Macromol. Symp. **2009**, 281, 197–205 DOI: 10.1002/masy.200950726

Functionalised Microgels for Acrylic Coatings

Jana Machotová, Jaromír Šňupárek*

Summary: Aqueous acrylic dispersions of hydroxy-functionalised copolymer microgel particles crosslinked with allyl methacrylate were synthesized by emulsion polymerization. The microgels were investigated as reactive polymer fillers in mixtures with a water-borne film-forming dispersion. Properties of coatings cast from mixtures of aqueous dispersion of hard microgel particles and film-forming water-borne dispersion were investigated. The swelling behaviour of microgels in selected solvents (aliphatic ketones) as a function of microgel composition is discussed as well. It was found that the swelling ability of microgels decreased with growing degree of crosslinking. Microgels comprising copolymerised butyl methacrylate swelled less in aliphatic ketones than microgels without this comonomer. This work was focused mainly on the influence of microgels incorporated in the commercial solvent-borne acrylic binders on the properties of coatings. It was shown that the application of microgels that were redispersed in acetone did not affect the surface appearance and transparency of coatings. Moreover, the presence of microgel network precursors accelerated film curing at ambient temperature and improved the final hardness of coatings.

Keywords: acrylic latexeces; emulsion polymerisation; microgels; network precursors; swelling

Introduction

The present paper deals with functionalised microgels, also called reactive microgels. These materials can be defined as submicron crosslinked structured latex particles which contain substantial amounts of reactive functional groups in their interior and/or at their surface. They can be prepared by the inclusion of monomers carrying the desired type of functional groups (e.g. epoxy or hydroxy) during the polymerisation. The functional groups do not participate in the polymerisation. They react with an appropriate reaction partner, e.g. in the reaction of microgels containing surface hydroxy groups with a polyisocyanate crossllinker. Another method of preparation of reactive microgels involves polymerisation of polyfunctional monomers based on diacrylates or divinylbenzene. Not all functional groups of multifunctional monomers can participate in the network formation for steric reasons; therefore, microgel particles contain some residual unreacted groups which are then available for further reactions.

In general, microgels are made by radical polymerisation either in dilute solutions or, more commonly, by emulsion polymerisation, normally in aqueous medium. Preparation of microgels using the emulsion polymerisation is a complex process that is affected by the used monomers, surfactants and initiator and also by the polymerisation itself.[1] The latex particles originate either from micelles (hydrophobic monomers and surfactant concentrations above the critical micelle concentration) according to the Smith-Ewart theory[2] or by homogeneous nucleation (more water-soluble monomers) as required by the theory of Fitch and Tsai.[3]

Institute of Polymeric Materials, Faculty of Chemical Technology, University of Pardubice, 532 07 Pardubice, Czech Republic
E-mail: jana.machotova@upce.cz

The semicontinuous process is the most frequent as it enables the control of the polymerisation heat as well as the control of the composition of the copolymers comprising several types of monomer units.[4] Microgel emulsions can be used as such, e.g. in aqueous coatings[5,6] or, after replacing water with an organic medium, in solvent-borne coatings.[7]

Microgels have found use in the surface coatings industry, optics, magnetism, electronics, colloid chemistry, biochemistry and medicine. The utilization of microgels in coating systems provides the advantage of obtaining a higher solid content than it would otherwise be possible without causing concurrently an increase in viscosity compared with systems without microgels. The properties of coatings and films such as rheology of compositions, aesthetic properties and transparency of films, and orientation of pigments are significantly influenced by the inclusion of microgels.

This study relates to hydroxy-functionalised microgels, to their swelling behaviour in selected organic solvents frequently used in the coating formulations, and to coating compositions containing the microgels.

Experimental Part

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 poly(oxyethylene) sulfate (Henkel, Germany), ammonium persulfate (Air Products), propan-2-one, butan-2-one, pentan-2-one, 3-methylbutan-2-one, hexan-2-one, 4-methylpentan-2-one, heptan-2-one, 5-methylhexan-2-one (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, hexamethylene diisocyanate (HDI) trimer (Bayer, Germany), Desmodur N 3600 – hydrophobic aliphatic polyisocyanate, HDI trimer (Bayer, Germany).

Table 1.
Composition of monomer feeds (wt.%).

Sample:	A1	A2	A3	A4	A5
Series A (10 wt.% HEMA, 0 wt.% BMA; MMA and AMA variable)					
MMA	90	89	88	87	86
AMA	0	1	2	3	4
Sample:	B1	B2	B3	B4	B5
Series B (10 wt.% HEMA, 50 wt.% BMA; MMA and AMA variable)					
MMA	40	39	38	37	36
AMA	0	1	2	3	4

Microgel Preparation

Two series of emulsion copolymers were synthesized with variable contents of methyl methacrylate and allyl methacrylate, which was employed as the cross-linking monomer (Table 1). The microgels were produced in a 2500-ml glass reactor by semicontinuous non-seeded emulsion polymerisation under nitrogen atmosphere at 85 °C. The reactor was charged and heated to the polymerisation temperature. Then the monomer emulsion was introduced into the stirred reactor during 3 h (at a feeding rate of ca. 10 ml/min). The polymerisation was complete after 2 h. The aqueous microgel dispersion was cooled to room temperature and filtered to remove any coagulum. The reactor charge and monomer emulsion composition of the prepared microgel dispersions are shown in Table 2.

Table 2.
Recipe for 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 3.
Microgel characterisation.

Microgel	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
T_g (°C)	116.9	118.5	121.3	123.4	126.3	67.8	69.7	71.8	74.8	76.5
Particle size in water phase d_0 (nm)	130	127	111	109	125	169	145	176	192	173

Microgel Characterisation

The glass transition temperatures (T_g) of vacuum-dried and ground microgel copolymers were determined by differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). The measurements were carried out on the isolated and vacuum-dried microgels at a heating rate of 10 °C min^{-1}. Particle sizes of microgels in the water phase were obtained by dynamic light scattering (DLS) measurements on a Coulter N4 Plus instrument (Coulter Corp., UK). All the DLS measurements were conducted at 25 °C. The measured microgel dispersion contained ca 0.05 wt.% of solids. The characteristic properties of the microgels are given in Table 3.

Microgel Swelling

To remove the surfactant, the aqueous microgel dispersions were diluted with distilled water to the microgel content ca 10 wt.% and purified thoroughly by the serum replacement [8] using the ultrafiltration Nylon membrane Magna (Osmonics) of nominal pore size 0.1 μm and distilled water (conductivity 2–3 μScm^{-1}). The microgels were subsequently isolated as powders by drying at ambient temperature in air and grinding using a vibrational mill VM-4 (OPS Přerov, Czech Republic). A representative SEM image of vacuum-dried and ground microgels is shown in Figure 1.

The vacuum-dried and ground microgels were added to aliphatic ketones (Table 4) at a concentration of ca 2 wt. %. All samples were allowed to equilibrate for 30 days prior to determination of the swelling changes. The particle sizes of the swollen microgels were determined on a dynamic light scattering apparatus Coulter N4 Plus (Coulter Corp., UK) at the conditions and dispersion concentration mentioned above. The viscosity values and refractive indices of the solvents were taken from literature.[9] The swelling was characterized by the swelling ratio (α) which was defined as the ratio of the particle size in aliphatic ketone (diameter d) to that of the collapsed particle in the water phase (diameter d_0), i.e. $\alpha = (d/d_0)^3$.

Further, the swelling of microgels was expressed in terms of the content of accessible hydroxy groups in the copolymer

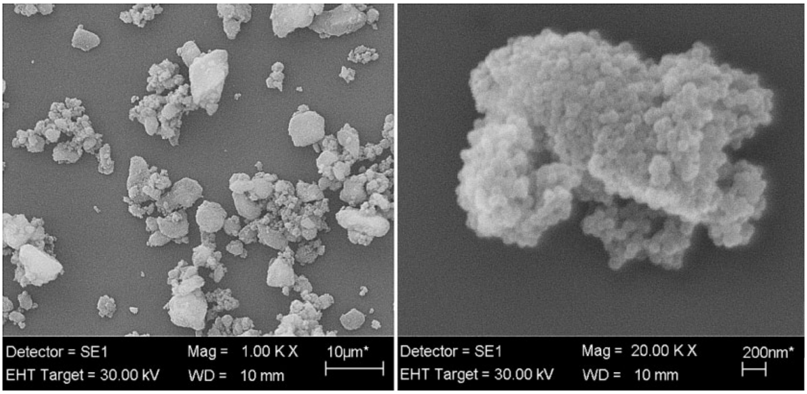
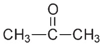
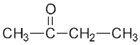
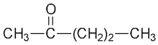
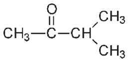
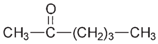
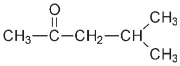
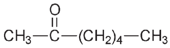
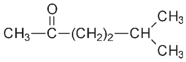


Figure 1.
SEM images of vacuum-dried and ground microgels A2: (a) magnification 100x, (b) magnification 30 000x.

Table 4.
The used aliphatic ketones.

Name	Code	Formula	Solubility parameter $\delta .10^{-3}$ ($J^{1/2}m^{-3/2}$)
propan-2-one (acetone)	Ac	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	19.7
butan-2-one (ethyl methyl ketone)	MEK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3$	19.0
pentan-2-one (methyl propyl ketone)	MPK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-(CH_2)_2-CH_3$	18.3
3-methylbutan-2-one (isopropyl methyl ketone)	MiPK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH{\substack{\diagup CH_3\\ \diagdown CH_3}}$	17.9
hexan-2-one (butyl methyl ketone)	MBK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-(CH_2)_3-CH_3$	18.1
4-methylpentan-2-one (isobutyl methyl ketone)	MiBK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH{\substack{\diagup CH_3\\ \diagdown CH_3}}$	17.2
heptan-2-one (methyl pentyl ketone)	MAK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-CH_3$	17.4
5-methylhexan-2-one (isopentyl methyl ketone)	MiAK	 $CH_3-\overset{\overset{O}{\parallel}}{C}-(CH_2)_2-CH{\substack{\diagup CH_3\\ \diagdown CH_3}}$	16.7

measured by potentiometric titration in which the hydroxy groups are reacted with an excess of acetic anhydride and the unreacted anhydride is titrated with a methanolic solution of KOH. Potentiometric titrations were carried out with microgel dispersions containing ca 2 wt.% of solids at 25 °C using a TitroLine alpha plus digital system (Schott, Germany). The samples were allowed to equilibrate for 30 days prior to the determination of the content of hydroxy groups present in the swollen microgel.

Coating Preparation

Water-Borne Systems

Aqueous emulsion copolymers A2 were mixed with a film-forming latex (a water-borne dispersion based on the copolymer BA/BMA/HEMA/AA, 28:60:10:2, 40 wt.% of solids). The amount of microgels was 0, 10, 20, 30, 40, 50, 60, 70 wt.% of the total solid content in the composition. Two series of samples were made, the first without curing, the other with the hardener Desmodur N 3600. Films were cast on a glass substrate using a blade applicator. A typical wet thickness was 100 μm.

Solvent-Borne Systems

Vacuum-dried and ground microgels A2 were added in acetone to obtain a concentration of 10 wt.% until cloudy microgel dispersion appeared, (after 4 weeks of spontaneous dispergation). The dispergation could be accelerated by sonication. The microgels in the form of acetone dispersion were stirred into the solvent-borne acrylic binder Synthalat A 125 HS. The content of microgels was 0, 10, 20, 30, 40, 50 wt.% of the total solid content in the acrylic coating composition. The system was thickened to 60 wt.% solids by evaporating solvents at ambient temperature while stirring. After mixing with the isocyanate hardener Desmodur N 3390 BA, films were cast on a glass substrate using a blade applicator. Typical wet thickness was 200 μm.

Table 5.
Particle sizes of swollen microgels containing 1 wt. % of AMA in the copolymer in aliphatic ketones and the corresponding swelling ratios.

Solvent	A2		B2	
	Swollen particle size (nm)	α	Swollen particle size (nm)	α
Acetone	234	6.26	184	2.04
MEK	223	5.41	165	1.47
MPK	221	5.27	205	2.83
MiPK	235	6.34	192	2.32
MBK	201	3.96	160	1.34
MiBK	209	4.46	173	1.70
MAK	185	3.09	169	1.58
MiAK	176	2.66	186	2.11

Coating Evaluation

The pendulum hardness of test films was measured with a tester Automatic 500 with a 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

Microgel Characterisation

Table 3 demonstrates the differences between microgels in terms of their glass transition temperature and mean particle size in water phase (determined by dynamic light scattering). It was proved that the content of the introduced crosslinking comonomer AMA influenced the glass transition temperature of microgels. The increasing cross-linking density was found to depend on an increase in T_g. Microgels of series A (A1–A5) exhibited higher values of T_g in contrast to microgels of series B comprising BMA comonomer.

Microgel Swelling

Swelling of microgels A2 and B2 containing 1 wt.% of AMA crosslinker was investigated by DLS in all the aliphatic ketones listed in Table 4. The results are summarized in Table 5. It is worth attention that microgels A2 (polymerized without BMA) exhibited a higher swelling ability in all the ketones than microgels B2 containing BMA units. This fact may be explained by higher difference in polarity of the solvent and BMA units in contrast to MMA-based polymers of microgels A2. The effects of solvent molecule size and of solubility parameters on the swelling ratio were observed in more polar microgels A2. Acetone was found to be the strongest swelling solvent, while MiAK (methyl isopentyl ketone) the weakest. The higher is the value of δ, the higher swelling ratio. Also, large MiAK molecules did not allow a high extent of microgel swelling due to steric hindrance effects. The elastic forces opposing the swelling increased with the rising size of solvent molecules.

Table 6 demonstrates the swelling behaviour of crosslinked microgels A2–A5 and B2–B5 in acetone, showing the highest value of solubility parameter and the smallest solvent molecules, and in MiAK, exhibiting the lowest δ and the largest solvent molecules. The crosslinked microgels of Series A (containing no BMA units swell more in acetone than in MiAK and their swelling ratios in both solvents decreased with the growing content of AMA in the copolymer. In this case the swelling is believed to be affected by the size of solvent molecules on one hand and by crosslinking density of microgels on the other. On the contrary, microgels of series B displayed low swelling ability in both

Table 6.
Swollen particle sizes d and swelling ratios α of microgels in acetone and 5-methylhexan-2-one as a function of the crosslinker content.

Microgel	AMA	Acetone		MiAK	
	(wt. %)	d (nm)	α	d (nm)	α
A2	1	234	6.26	176	2.64
A3	2	212	6.97	173	3.80
A4	3	175	4.14	141	2.18
A5	4	127	1.05	142	1.46
B2	1	184	2.04	186	2.11
B3	2	248	2.80	194	1.33
B4	3	215	1.40	209	1.30
B5	4	222	2.11	209	1.75

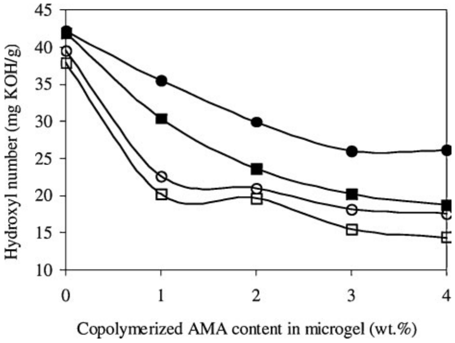


Figure 2.
Dependence of the hydroxyl number corresponding to accessible hydroxy groups in microgels swollen in acetone and MiAK (5-methylhexan-2-one) on the crosslinker content in microgel copolymers: Series A microgels in acetone (●), Series B microgels in acetone (■), Series A microgels in MiAK (○), Series B microgels in MiAK (□).

acetone and MiAK and their swelling behaviour was not affected by the crosslinker content. The reason is obviously related to the polarity aspect, which has been mentioned above.

Nevertheless, all the DLS measurements proved that the crosslinked microgels of both Series A and Series B could be redispersed in all the used aliphatic ketones and that they form stable microgel dispersions of swollen particles without any significant agglomeration.

As the functionalised microgels are assumed to be utilised first of all in solvent-borne coatings, it is important that the functional groups are accessible to crosslinking reactions. It is believed that the solvent should sufficiently swell the microgel particles to enable the reagent diffusion into the particle and the reaction of hydroxy groups in the swollen copolymer particle. The different extents of swelling in different solvents lead to different accessibility of functional groups. The results of the swelling studies based on the determination of accessible hydroxy groups in microgels are shown in Figure 2. Microgels A1 and B1 polymerized without the crosslinker exhibited values of the hydroxyl number close to the theoretical value (43.1 mg KOH/g polymer as calculated for a copolymer containing 10 wt. % of HEMA). It can be assumed that all hydroxy groups were accessible to the reaction with acetic anhydride. This indicates a total solubility of microgels A1 and B1 in both investigated solvents (acetone and MiAK). Figure 2 demonstrates that the higher is the AMA content in the microgel structure, the lower are the hydroxyl numbers. That means that the swelling ability of microgels decreased with the growing degree of crosslinking. It was shown again that microgels of series A swelled more extensively in acetone than those of series B. On the other hand, the same swelling tendency was observed for microgels of series A and B in MiAK. It was found as well that acetone was a better solvent for all microgels, because small acetone molecules penetrate more easily into the microgel.

Microgels as Reactive Network Precursors in Acrylic Coatings

Water-Borne Systems

The functionalised microgels were investigated as reactive network precursors in mixtures with water-borne film-forming acrylic dispersions. It was shown that the addition of an aqueous dispersion of hard functionalised microgel particles A2 (polymerized without BMA) into a film-forming water-borne dispersion caused an increase in coating hardness as shown in Figure 3. The high values of hardness were caused by

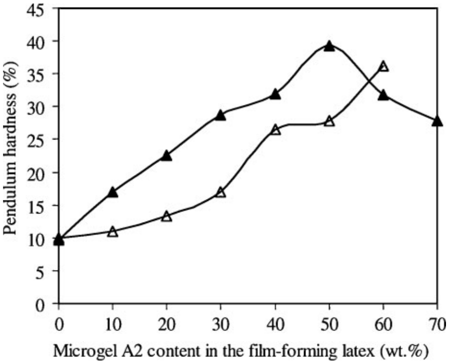


Figure 3.
Effect of the microgel A2 content in the film-forming water-borne dispersion on the pendulum hardness of coatings: without curing (△), cured with an isocyanate hardener (▲).

the presence of microgels A2 with high T_g. Cure with the isocyanate hardener resulted in an increase in the coating hardness (at the same content of microgel precursors A2). Urethane chemical links between the latex particles of the acrylic dispersion and microgel particles A2 were probably formed, thus compensating poor coalescence properties of microgel particles A2.

Solvent-Borne Systems

A pronounced swelling ability was observed especially in slightly crosslinked microgel particles A2 in acetone. For these reasons microgels A2 in the form of a dispersion of swollen microgel particles in acetone were chosen as reactive network precursors for the preparation of solvent-borne acrylic coating systems. The addition of the precursors to the thermosetting acrylic binder Synthalat A 125 HS did not affect the film clarity as shown in Figure 4. Smooth and continuous films without any defects were obtained, which suggests a regular distribution of microgel particles in the polymeric binder. Moreover, the incorporated microgels of the size around 100 nm were found to retain the coating transparency. The cryo-fracture images of coatings without any microgels were compared with those containing 40 wt. % microgel network precursors A2 (Figure 5). Separate spherical microgel particles of the size around 100 nm were observed distinctly in coatings containing microgel network precursors. It can be clearly seen that microgels were distributed regularly inside the coating film.

Figure 6 demonstrates the effect of microgel A2 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 rising with time due to the progressing crosslinking reaction associated with an increase in the T_g of the coating. It was found that the addition of functionalised microgel network precursors

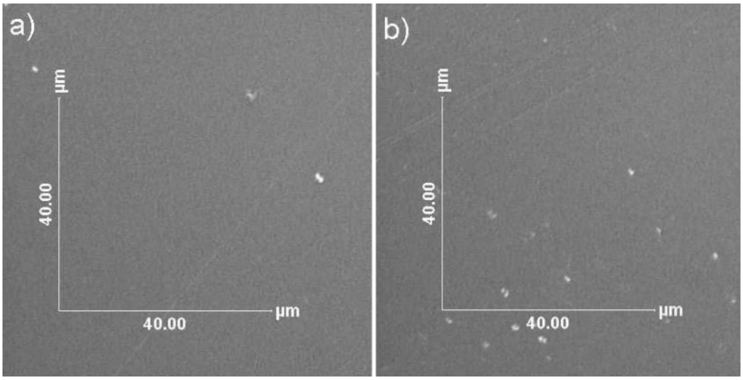


Figure 4.
Appearance of coatings based on the acrylic binder Synthalat A 125 HS containing a) 0 wt.% microgels, b) 40 wt.% microgels A2.

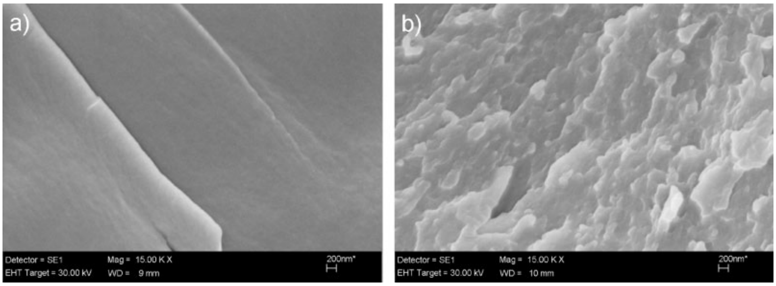


Figure 5.
Cryo-fracture surface of the coating based on the acrylic binder Synthalat A 125 HS a) without addition of microgels, b) containing 40 wt.% of microgel A2.

accelerated the curing process. The coatings containing high amounts of microgels exhibited high values of hardness after a short curing (1 or 2 days) in contrast to the films containing low (or zero) amounts of microgels. It is believed that the initial high values of coating hardness were caused by the addition of microgels with high T_g. However, at later stages of filmformation, the coating hardness was governed also by the formed cross-linked polymeric structure of the thermosetting binder Synthalat A 125 HS. It was found as well that the values of pendulum hardness of coating films cured for 30 days at ambient temperature increased with the growing content of microgels in the acrylic binder. This indicates the increased crosslinking density of the final polymer network.

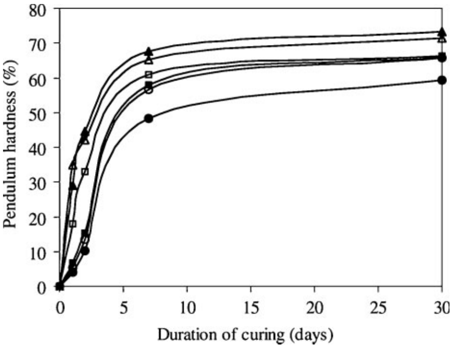


Figure 6.
Effect of time and microgel A2 content in the acrylic binder Synthalat A 125 HS on the pendulum hardness of coatings. The content of microgels 0 wt.% (●), 10 wt.% (○), 20 wt.% (■), 30 wt. % (□), 40 wt.% (▲), 50 wt.% (△) is related to the total amount of solids in the coating.

Conclusion

Microgels synthesized by standard emulsion polymerisation, dried at ambient temperature and ground in a mill could be redispersed in the aliphatic ketones listed above to form a stable microgel dispersion of swollen particles. It was confirmed that the crosslinking density of microgels had a pronounced effect on the microgel swelling behaviour. The swelling ability of microgels decreased with the growing degree of cross-linking. Microgels comprising copolymerized butyl methacrylate swelled less in the used aliphatic ketones than microgels without BMA. Out of all the investigated solvents acetone was found to be the best solvent, while 5-methylhexan-2-one (methyl isopentyl ketone) was shown to be the poorest.

The effect of the addition of functionalised crosslinked microgel particles redispersed in acetone on the surface appearance and hardness of the thermosetting commercial solvent-borne acrylic binder was investigated. It was found that the final hardness of coating films rose with the growing content of microgel network precursors in the acrylic binder. It was shown as well that the addition of microgels accelerated curing as it was found that coatings containing high amounts of microgels exhibited a steeper increase in pendulum hardness at early stages of film-curing in contrast to films containing low (or zero) amount of microgels. The presence of microgels did not affect the surface appearance and the transparency of coatings.

Acknowledgements: The Ministry of Education of the Czech Republic (MSM 0021627501) is gratefully acknowledged for support of this work.

[1] J. Šňupárek, M. Kaška, G. Baghaffar, O. Quadrat, *Macromol. Symp.* **2002**, *179*, 89.

[2] W. V. Smith, R. H. Ewart, *J. Chem. Phys.* **1948**, *16*, 592.

[3] R. M. Fitch, C. H. Tsai, *Polymer Colloids*, Plenum Press, New York **1971**, p. 103.

[4] J. Šňupárek, *Prog. Org. Coat.* **1996**, *29*, 225.

[5] P. Bradna, P. Štern, O. Quadrat, J. Šňupárek, *Colloid Polym. Sci.* **1995**, *273*, 234.

[6] O. Quadrat, L. Mrkvičková, Z. Walterová, P. Štern, P. Bradna, J. Šňupárek, *Prog. Org. Coat.* **2003**, *46*, 1.

[7] H. J. Wright, D. P. Leonard, R. A. Etzell, EP Patent 0 029 637 **1980**.

[8] S. M. Ahmed, M. S. El-Aasser, G. H. Pauli, G. W. Poehlein, J. W. Vanderhoff, *J. Colloid Interface Sci.* **1980**, *73*, 388.

[9] J. Vohlídal et al., *Chemical and Analytic Tables*, Grada Publ., Praha, **1999**.