Study of electrokinetic properties of nanofillers used for the preparation of nanocomposites

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Abstract. The aim of the studies was to determine, how the zeta potential and particle size of nanofillers affect the stability of the dispersion of nanoparticles in the electroinsulating varnish, and consequently can influence the varnish properties. We have investigated the nanofillers that had been used for the preparation of nanocomposites in our earlier works. It has been found that in toluene the zeta potential of all nanofillers is much increased. It enables modifying of nanofillers. Correlation between the properties of the nanocomposite and the results of the particle size measurements has been observed. Thus studies of electrokinetic properties can be used during the preparation of nanocomposites, as well to determine the factors affecting the nanoparticles deagglomeration and a preliminary determination of the optimal technological parameters of process of preparing of nanocomposites.

1. Introduction
Polymer nanocomposite generally comprises very small filler particles dispersed in the polymer matrix. If the nanocomposite is prepared by direct mixing of the filler into a polymeric matrix in solution or in melt, we can get a colloidal dispersion. A key indicator of the stability of colloidal dispersions is the zeta potential. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. Colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. Zeta potential measurements can contribute to improve formulation stability and reduce formulation time and cost [1-7].

We have studied the zeta potential and particle size of nanofillers that were used for the preparation of nanocomposites in our earlier works. The aim of our research was to determine in what way the electrokinetic properties of nanofillers affect the stability of the dispersion of nanoparticles in the electroinsulating polyesterimide and influence the varnish properties.

2. Experimental
Zeta potential and particle size of various nanofillers in different solvents was measured using Zetasizer Nano ZS Malvern Instruments. The following commercial nanoparticles have been studied: (i) fumed nanosilicas: Aerosil 200 (hydrophilic), Aerosil 380 (hydrophilic), Aerosil R202 (hydrophobic, after treated with a polydimethylsiloxane) – the all from Evonik Industries AG as well as Orisil 200 (hydrophilic, Orisil-Farm, Ukraine); (ii) nanopowders of metal oxides: Aerioxide Alu130, Aerioxide TiO₂P90 and VPZnO20 (Evonik Industries AG); (iii) montmorillonites: Rheospan AS31740 and Nanocor I.22E (Nanocor); (iv) conductive nanofillers: carbon nanotubes High Purity MWNT and...
Industrial Grade MWNT as well as a nanosilver 47MN-03 (Inframat Advanced Materials). The zeta potential study was performed as a function of pH of water. Nanoparticles dispersed in polar solvents (water, methanol) and non-polar solvent (toluene) were also tested. Furthermore, we have determined the ζ-potential as a function of time in solvents. Then we have attempted to relate the obtained electrokinetic parameters to properties of nanocomposites based on polyesterimide varnish with mentioned nanoparticles.

3. Results and discussion
The influence of water pH on the zeta potential of various nanoparticles is presented in Fig. 1-4. Curves of zeta potential versus pH of hydrophilic nanosilicas are similar, whereas the curve of hydrophobic Aerosil R 202 shows two isoelectric points (Fig. 1). Metal oxide particles exhibit large changes in the zeta potential with the change of the pH values of the solution, going from positive values to negative (Fig. 2). Zeta potential is negative in the montmorillonites, only for Nanocor I.22 at lowest pH value is positive (Fig. 3). The same is true for conductive nanoparticles (Fig. 4).

The maximum of absolute value of zeta potentials of the nanofillers are presented in Fig. 5. The value of ζ-potential of the all nanoparticles was less than 30 mV, so they did not form a stable colloid in water.

Absolute zeta potential of the nanoparticles dispersions in various solvents including pure water, methanol and toluene is illustrated in Fig. 6. It is clear that ζ-potential of the all nanofillers much increases in toluene. This increase is particularly high for carbon nanotubes, montmorillonites and aluminum oxide, so that toluene can be used to modifying of nanofillers [7].

In turn, measurements of the nanofillers particle size in water confirmed the formation of agglomerates. For example, nominal size of grain of nanosilicas ranges from a few to several micrometers while the measured size is more than one orders greater (Fig. 7).
It was observed that residence time of nanofiller in a solvent influences the average particle size of hydrophilic and hydrophobic nanosilica. It was shown in Figures 8 and 9 for hydrophilic and hydrophobic nanosilica.

Figure 5. Absolute value of maximum ζ-potential in water for various pH values

Figure 6. Absolute ζ-potential in various solvents

Figure 7. Measured Average particle size of nanofillers

Figure 8. Average particle size of the silica nanoparticles in water, and after 48 h in water

Figure 9. Average particle size of the silica nanoparticles in styrene, and after 48 h in styrene

Figure 10. Absolute zeta potential of the nanoparticles in water after 48 hours
The average particle size of hydrophilic nanosilica (Aerosil 200) is distinctly diminished (deagglomeration) after period of 48 h staying in a solvent such as water or styrene. This phenomenon does not occur for the hydrophobic nanosilica (Aerosil R 202). A beneficial effect on the nanocomposite seems to have using of a stabilization period of certain nanofillers in the varnish.

Polyesterimide varnishes filled with the nanoparticles had been investigated in our previous works as it has been mentioned above. A qualitative assessment of the properties of varnishes filled by the nonconductive nanoparticles compared with the properties of the base varnish is shown descriptively in Table 1. The table comprises also the values of absolute zeta potential of nanofillers in water and in water after period of 48 hours. Correlation between zeta potential nanofillers in the water after 48 h and the properties of nanocomposites contained the tested nanofillers has been found.

Absolute zeta potential of the nanoparticles dispersions in water after 48 hours is presented in Fig. 10. On the right side of a black line are nanoparticles which, when introduced using the same method of dispersing into the varnish have resulted in improved properties of the nanocomposites. This could mean that by examining the zeta potential in water after 48 hours, we can preselect the nanofillers.

### Table 1. Summary of the properties of nanofilled varnishes that contain various nonconductive nanoparticles and their zeta potential in water as well after period of 48 hours in water.

| Nanofiller   | Mechanical properties | Dielectric properties | Gelling process (TGA/DSC) | Absolute $\zeta$-potential in water [mV] | Absolute $\zeta$-potential in water after 48 h [mV] |
|--------------|-----------------------|-----------------------|----------------------------|------------------------------------------|-----------------------------------------------|
| Rheospan AS  | +                     | –                     | –                          | disturbed 8.3                           | 3.8                                           |
| Aerosil R202 | 0                     | –                     | –                          | disturbed 7.5                           | 4.1                                           |
| NanocorI.22E | 0                     | 0                     | –                          | disturbed 1.7                           | 4.3                                           |
| VP ZnO20     | ++                    | 0                     | ++                         | normal 9.8                               | 5.3                                           |
| Aerosil 380  | +                     | +                     | +++                        | normal 6.8                               | 7.9                                           |
| Aerosil 200  | ++                    | ++                    | +++                        | normal 12.6                              | 9.1                                           |
| Orisil 200   | ++                    | ++                    | +                          | normal 7.1                               | 10.6                                          |
| TiO$_2$ P90  | +                     | ++                    | +                          | normal 9.6                               | 12.9                                          |
| Alu 130      | ++                    | ++                    | +++                        | normal 20.7                              | 17.8                                          |

- worse; – – significant worse; 0 no changes; + improved; ++ much improved; +++ very much improved.

### 4. Conclusions

Study of influence of electrokinetic properties of nanofillers used for preparing of nanofilled varnishes indicate that: (i) None of used nanofillers does not form a stable colloid in water at different pH and a correlation between zeta potential nanofillers in the water with properties of nanocomposites was not found; (ii) the particle size of all nanofillers measured in the water indicate the formation of agglomerates; (iv) For all nanofillers $\zeta$-potential much increases in toluene; (v) correlation can be found between the particle size and the properties of nanocomposites; (vi) A clear correlation between the potential of nanofillers after 48 in water with the properties of the resulting nanocomposites has been found.
5. References
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