

SCIENTIFIC PAPERS  
OF THE UNIVERSITY OF PARDUBICE  
Series A  
Faculty of Chemical Technology  
22 (2016)

**ACRYLIC COATINGS MODIFICATION BY  
REACTIVE NANOGELS PREPARED BY EMULSION  
POLYMERISATION: A STUDY**

Jana MACHOTOVÁ<sup>1</sup>, Jaromír ŠŇUPÁREK, Luboš POKŮPEK,  
and Miroslav VEČEŘA  
Institute of Chemistry and Technology of Macromolecular Materials,  
The University of Pardubice, CZ-532 10 Pardubice

Received January 6, 2016

*In this paper, the influence of hydroxyl-functionalised acrylic nanogels incorporated into solvent-borne and water-borne acrylic binder system on the properties of coating films is described. Our approach has been to show the usefulness of prepared reactive nanogels as network precursors. As found out, the application of nanogels did not affect the surface appearance and the transparency of solvent-borne thermosetting coatings. Moreover, the presence of nanogel network precursors accelerated the cure at ambient temperature, thus improving the final hardness of coatings.*

---

<sup>1</sup> To whom correspondence should be addressed.

## Introduction

The reactive nanogels described in this paper are defined as the submicron intramolecularly crosslinked latex particles, which — after the respective synthesis — contain substantial amounts of reactive functional groups in their interior and at their surface. Their molecular weight is comparable with high molecular weight linear polymers. However, their internal structure resembles a typical crosslinked polymer (macrogel). The majority of nanogels used in the coatings industry are based on acrylic, styrene, and divinylbenzene monomers. Non-aqueous nanogel dispersions (especially those with high solids content), have widely been used as additives to improve pseudoplastic/thixotropic properties of coating compositions [1], and mechanical properties of the resulting coating films [2,3]. Nanogel containing formulations were also found to improve the film formation and, therefore, fewer coats were needed for comparison with conventional compositions. Nanogels may decrease problems connected with a slow rate of the film formation in water-based paints. In metallic coatings, nanogels improve the levelling and orientation of the metallic flakes added and being parallel to the substrate surface [4].

In general, nanogels are made by processes of the free-radical polymerisation either in a dilute solution or — more commonly — by emulsion polymerisation; normally, in an aqueous medium. Solution polymerisation is generally more suitable when large proportions of the crosslinking monomers are used and for which the intramolecular crosslinking is favoured [5]. However, during polymerisations in solution, the formation of large coarse particles usually occurs; particularly, where the concentration of the reactants is high and almost total conversions are desired. Emulsion polymerisation is thus more effective in avoiding a macroscopic network formation. Otherwise, it is a versatile technique that yields particles of spherical shape and with narrow size distributions. Conventional emulsion polymerisation enables the preparation of very small particles (with diameter less than 150 nm). Preparation of nanogels using the emulsion polymerisation is a complex process that can be affected by the monomers used, surfactants, the initiator selected, and also, by the polymerisation process itself [6]. The latex particles originate either from micelles (in the case of hydrophobic monomers and surfactant concentrations above the critical micelle concentration) according to Smith–Ewart theory [7] or by homogeneous nucleation (when using more water-soluble monomers) as required by the theory of Fitch and Tsai [8]. Nanogel emulsions can be used as they are; e.g., in aqueous coatings [9-12] or, in solvent-borne coatings, after replacing water with an organic medium, [13].

The main objective of this work was to prepare hydroxyl-functionalised acrylic nanogels *via* the emulsion polymerisation technique. The reactive nanogels were incorporated into solvent-borne and water-borne acrylic binder systems,

respectively, and the effect of nanogel addition on the surface appearance and mechanical properties of the coatings prepared investigated.

## Experimental

### Materials

Methyl methacrylate (MMA), butyl methacrylate (BMA), allyl methacrylate (AMA), 2-hydroxyethyl methacrylate (HEMA), butyl acrylate (BA), acrylic acid (AA) – technical grade (Roehm, Darmstadt, Germany), Disponil AES 60 – sodium salt of alkyl aryl polyoxyethylene sulfate (Henkel, Germany), ammonium persulfate – (Air Products), 2-propanone – (Sigma-Aldrich), Synthalat A 125 HS – polyisocyanate-curing acrylic resin in butyl acetate and Shellsol A (Synthopol Chemie, Germany), Veropal D 709 – thermoplastic acrylic binder based on BMA/MMA in xylene (Synpo, Czech Republic), Desmodur N 3390 BA – aliphatic polyisocyanate in butyl acetate, HDI trimer (Bayer, Germany), Desmodur N 3600 – hydrophobic aliphatic polyisocyanate, HDI trimer (Bayer, Germany).

Table I Recipe of emulsion polymerisation

Reactor charge	
Water	400 g
Disponil AES 60	3 g
Ammonium persulphate	4 g
Monomer emulsion	
Water	700 g
Disponil AES 60	52 g
Ammonium persulphate	4 g
Monomers	800 g

### Nanogel Preparation

Nanogel emulsion copolymers were synthesized from a mixture comprising 89 wt. % of MMA, 10 wt. % of HEMA and 1 wt. % of AMA; the last reagent being employed as the crosslinking monomer. The nanogels were produced in a 2500 ml glass reactor by semi-continuous and non-seeded emulsion polymerisation under nitrogen atmosphere at 85 °C. This procedure ensured relatively homogeneous

nanogel particles of statistical copolymers. The reactor charge was put into the reactor and heated up to the polymerisation temperature. Then, the monomer emulsion was fed into the stirred reactor during 3 h (at feeding rate about 10 ml min<sup>-1</sup>). After that, during 2 h of hold period, the polymerisation was completed. The aqueous nanogel dispersion was cooled down to room temperature and filtered to remove any coagulum. The reactor charge and monomer emulsion composition of the nanogel dispersions prepared is shown in Table I.

## Nanogel Characterisation

The glass transition temperatures ( $T_g$ ) of the vacuum-dried and grinded (grinding achieved by a vibrational mill (model VM-4, OPS Přerov, the Czech Republic), nanogel copolymers were determined by means of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). Particle sizes of nanogels after isolation by drying at ambient temperature and grinding in a mill were estimated by scanning electron microscopy. SEM images were obtained using a LEO Gemini DSM 982 instrument (Zeiss, Germany). Particle sizes of nanogels in the water phase were obtained from dynamic light scattering experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). All the DLS measurements were conducted at 25 °C. The concentration of the measured nanogel dispersion was around 0.05 wt. % of solids. The characteristic properties of the nanogels are listed in Table II.

Table II Nanogel characterisation in terms of glass transition temperature and particle size in the water phase (determined by DLS) and after drying (according to SEM)

Property	Numerical value
$T_g$ , °C	119
Particle size in aqueous phase, nm	127
Particle size after drying, nm	105

## Coatings Preparation

### *Water-borne Systems*

Aqueous emulsion nanogels were mixed with a film-forming latex (a water-borne dispersion based on the copolymer BA/BMA/HEMA/AA, 28:60:10:2 % by weight, solids content of 40 wt. %). The amount of nanogels was 0, 10, 20, 30, 40, 50, 60, 70 % (by weight) related to the total amount of solids in the composition. Two series of samples were made, the first one without curing, the other one with

the hardener Desmodur N 3600. Films were cast on a glass substrate using a blade applicator. Their typical wet thickness was 100  $\mu\text{m}$ .

### *Solvent-borne Systems*

The vacuum-dried and grinded nanogels were added into acetone at a concentration of 10 % by weight until cloudy nanogel dispersion was obtained, which was achieved after 4 weeks of spontaneous dispergation. The dispergation could be accelerated by ultrasonic treatment. The nanogels in the form of acetone dispersion were stirred into the solvent-borne acrylic binder Synthalat A 125 HS or Veropal D 709, respectively. The content of nanogels was 0, 10, 20, 30, 40, 50 % (by weight) of the total amount of solids in the acrylic coating composition. The system was thickened to 60 wt. % of solids by evaporating solvents to dryness at ambient temperature while permanently stirring. After mixing with the isocyanate hardener Desmodur N 3390 BA (only in the case of coating compositions based on the binder Synthalat A 125 HS) films were cast on a glass substrate using a blade applicator. Their typical wet thickness was 200  $\mu\text{m}$ .

### Coatings Evaluation

The pendulum hardness of test films was measured by a special tester with “Persoz” pendulum (model Automatic 500; Tesla, the Czech Republic). The surface appearance of solvent-borne coatings was evaluated by optical microscopy performed using an Axiotech KS 100 instrument (Zeiss, Germany). The cryofractures of solvent-borne coatings containing 0 and 40 wt. % of microgels were compared using a scanning electron microscope (model LEO Gemini DSM 982; Zeiss, Germany).

## **Results and Discussion**

### Nanogel Characterisation

It is evident (from Table II) that the investigated nanogels having the  $T_g$  value of 119 °C represents hard and rigid materials without film-forming properties at ambient temperature. By comparing the results of both DLS and SEM, it can be assumed that the nanogels are solvated and swollen by water molecules due to their hydrophilic nature. Their mean particle sizes in water phase were found to be higher than the corresponding particle sizes in the dry state. A representative SEM image of vacuum-dried and grinded nanogels is shown in Fig. 1.

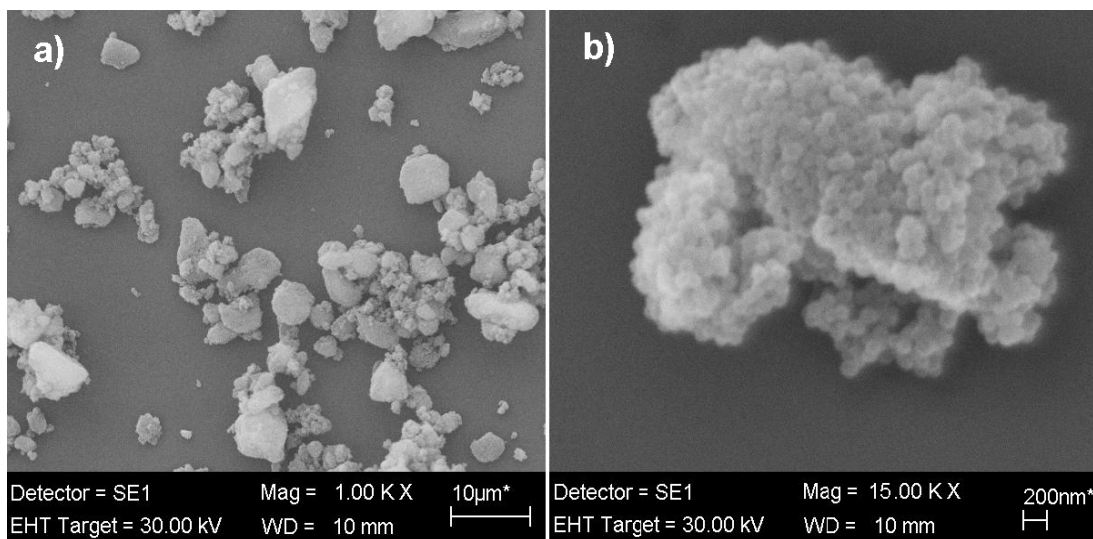


Fig. 1 SEM image of vacuum-dried and grinded nanogels: a) magnification 100×, b) magnification 30 000×

## Water-borne Systems

The functionalised nanogels were investigated as reactive network precursors in mixtures with a water-borne film-forming acrylic dispersion. As found, addition of aqueous dispersion of hard functionalised nanogel particles into a film-forming water-borne dispersion has caused an increase in coating hardness, which is illustrated in Fig. 2 and indicating that the high values of hardness have been caused by the presence of nanogels having a high value of  $T_g$ .

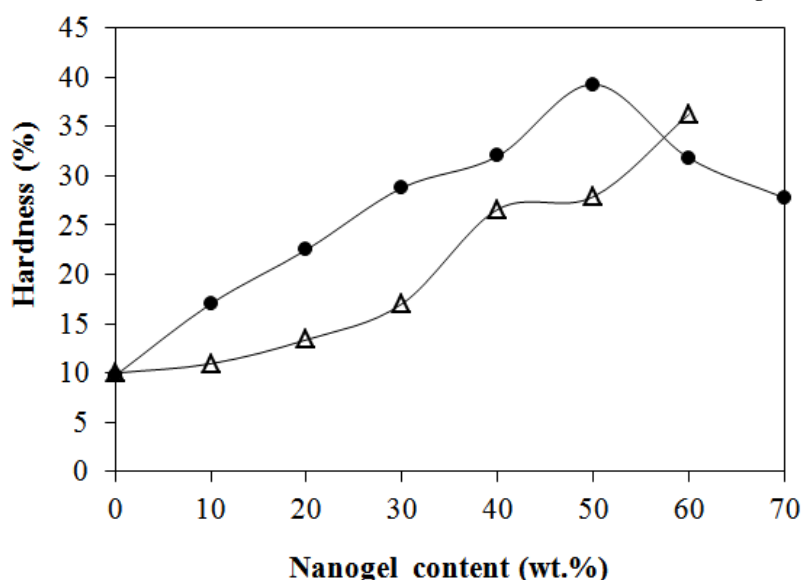


Fig. 2 Effect of nanogel content in the film-forming water-borne dispersion on the pendulum hardness of coatings: without curing ( $\Delta$ ), cured with the isocyanate hardener ( $\bullet$ )

Cure with the isocyanate hardener then resulted in an increase in the coating hardness (compared to the uncured coatings containing the same amount of nanogel precursors). The urethane chemical links between the film-forming latex particles of the acrylic dispersion and nanogel particles were probably formed, thus compensating the poor coalescence properties of nanogel particles.

### Solvent-borne Systems

The addition of nanogel network precursors into the thermosetting acrylic binder Synthalat A 125 HS did not affect the surface appearance of coatings as shown in Fig. 3. Smooth and continuous films without any defects were obtained, suggesting a regular distribution of nanogel particles in the polymeric binder.

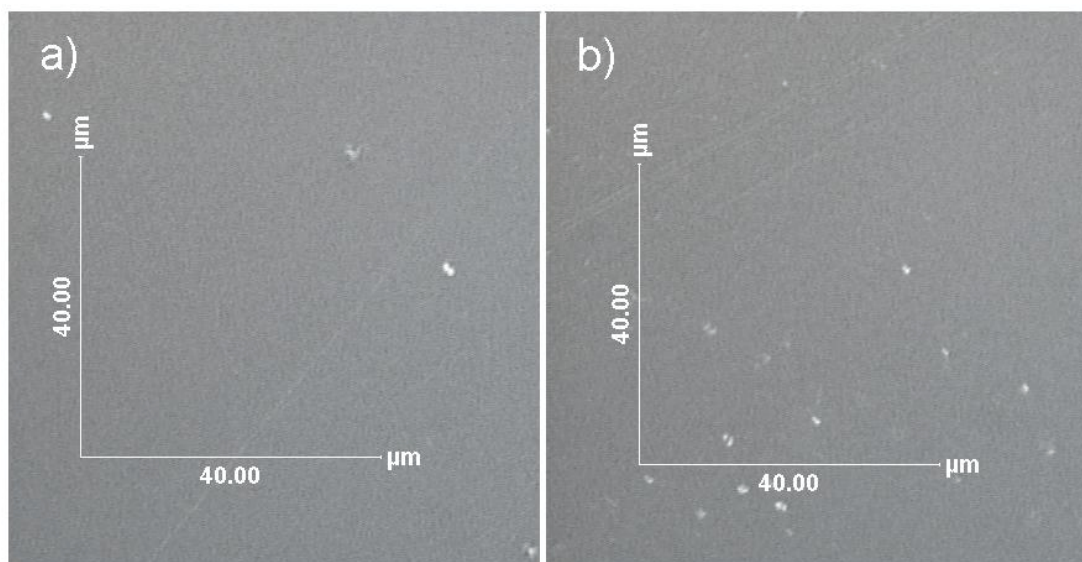


Fig. 3 Appearance of coatings based on the acrylic binder Synthalat A 125 HS containing a) 0 wt. % of nanogels, b) 40 wt. % of nanogels

Moreover, the incorporated nanogels of size around 100 nm (see Table II) were found to retain the coating transparency. On the other hand, the presence of nanogels in the thermoplastic acrylic binder Veropal D 709 had resulted in rough surface of coating films accompanied with loss of transparency (see Fig. 4).

The undesirable worsening of coatings appearance was probably caused by xylene (the starting amount of xylene in the binder was 60 wt. %) that might induce a phase separation of nanogel particles and the pure binder.

The cryo-fracture images of coatings without any nanogels were compared with those containing 40 wt. % of nanogel network precursors (see Figs 5 and 6). Separate spherical nanogel species with particle size of around 100 nm were noticed in the case of coatings containing the nanogel network precursors. It can be seen clearly that nanogels have been distributed regularly inside the coating



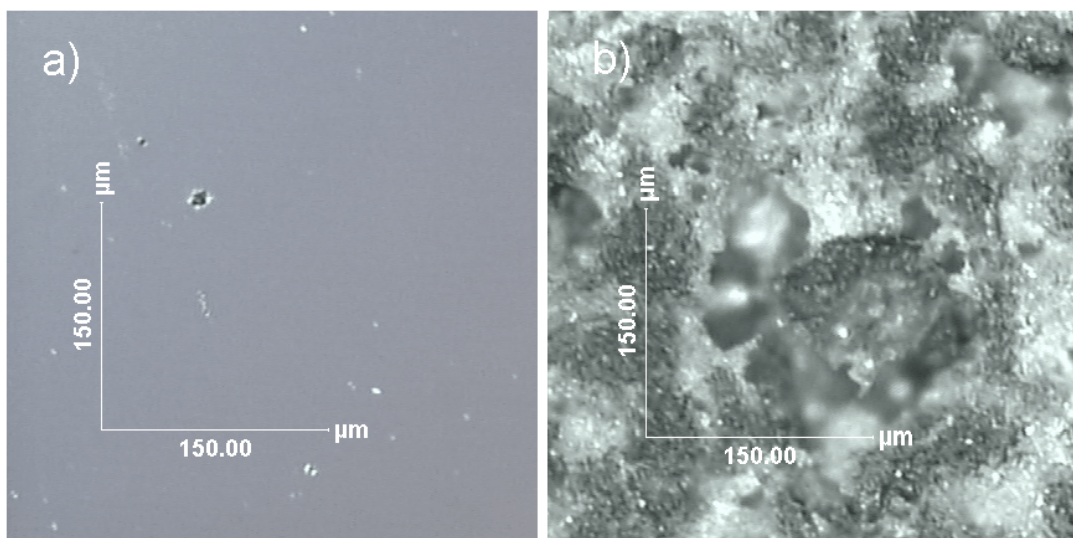


Fig. 4 Appearance of coatings based on the acrylic binder Veropal D 709 containing a) 0 wt. % of nanogels, b) 40 wt. % of nanogels

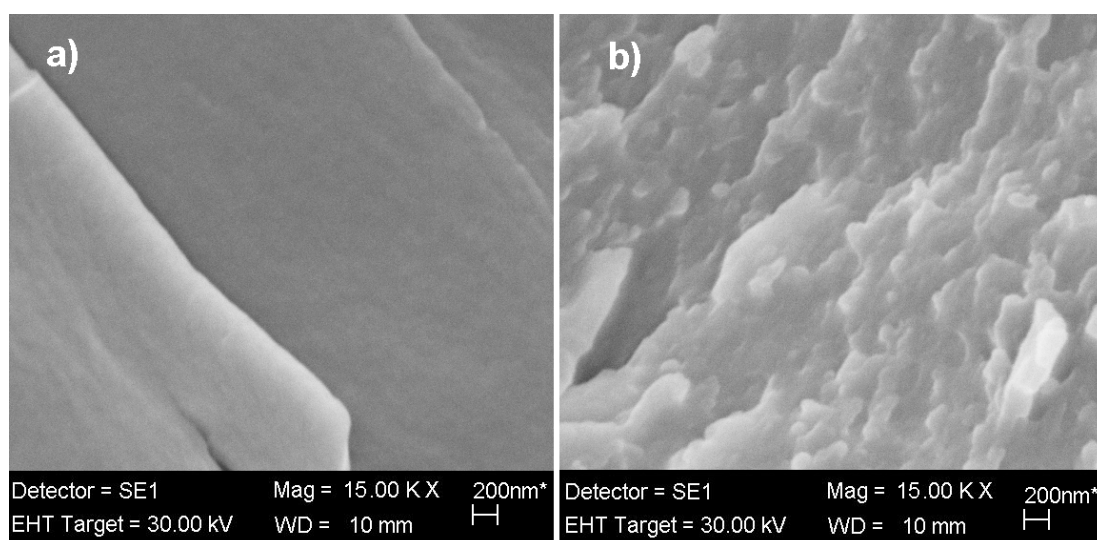


Fig. 5 Cryo-fracture surface of the coating film based on the acrylic binder Synthalat A 125 HS a) without addition of nanogels, b) with 40 wt. % of nanogels

film in the case of the binder Synthalat A 125 HS, whereas the formation of domain-like structure of nanogel-rich and nanogel-pure binder areas characterized in the coating film based on the binder Veropal D 709.

Figures 7 and 8 demonstrate the effect of nanogel addition on the pendulum hardness of acrylic coatings cured at ambient temperature. It is evident that the pendulum hardness values of all the prepared coating films have been raising with time due to the progressing crosslinking reaction connected with increase in  $T_g$  of the coating system.

It was found that the addition of functionalised nanogel network precursors had accelerated the curing process. The coatings containing a high amount of nanogels exhibited high values of hardness after a short duration of curing (1 or



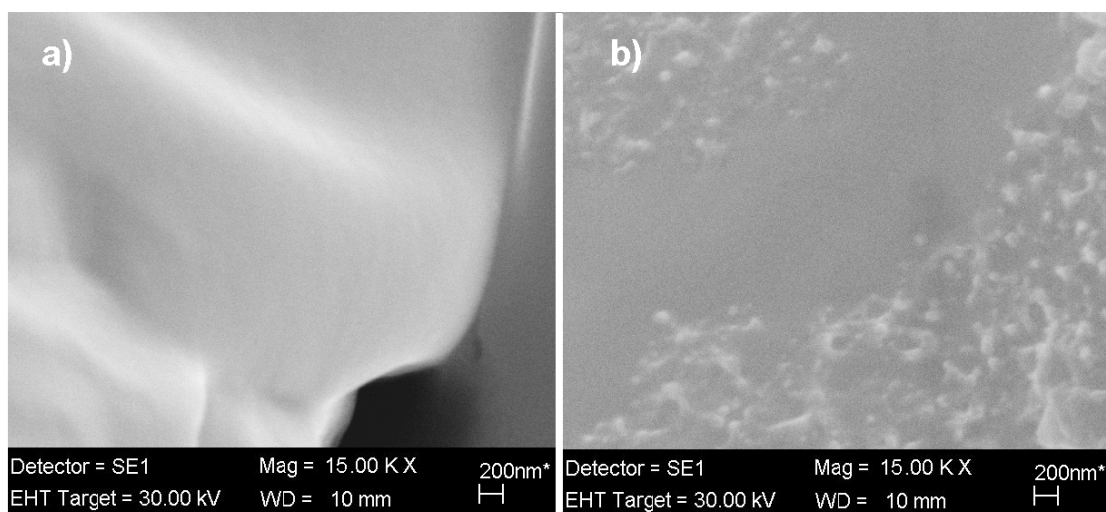


Fig. 6 Cryo-fracture surface of the coating film based on the acrylic binder Veropal D 709 a) without the addition of nanogels, b) containing 40 wt. % of nanogels

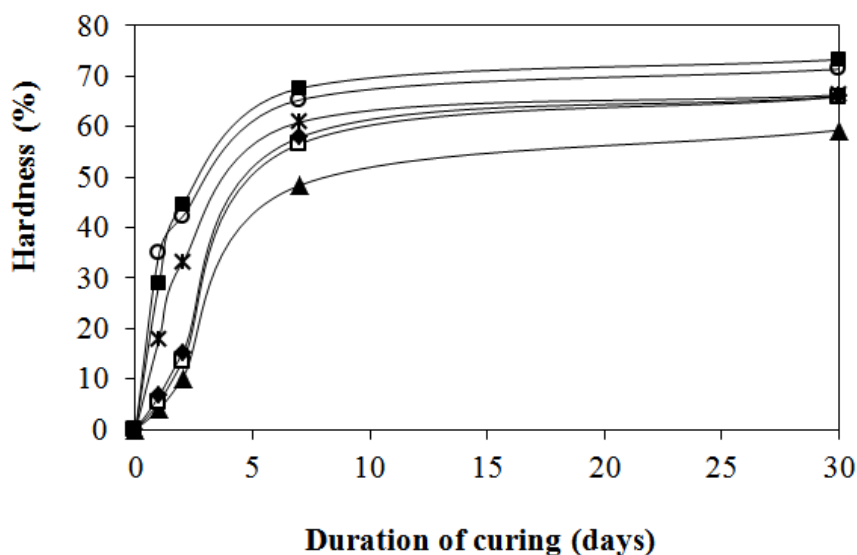


Fig. 7 Effect of time and nanogel content in the acrylic binder Synthalat A 125 HS on the pendulum hardness of coatings. The content of nanogels: 0 wt. % (▲), 10 wt. % (◻), 20 wt. % (◆), 30 wt. % (\*), 40 wt. % (■), 50 wt. % (○) is related to the total amount of solids in the coating

2 days) in contrast to the films containing a low (or zero) amount of nanogels. It is believed that the initial high values of coating hardness have been caused just by the addition of nanogels having a high value of  $T_g$ . In later stages of film-formation, however, the coating hardness was governed also by the formed cross-linked polymeric structure of the thermosetting binder Synthalat A 125 HS (see Fig. 7). As found as well, the values of pendulum hardness of coating films cured for 30 days at ambient temperature had increased with the increasing content of nanogels in the acrylic binder. This indicates enhanced crosslinking density of the final polymer network structure.

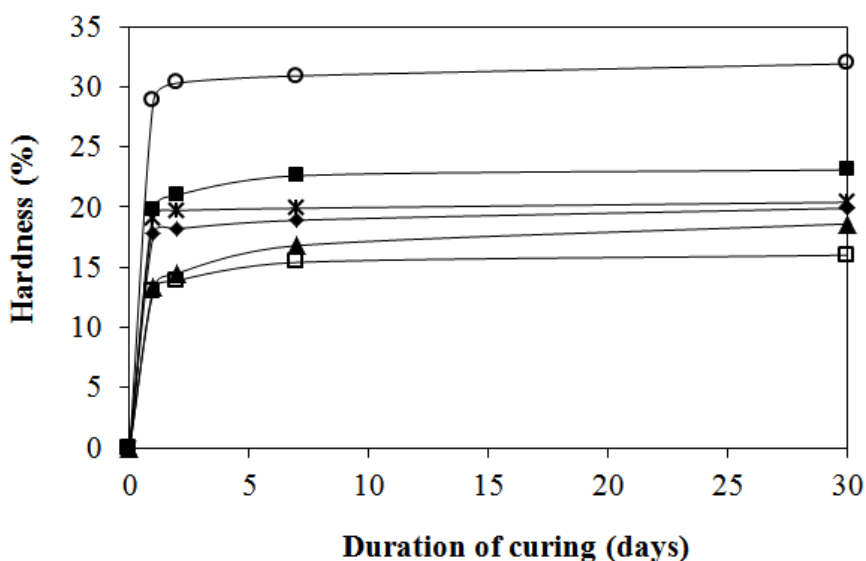


Fig. 8 Effect of time and nanogel content in the acrylic binder Veropal D 709 on the pendulum hardness of coatings. The content of nanogels: 0 wt. % (▲), 10 wt. % (◻), 20 wt. % (◆), 30 wt. % (\*), 40 wt. % (■), 50 wt. % (○) is related to the total amount of solids in the coating

## Conclusion

Crosslinked reactive nanogels composed — mainly, of the methylmethacrylate and 2-hydroxyethylmethacrylate type — were prepared in the form of particles in an aqueous emulsion *via* the semi-batch emulsion copolymerisation. It has been shown that the addition of aqueous dispersion of hard hydroxyl-functionalised nanogel particles into a film-forming water-borne dispersion caused an increase in coating hardness. This was due to the presence of nanogels with a high value of  $T_g$ . Furthermore, a cure with the isocyanate hardener resulted in the increase in coating hardness, suggesting us the formation of urethane chemical links between the film-forming latex particles and nanogel particles and thus compensating the poor coalescence properties of nanogels. Finally, the effect of addition of the reactive crosslinked nanogel particles redispersed in acetone on the surface appearance and the hardness development of two commercial solvent-borne acrylic binders were investigated as well. In the case of the thermosetting acrylic binder, the presence of nanogels did not affect the surface appearance and the transparency of coatings. As found out, the final hardness of coating films increased with the growing content of nanogel network precursors in the acrylic binder. Also, it was shown that the addition of nanogels had accelerated curing, as ascertained with the coatings containing a high amount of nanogels and exhibiting a steeper increase in pendulum hardness in the early stages of film-curing in contrast to films with low (or zero) amount of nanogels.

## References

- [1] Backhouse A.J.: *J. Coat. Technol.* **54**, 83 (1982).
- [2] Machotová J., Šňupárek J., Černošek Z., Svoboda L.: *Prog. Org. Coat.* **62**, 71 (2008).
- [3] Machotová J., Šňupárek J., Prokůpek L., Rychlý T., Vlasák P.: *Prog. Org. Coat.* **63**, 175 (2008).
- [4] Saatweber D., Vogt-Birnbrich B.: *Prog. Org. Coat.* **28**, 33 (1996).
- [5] Antionetti M., Rosenauer C.: *Macromolecules* **24**, 3434(1991).
- [6] Šňupárek J., Kaška M., Baghaffar G., Quadrat O.: *Macromol. Symp.* **179**, 89 (2002).
- [7] Smith W.V., Ewart R.H.: *J. Chem. Phys.* **16**, 592 (1948).
- [8] Fitch R.M., Tsai C.H.: *Polymer Colloids*, Plenum Press, New York, 1971, p. 103.
- [9] Bradna P., Štern P., Quadrat O., Šňupárek J.: *Colloid Polym. Sci.* **273**, 234 (1995).
- [10] Quadrat O., Mrkvičková L., Walterová Z., Štern P., Bradna P., Šňupárek J.: *Prog. Org. Coat.* **46**, 1 (2003).
- [11] Zhang S.F., Wang R.M., He Y.F., Song P.F., Wu Z.M.: *Prog. Org. Coat.* **76**, 729 (2013).
- [12] Sa S.S., Zhang B.H., Yang Q., Wang X.Q., Mao Z.P.: *J. Shanghai Univ. (Engl. Ed.)* **13**, 67 (2009).
- [13] Nie L., Jiang W., Yang W., Wang Ch, Fu S: *J. Macromol. Sci. A* **42**, 623 (2005).