadto środki ułatwiające zwilżanie i dyspergowanie nanonapełniaczy oraz substancje sprzyjające odpowietrzaniu. Oceniono właściwości przetwórcze, mechaniczne, elektryczne, barierowe i cieplne lakieru standardowego bądź zmodyfikowanego (tabela 1—3, rys. 1—4). Stwierdzono, że obecność już niewielkich ilości użytych nanonapełniaczy umożliwia poprawę właściwości dielektrycznych (wytrzymałość elektryczna i trwałość w warunkach działania napięcia impulsowego) poliestrowych lakierów elektroizolacyjnych. Lakiery z nanocząstkami wykazują również wzrost (w stosunku do odpowiedniej wartości lakierów nienapełnionych) odporności cieplnej oraz siły wiążącej jak również mniejszą chłonność wody.

Słowa kluczowe: lakiery elektroizolacyjne, poliestry, nanonapełniacze, właściwości dielektryczne.

Nanotechnology enable to develop the new advanced dielectrics which show not only better mechanical, thermal and barrier properties [1—4] but also display the better dielectric properties because the large development of surface activity in nanofilled polymers results in reduced charge mobility, what in turn should bring the significant change in electrical properties [5—7]. If the size of the incorporated particles approaches that of the polymer chain length, the particles stop to behave like foreign inclusions and space charge densities are very small. The micron scale fillers produce significant Maxwell—Wagner interfacial polarization; it is negligible in a case of nanofillers.

Polymer nanocomposites for dielectric application are therefore very promising [8—14].

The developing of the new, modified by nanofillers, varnishes may be useful for the modern electrical motors applications. In this paper we present our study on improvement of properties of varnishes, especially dielectric properties, by an incorporation of various nanofillers.

EXPERIMENTAL

Materials

The impregnating polyester (PES) varnish was modified by adding of various nanoparticles: fumed nanosilica, nanosilica and titanium dioxide obtained *via* solgel process, zinc oxide or montmorillonite (MMT) at loading 1— 3 % by weight.

The following materials were used in this work:

— PES — polyester/styrene two component solventless varnish for impregnation of electrical machines and apparatus for thermal class F of insulation systems, suitable for processing on trickle-feed machines; density

1.02—1.06, viscosity (flow cup 4) 20—26 s, flash point > 32 °C, gelation time at 100 °C 8—10 s and at 120 °C 3—4 s, (Polifarb C-W);

— ZnO — titanium dioxide, a specific surface area of 42 m^2/g, density 5.3 g/cm^3 (Institute of High Pressure Physics of Polish Academy of Sciences);

— fumed silica — hydrophilic fumed silica "Aerosil 380", a specific surface area of 380 m^2/g, average particle size 7 nm (Degussa AG);

— SiO_2 (sol-gel) — silica nanospheres, prepared *via* the sol-gel technique, 400 nm diameter (Wroclaw University of Technology);

— TiO_2 (sol-gel) — nanospheres, prepared *via* the sol-gel technique, 100—200 nm diameter (Wroclaw University of Technology);

— MMT — montmorillonite (Szczecin University of Technology).

Preparation of the compositions

The nanofillers had been dried and also milled or deaglomerated by sonication and then dispersed in standard PES varnish at ambient temperature. The special additives were used to enhance wetting and dispersing (d) of nanoparticles and also air releasing of dispersion (a) to reduce the amount of voids caused by the air bubbles.

The following composition were prepared:
— PES standard,
— PES + 1 wt. % of ZnO + d + a,
— PES + 1 wt. % of fumed silica + d + a,
— PES + 3 wt. % of nanospheres SiO_2 + d,
— PES + 1 wt. % of TiO_2 + d + a,
— PES + 3 wt. % of MMT + d.

Methods of testing

The processing properties were determined by measurement of viscosity according to ISO 2431 and range of the gelation parameters utilizing thermoanalytical testing (simultaneous TG/DTG/DTA curves) of liquid varnishes with use of derivatograph "OD-102 MOM". The applied test parameters were as following: temperature range 25—800 °C, rate of heating 10 °C/min, sample weight 100 mg, test environment air, reference substance Al_2O_3.

The measurements of bond strength and electrical strength at elevated temperatures as well as the water absorption were performed according to IEC 60455-2.

The temperature of varnish decomposition for cured samples were determined from TG curve as the temperature of 5 % weight loss.

The loss factor tan δ was determined in temperature range 23 °C — 180 °C at frequency 1 kHz (the test specimens in a form of impregnated twisted pairs from enamelled wire according to IEC 60851-5).

Dielectric permittivity ε at frequency 1 kHz and electrical resistivity ρ under test voltage 1 V were also measured (the test specimens in a form of steel panels coated with varnish and cured according to IEC 60464-2, the diameter of top electrode 75 mm, bottom electrode—the metal sheet of coated panel).

Life time under pulse voltage have been determined using special generator of sharp square voltage pulses which simulated "Pulse Width Modulation" inverter pulses. The testing was made under voltage amplitude 1.1 kV and frequency 20 kHz. All tests were performed for both basic pure varnish and varnish with nanofiller.

RESULTS AND DISCUSSION

The examination of properties of electroinsulating varnishes after adding the nanofillers indicated that the processing properties were almost unchanged while nanofilled varnishes exhibited increased temperature of varnish decomposition by 10—30 °C which should be correlated with the better thermal endurance (Table 1). The fact that the processing parameters stay still in requirement limits after application of nanofiller is very important for the impregnation processes of motor windings.

Varnishes modified with nanofillers have shown higher varnish bond strength, on average by about 20 % to 40 % (Fig. 1), while at ambient temperature the rise came to above 50 % (Table 2). For all versions containing an air release additive water absorption was smaller than for pure varnish (Fig. 2), due to mechanism of barrier enhancement [4].

Table 1. Results of thermoanalytical testing of impregnating PES varnishes modified with various nanofillers

Composition	Viscosity, s	Range of gelation temperature, °C			Loss of solvent % (± 2 %)	Initial temp. of decomposition, °C
		$T_{initial}$	T_{max}	T_{end}		
PES	20	95	135	185	14	330
PES + 1 wt. % of ZnO	23	100	130	170	17	340
PES + fumed SiO_2	24	100	140	190	17	360
PES + 3 wt. % of SiO_2 nanospheres (sol-gel)	25	100	140	190	17	345
PES + 1 wt. % of TiO_2	23	100	140	200	17	330
PES + 3 wt. % of MMT	30	90	125	180	17	345

T a b l e 2. Ratios of the bond strength of nanofilled varnish and pure varnish at ambient temperature

PES	PES + 1 wt. % of ZnO	PES + 1 wt. % of fumed SiO_2	PES + 3 wt. % of SiO_2 nanospheres (sol-gel)	PES + 1 wt. % of TiO_2 (sol-gel)	PES + 3 wt. % of MMT
1.00	1.57	1.72	1.90	1.78	1.68

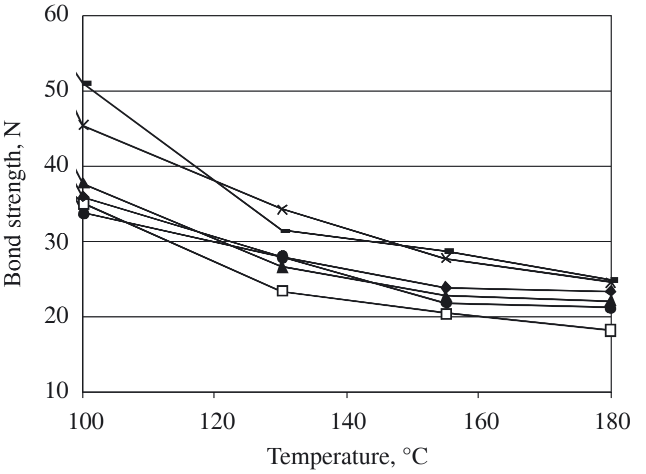

Fig. 1. Temperature dependence of bond strength for pure and nanofilled varnishes: ☐ pure PES varnish, – PES + 1 wt. % of ZnO, ● PES + 1 wt. % of fumed nanosilica, × PES + 3 wt. % of SiO_2 nanospheres (sol-gel), ▲ PES + 1 wt. % of TiO_2 (sol-gel), ♦ PES + 1 wt. % of MMT

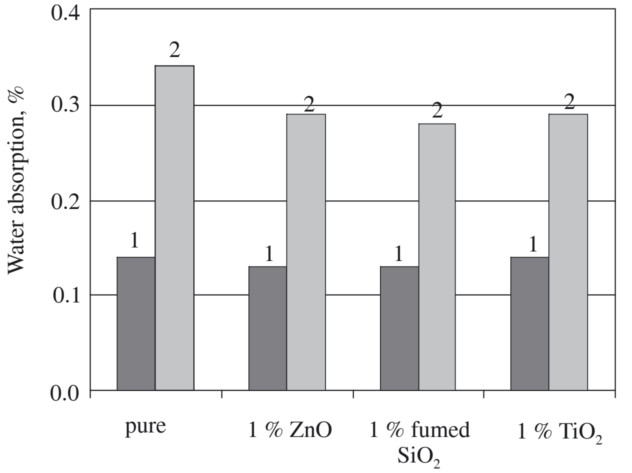

Fig. 2. Water absorption of pure and nanofilled PES varnishes: 1 — after 24 h in water, 2 — after 120 h in water

The results of the dielectric properties investigations are presented in Table 3. The varnishes PES included zinc oxide, nanosilica or titanium dioxide have shown the decrease in dielectric permittivity and maintained similar level of electrical resistivity and thermal dependence of dielectric loss factor (Fig. 3) as of standard varnish. The permittivity tends to decrease if nanostructuration takes place properly. It is ascribed to the restriction of polymer chain movement by nanoparticles [5].

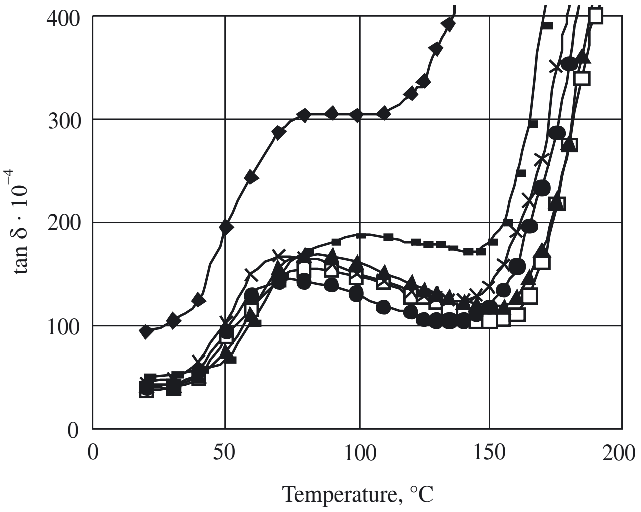

Fig. 3. Temperature dependence of loss factor tan δ at frequency 1 kHz for pure and nanofilled varnishes: ☐ pure varnish PES, – PES + 1 wt. % of ZnO, ● PES + 1 wt. % of fumed nanosilica, × PES + 3 wt. % of SiO_2 nanospheres (sol-gel), ▲ PES + 1 wt. % of TiO_2 (sol-gel), ♦ PES + 1 wt. % of MMT

Only two from the compositions, *i.e.* PES + SiO_2 obtained by sol-gel method and PES + MMT, exhibited not diminished permittivity accompanied by deterioration of other electrical properties (a higher losses, reduced resistivity and diminished electrical strength). It is possibly due to inhomogeneous dispersion and agglomeration accompanying the microstructuration in the case.

PES varnish modified with fumed nanosilica exhibited much increasing electrical strength at higher temperatures (Table 3) and also much better resistance to impulse voltage and partial dischargers (Fig. 4) which can appear in inverter-fed motors. The presence of inor-

T a b l e 3. Dielectric properties of impregnating PES varnishes modified by different nanofillers

Electrical properties	PES	PES + 1 wt. % of ZnO	PES + 1 wt. % of fumed SiO_2	PES + 3 wt. % of SiO_2 nanospheres (sol-gel)	PES + 1 wt. % of TiO_2 (sol-gel)	PES + 3 wt. % of MMT
Electrical strength, at 180 °C, kV/mm	67.1	67.5	93.1	64.7	69.6	30.9
Dielectric permittivity ε	3.3	2.7	2.7	3.3	2.8	3.2
Electrical resistivity $\rho \cdot 10^{12}$ Ω	246	207	194	49	114	33
Loss factor tan δ at 60 °C, $\cdot 10^{-4}$	114	102	129	148	110	243

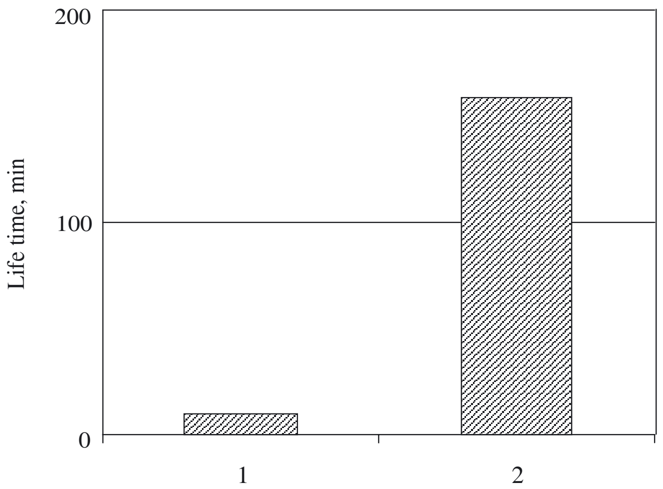

Fig. 4. Life time under impulse voltage 1.1 kV / 20 kHz for PES (1) and PES + 1 wt. % of fumed SiO_2 *(2) varnishes*

ganic particles could cause the barrier effect and inhibited erosion of surface under partial discharges [10].

CONLUSIONS

Improvement in dielectric properties of varnishes used in electrical insulation, especially in electrical strength and resistance to partial discharges, is possible by incorporation of small quantity (1 wt. %) of nanoparticles. Nanofilled varnishes exhibit also the increased thermal endurance, bond strength and smaller susceptibility to water absorption.

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