STUDY OF ACRYLIC COATINGS MODIFICATION BY REACTIVE NANOGELS PREPARED BY EMULSION POLYMERISATION

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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 in this paper. Our approach has been to show the usefulness of prepared reactive nanogels as network precursors. It was shown that the application of nanogels did not affect the surface appearance and transparency of solvent-borne thermosetting coatings. Moreover, the presence of nanogel network precursors accelerated curing at ambient temperature and improved final hardness of coatings.

Introduction

The reactive nanogels described in this paper are defined as submicron intramolecularly crosslinked latex particles, which after their synthesis have 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 been widely used as additives to improve pseudoplastic/thixotropic properties of coating compositions [1], and mechanical properties of resulting coating films [2,3]. Nanogel containing formulations

were also found to improve film build and therefore fewer coats were needed as compared with conventional compositions. Nanogels may decrease problems connected with slow rate of film formation in water-based paints. In metallic coatings, nanogels improve levelling and orientation of added metallic flakes parallel to the substrate surface [4].

In general, nanogels are made by processes of free radical polymerisation either in dilute solution or more commonly by emulsion polymerisation, normally in an aqueous medium. Solution polymerisation is generally more suitable when large proportions of crosslinking monomers are used in which case intramolecular crosslinking, is favoured [5]. But the formation of large coarse particles is difficult to avoid in solution polymerisations, particularly where the concentration of reactants is high and high conversions are desired. Emulsion polymerisation is more effective in avoiding macroscopic network formation. It is a versatile technique which yields particles of spherical shape and narrow size distributions. Conventional emulsion polymerisation enables the preparation of very small particles (particle diameter less than 150 nm). Preparation of nanogels using the emulsion polymerisation is a complex process that is affected by used monomers, surfactants and initiator selection and also by the polymerisation process itself [6]. The latex particles originate either from micelles (in case of hydrophobic monomers and surfactant concentrations above the critical micelle concentration) according the Smith-Ewart theory [7] or by homogeneous nucleation (in the case of 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, after replacing water with an organic medium, in solvent-borne coatings [13].

The main objective of the present work was to prepare hydroxyl-functionalised acrylic nanogels via 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 surface appearance and mechanical properties of prepared coatings was 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).

Nanogel preparation

Nanogel emulsion copolymers were synthesized comprising 89 wt. % of MMA, 10 wt. % of HEMA and 1 wt. % of AMA which was employed as the crosslinking monomer. The nanogels were produced in a 2500 ml glass reactor by semi-continuous 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 to the polymerisation temperature. Then the monomer emulsion was fed

into the stirred reactor during 3 hours (at feeding rate about 10 ml/min). After that, during 2 hours of hold period the polymerisation was completed. The aqueous nanogel dispersion was cooled to room temperature and filtered to remove any coagulum. The reactor charge and monomer emulsion composition of prepared nanogel dispersions is shown in Table 1.

Nanogel characterisation

The glass transition temperatures (T_g) of the vacuum-dried and grinded (grinding achieved by a vibrational mill VM-4, OPS Přerov, 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 2.

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 μm.

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 at ambient temperature while 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 μm.

Coatings evaluation

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

Results and discussion

Nanogel characterisation

It is evident (see Table 2) that the investigated nanogels having the T_g value of 119 °C represent hard and rigid materials without film-forming properties at ambient temperature. From the comparison of DLS and SEM results 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 corresponding particle sizes in the dry state. A representative SEM image of vacuum-dried and grinded nanogels is shown in Fig. 1.

Water-borne systems

The functionalised nanogels were investigated as reactive network precursors in mixtures with a water-borne film-forming acrylic dispersion It was shown that the addition of aqueous dispersion of hard functionalised nanogel particles into a film-forming water-borne dispersion caused an increase in coating hardness, as shown in Fig. 2. The high values of hardness were caused by the presence of nanogels having a high value of T_g. Cure with the isocyanate hardener resulted in increase in coating hardness (when comparing the uncured coatings containing the same content 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, which suggests a regular distribution of nanogel particles in the polymeric binder. Moreover, the incorporated nanogels of size around 100 nm (see Table 3) were found to retain the coating transparency. On the other hand, the presence of nanogels in the thermoplastic acrylic binder Veropal D 709 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 may have induced 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 particles of size around 100 nm were observed distinctly in the case of coatings containing nanogel network precursors. It can be seen clearly that nanogels were distributed regularly inside the coating film in the case of the binder Synthalat A 125 HS whereas formation of domain-like structure of nanogel-rich and nanogel-pure binder areas appeared in the coating film based on the binder Veropal D 709.

Figs. 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 were 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 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 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 were 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). It was found as well that the values of pendulum hardness of coating films cured for 30 days at ambient temperature increased with growing content of nanogels in the acrylic binder. This indicates the increased crosslinking density of the final polymer network structure.

Conclusion

Crosslinked reactive nanogels composed mainly of methylmethacrylate and 2-hydroxyethylmethacrylate were prepared as particles in an aqueous emulsion via the semi-batch emulsion copolymerisation. It was 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 effect was apparently caused by the presence of nanogels having a high value of T_g. Cure with the isocyanate hardener resulted in increase in coating hardness, which suggests the formation of urethane chemical links between film-forming latex particles and nanogel particles, thus compensating poor coalescence properties of nanogels. The effect of the addition of reactive crosslinked nanogel particles redispersed in acetone on the surface appearance and hardness development of two commercial solvent-borne acrylic binders was 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. It was found that the final hardness of coating films rose with the growing content of nanogel network precursors in the acrylic binder. It was shown as well that

the addition of nanogels accelerated curing, as it was found that coatings containing a high amount of nanogels exhibited steeper increase in pendulum hardness in early stages of film-curing in contrast to films containing a low (or zero) amount of nanogels.

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Table 1   Recipe of emulsion polymerisation

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

Table 2   Nanogel characterisation in terms of glass transition temperature and particle size in water phase (determined by DLS) and after drying (according to SEM)

Property	Numeric value
T_g (°C)	119
Particle size in water phase (nm)	127
Particle size after drying (nm)	105

Fig. 1   The SEM image of vacuum-dried and grinded nanogels: a) magnification 100x, b) magnification 30 000x
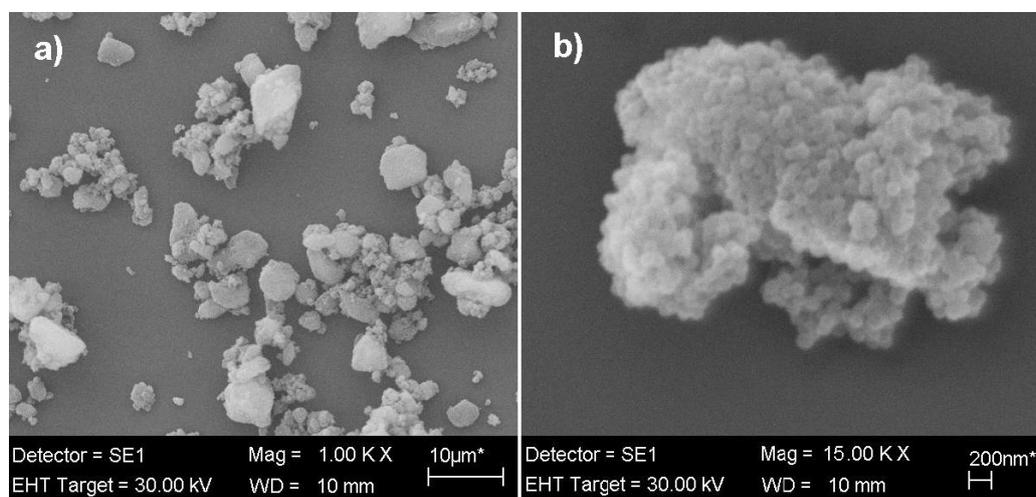
Fig. 2   Effect of nanogel content in the film-forming water-borne dispersion on the pendulum hardness of coatings: without curing (△), cured with the isocyanate hardener (●)
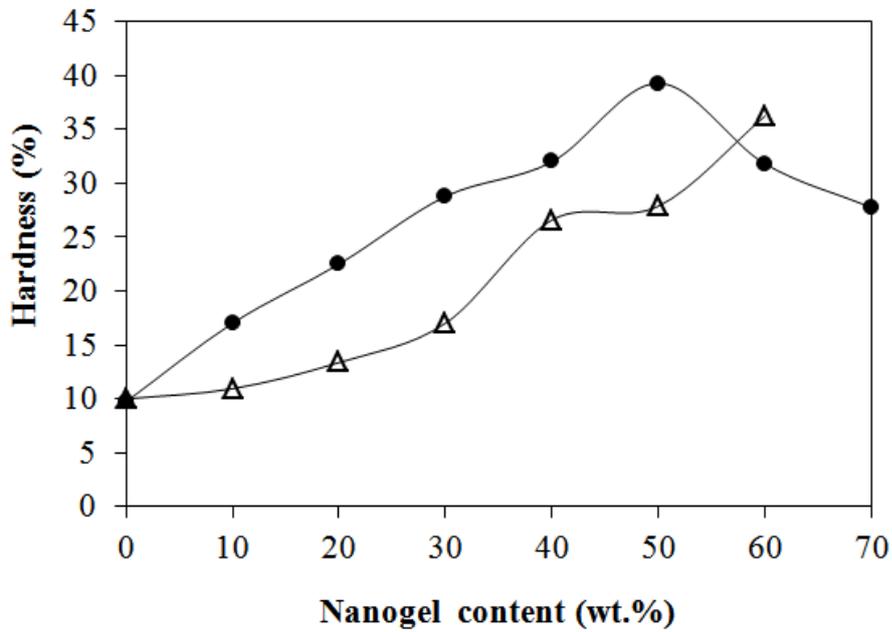
Fig. 3   Appearance of coatings based on the acrylic binder Synthalat A 125 HS containing a) 0 wt. % of nanogels, b) 40 wt. % of nanogels
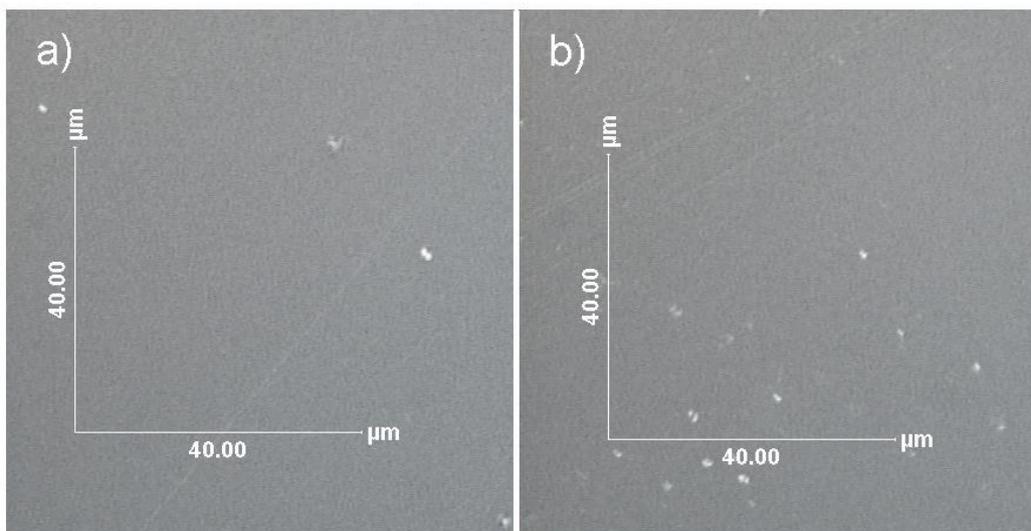
Fig. 4   Appearance of coatings based on the acrylic binder Veropal D 709 containing
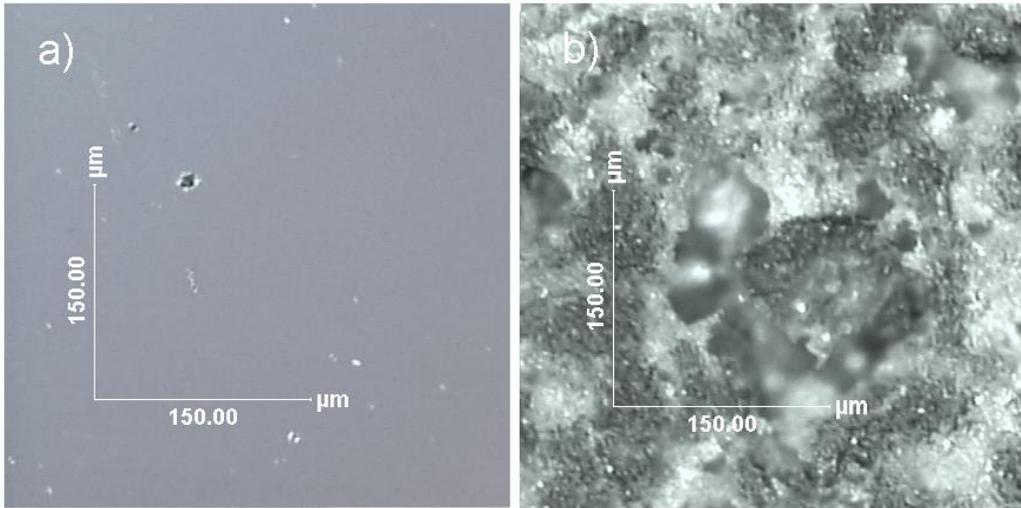
a) 0 wt. % of nanogels, b) 40 wt. % of nanogels

Fig. 5   Cryo-fracture surface of the coating film based on the acrylic binder Synthalat A

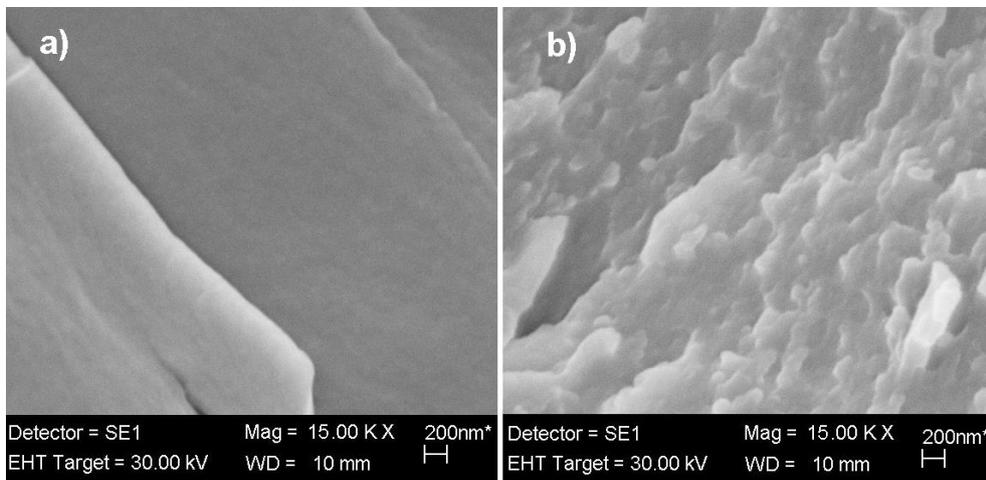125 HS a) without the addition of nanogels, b) containing 40 wt. % of nanogels

Fig. 6   Cryo-fracture surface of the coating film based on the acrylic binder Veropal D

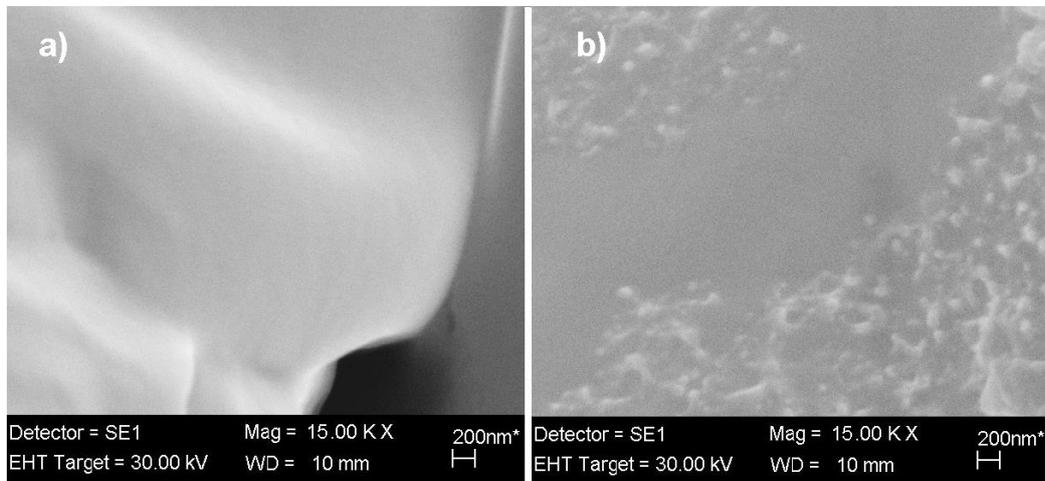709 a) without the addition of nanogels, b) containing 40 wt. % of nanogels

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
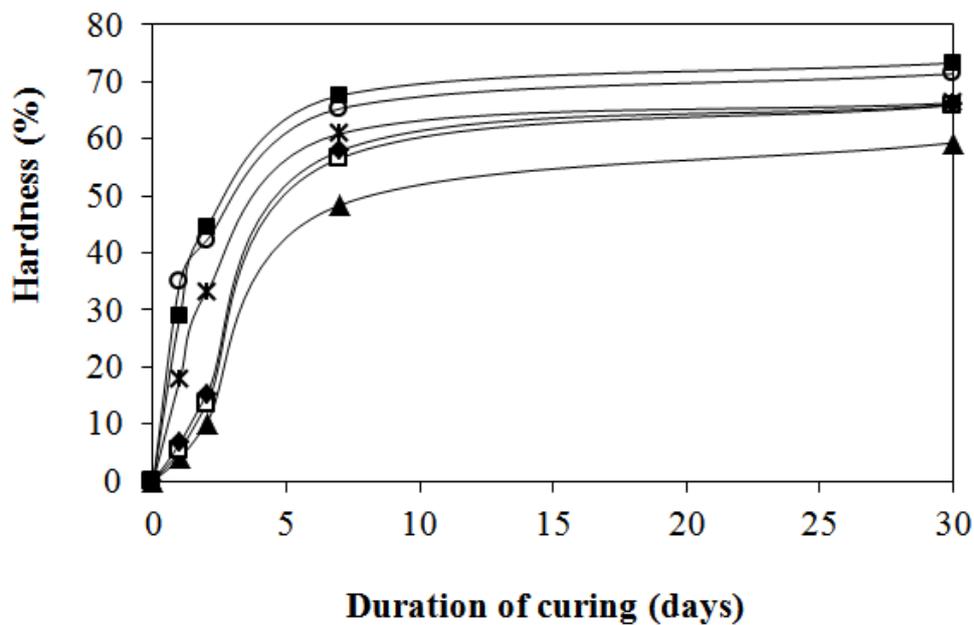
the total amount of solids in the coating

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