

Article

Studies on Synthesis and Characterization of Aqueous Hybrid Silicone-Acrylic and Acrylic-Silicone Dispersions and Coatings. Part I

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Abstract: The objective of the study was to investigate the effect of the method of synthesis on properties of aqueous hybrid silicone-acrylic (SIL-ACR) and acrylic-silicone (ACR-SIL) dispersions. SIL-ACR dispersions were obtained by emulsion polymerization of mixtures of acrylic and styrene monomers (butyl acrylate, styrene, acrylic acid and methacrylamide) of two different compositions in aqueous dispersions of silicone resins synthesized from mixtures of silicone monomers (octamethylcyclotetrasiloxane, vinyltriethoxysilane and methyltriethoxysilane) of two different compositions. ACR-SIL dispersions were obtained by emulsion polymerization of mixtures of the same silicone monomers in aqueous dispersions of acrylic/styrene copolymers synthesized from the same mixtures of acrylic and styrene monomers, so the compositions of ACR and SIL parts in corresponding ACR-SIL and SIL-ACR hybrid dispersions were the same. Examination of the properties of hybrid dispersions (particle size, particle structure, minimum film forming temperature, T_g of dispersion solids) as well as of corresponding coatings (contact angle, water resistance, water vapour permeability, impact resistance, elasticity) and films (tensile strength, elongation at break, % swell in toluene), revealed that they depended on the method of dispersion synthesis that led to different dispersion particle structures and on composition of ACR and SIL part. Generally, coatings produced from hybrid dispersions showed much better properties than coatings made from starting acrylic/styrene copolymer dispersions.

Keywords: aqueous polymer dispersions; silicone-acrylic; acrylic-silicone; hybrid particle structure; coatings

1. Introduction

Aqueous polymer dispersions are currently produced in quantities exceeding globally 20 million tons per annum [1] and are commonly used, inter alia, as binders for organic coatings, especially for aqueous dispersion-based architectural paints. The reason for a great increase in research and business interest in that specific group of products is not only the fact that they are environmentally friendly, but also the possibility of tailoring the composition and structure of dispersion particle in order to achieve desired performance characteristics of the final coating. If the particles have a hybrid (It is worth to

note that generally a “hybrid material” is a material that is composed of at least two components mixed at molecular scale [2] and although this term is normally used for polymer-inorganic structure composites [3], it can be also applied to polymer-polymer systems) structure (i.e., are composed of at least two different polymers) and their diameter is less than 100 nm they may be called “dispersion nanoparticles with hybrid structure” within which the occurrence of specific interactions between these polymers optionally leading to synergistic effect may be expected. Then, due to a synergistic effect, new and sometimes quite unexpected features of coatings or films made using such hybrid dispersions as binders may be found—see Figure 1.



Figure 1. Differences between mixture of two aqueous dispersions of different polymers (polymer 1—blue color and polymer 2—red color) and aqueous dispersion with hybrid particle structure composed of the same two different polymers. In the mixture of two dispersions (a) synergistic effect is much less probable than in dispersion with hybrid particle structure (b) [4].

Although some authors reported that certain specific properties of coatings could be improved by using blends of dispersions of different polymers (e.g., dirt resistance could be enhanced this way [5]), clear advantages of application of dispersions with hybrid particle structure as coating binders have been confirmed in the literature, e.g., [1,4,6] and descriptions of methods applied for synthesis of such dispersions can be found in books and review papers, e.g., [7–10]. The particle morphology that is most frequently referred to in the research articles is a “core-shell” structure, but other morphologies, like core-double shell, gradient, eye-ball-like, raspberry-like, fruit cake or embedded sphere can also be obtained [11,12]. It has been proved [8] that not only the hybrid dispersion particle size and chemical composition, but also its morphology can significantly affect the properties of both dispersions and coatings produced from such dispersions. Therefore, investigation of the hybrid dispersion systems is of great interest to many researchers.

According to [7], the following general approaches can be applied to synthesis of hybrid aqueous dispersions in the emulsion polymerization process:

- A process where monomer X is polymerized in aqueous dispersion of polymer Y or monomer Y is polymerized in aqueous dispersion of polymer X;
- A process where monomer X is added to aqueous dispersion of polymer Y or monomer Y is added to aqueous dispersion of polymer X and left for some time in order to achieve swelling of dispersion particles with the monomer, and only then is polymerization conducted;
- A process where a mixture of monomers X and Y is placed in the reactor before start of polymerization or is added dropwise during the polymerization. However, in this case formation of particles with hybrid structure would be possible only if the corresponding homopolymers are not compatible or either reactivities of monomers or their polymerization mechanisms differ significantly.

As is clear from the literature, e.g., [4,13] the aforementioned methods of hybrid aqueous dispersion synthesis can be successfully applied to obtain different dispersion particle morphologies, depending on the selection of the starting materials (polymers, monomers, surfactants, initiators etc.). It can be expected that if methods (1) or (2) are applied, the “core-shell” morphology will be the most probable one supposing that certain conditions are fulfilled: “core” polymer should be more hydrophobic than “shell” polymer and formation of separate particles of polymer X in the course of

polymerization in dispersion of polymer Y resulting from homolytic nucleation is retarded, e.g., by diminishing the monomer and surfactant concentration in the reaction mixture. The mechanism of hybrid particle formation in the emulsion polymerization process has been described in detail, e.g., in [4,13–15] and factors that determine creation of specific particle morphology have been identified. A review of fundamental theoretical aspects of the formation of dispersion particles with a hybrid structure has been published [16].

One of the hybrid aqueous dispersion systems that is most interesting from the point of view of practical application, especially as coating binders, is dispersion with particles containing organic polymer (usually polyacrylate) and silicone. This is because silicone-containing polymer systems allow for achieving specific features of coating surface like e.g., water repellency without affecting its general performance [17]. A comprehensive review of synthesis and characterization of such hybrid silicone-acrylic dispersions as well as of coatings and films or powders produced from them has been published in 2015 [11]. It has been proved in a number of research papers both referred to in that review paper and published later that the unique properties of coatings like e.g., high surface hydrophobicity and water resistance combined with enhanced water vapour permeability and good mechanical properties can be achieved by applying methods (1) to (3) described above to synthesize hybrid dispersions containing silicones where monomer X is acrylic monomer and monomer Y is silicone monomer—see e.g., [18–21] for method (1), [22–24] for method (2) or [24–26] for method (3). If fluoroacrylic monomer was used as monomer X [27–30], the surface hydrophobicity of coatings could be improved even more. It was also proved in our earlier studies [31–33] that the application of method (1) to emulsion polymerization of methyl methacrylate in aqueous silicone resin dispersions led to stable “core-shell” silicone-poly(methyl methacrylate) hybrid dispersions which, after drying, produced corresponding “nanopowders” that were later used as very effective impact modifiers for powder coatings.

In the present study we investigated the effect of the approach to synthesis (method (1) or method (2) as defined above) on the properties of hybrid aqueous dispersions and corresponding coatings. Two different silicone resin dispersions and two different acrylic/styrene copolymer dispersions were used as starting media in which emulsion polymerization of acrylic and styrene monomers or silicone monomers respectively was conducted. The mass ratio equal to 1/3 of silicone part (SIL 1 or SIL 2) to acrylic/styrene part (ACR A or ACR B) in the synthesis was selected based on the assumption supported by the literature [11] that this proportion would be sufficient to observe the influence of the presence of silicone in the dispersion particle on the properties of hybrid dispersions and coatings. Further studies on the effect of SIL/ACR ratio on the properties of hybrid dispersions and coatings are ongoing and will be published soon.

2. Materials and Methods

2.1. Starting Materials

Octamethylcyclotetrasiloxane (D4) was obtained from Momentive (Waterford, NY, USA). Other silicone monomers: vinyltriethoxysilane (VTES) and methyltriethoxysilane (MTES) were obtained from Evonik (Essen, Germany) under trade names Dynasylan® VTEO and Dynasylan® MTES. Surfactants dodecylbenzenesulphonic acid (DBSA) and Rokanol T18 (nonionic surfactant based on ethoxylated C16–C18 alcohols) were obtained from PCC Exol (Brzeg Dolny, Poland). Emulgator E30 (anionic surfactant based on C15 alkylsulfonate) was obtained from LeunaTenside GmbH (Leuna, Germany). Other standard ingredients used in the synthesis of dispersions (sodium acetate, sodium hydrocarbonate, potassium persulphate and aqueous ammonia solution) were obtained from Standard Lublin (Poland) as pure reagents. Biocide used to protect dispersions from infestation was Acticide MBS obtained from THOR (Wincham, UK). Starting acrylic/styrene copolymer dispersions (ACR A and ACR B) characterized by different T_{gs} were supplied by Dispersions & Resins (D&R, Włocławek, Poland). Monomers applied in synthesis of ACR A and ACR B dispersions by D&R were butyl

acrylate (BA) obtained from ECEM, Arkema, Indianapolis, IN, USA, styrene (ST) obtained from KH Chemicals, Helm, Zwijndrecht, The Netherlands, acrylic acid (AA) obtained from Prochema, BASF, Wien, Austria, and methacrylamide (MA) obtained from ECEM, Arkema. Acrylic and styrene monomers were used as received as mixtures designated as A and B with compositions corresponding to compositions of monomers applied to synthesize dispersions ACR A and ACR B, respectively. Exact compositions could not be revealed due to commercial secret, but were appropriately designed to get T_g of dispersion solids at a level of ca. +15 °C (ACR A) and of ca. +30 °C (ACR B). For structures of acrylic monomers—see Figure 2.

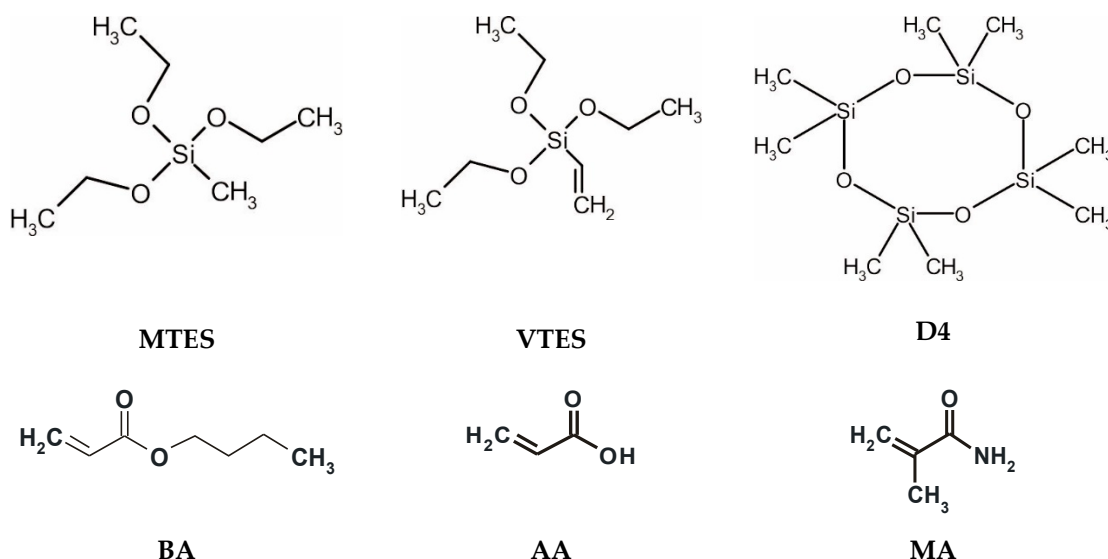


Figure 2. Structures of silicone monomers used in synthesis of silicone resin dispersions SIL 1 and SIL 2 and acrylic/styrene polymer dispersions ACR A and ACR B.

ACR A and ACR B dispersions were not neutralized after polymerization had been completed in order to ensure the low pH value (ca. 3) that was needed to conduct polymerization of silicone monomers in the process of synthesis of hybrid acrylic-silicone dispersions.

2.2. Synthesis of Silicone Resin Dispersions and Hybrid Silicone-Acrylic and Acrylic-Silicone Dispersions

Silicone resin dispersions (SIL 1 and SIL 2) were synthesized according to the procedure described in [31], although different functional silanes were used along with D4 as silicone monomers—see Figure 2 for the structures of these silicone monomers.

The compositions (wt.%) of mixtures of silicone monomers used in synthesis of SIL 1 and SIL 2 were as follows:

- Mixture designated as 1: D4—84.0%, MTES—9.5%, VTES—6.5%
- Mixture designated as 2: D4—88.0%, VTES—12%

DBSA was used as surfactant and D4 ring-opening catalyst. The reaction that proceeded in the process of SIL 1 and SIL 2 synthesis was simultaneous hydrolysis of trifunctional ethoxysilanes and breaking of Si-O bond in D4 leading to the formation of partially crosslinked poly(dimethylsiloxane) containing unsaturated bonds originating from VTES (see Figure 3).

After distillation of ethanol under vacuum no free VTES or MTES were detected by gas chromatography (GC) in the resulting SIL dispersions, although small amounts of D4 (ca. 0.8%) and ethanol (ca. 0.2%) were still present.

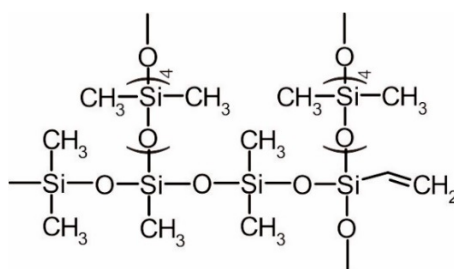


Figure 3. Simplified structure of partially crosslinked silicone resin obtained in synthesis of SIL 1 and SIL 2 dispersions.

Hybrid silicone-acrylic dispersions SIL-ACR 1-A and SIL-ACR 1-B were synthesized by emulsion polymerization of mixtures of acrylic and styrene monomers A and B, respectively, in silicone resin dispersion SIL 1. Hybrid silicone-acrylic dispersions SIL-ACR 2-A and SIL-ACR 2-B were synthesized by emulsion polymerization of mixtures of acrylic and styrene monomers A and B, respectively, in silicone resin dispersion SIL 2. Compositions of acrylic and styrene monomers mixtures A and B corresponded to compositions of acrylic and styrene monomers in starting acrylic/styrene copolymer dispersions ACR A and ACR B. Polymerization was carried out at 78–79 °C for 5 h. After cooling to room temperature, dispersions were neutralized with 25% aqueous NH_3 solution to reach pH ca. 6.0–6.5, then 0.15% of biocide was added and dispersions were filtered through 190 mesh net. Free acrylic and styrene monomers contents as tested by GC were <0.01%. No free VTES or MTES were detected by GC, although small amounts of D4 (ca. 0.4%) and ethanol (ca. 0.1%) were still present. Hybrid acrylic-silicone dispersions ACR-SIL A-1 and ACR-SIL A-2 were synthesized by emulsion polymerization of mixtures of silicone monomers 1 and 2, respectively, in acrylic/styrene copolymer dispersion ACR A. Hybrid acrylic-silicone dispersions (ACR-SIL B-1 and ACR-SIL B-2) were synthesized by emulsion polymerization of mixtures of silicone monomers 1 and 2, respectively, in acrylic/styrene copolymer dispersion ACR B. Compositions of silicone monomers mixtures 1 and 2 corresponded to compositions of silicone monomers in starting silicone resin dispersions SIL 1 and SIL 2. Polymerization was carried out at 88–89 °C for 4 h and then ethanol that was formed in hydrolysis of VTES and MTES was distilled off under vacuum for 3 h. After cooling to room temperature, dispersions were neutralized with 25% NH_3 solution to reach pH ca. 6.0–6.5, then 0.15% of biocide was added and dispersions were filtered through 190 mesh net. No free VTES or MTES or acrylic and styrene monomers were detected by GC in the resulting dispersions, though small amounts of D4 (ca. 0.4%) and ethanol (ca. 0.1%) were still present.

It was essential that the composition and concentration of surfactants remained the same in SIL-ACR and ACR-SIL dispersions, so their properties (and properties of coatings obtained from them) could be compared.

2.3. Characterization of Dispersions

All dispersions were characterized by:

- Solids content, wt.%—percentage of sample mass remaining after drying for 1 h at 80 °C followed by 4 h at 125 °C. The measurements were conducted three times and the mean value was taken.
- pH—using standard indicator paper.
- Viscosity—using Bohlin Instruments CVO 100 rheometer (Cirencester, UK), cone-plate 60 mm diameter and 1° measuring device, shear rate 600 s^{-1} .
- Coagulum content—after filtration of dispersion on 190 mesh net the solids remaining on the net were dried and weighed. Coagulum content (wt.%) was calculated from equation $m_c/m_d \times 100\%$ where m_c was mass of dry coagulum remaining on the net and m_d was mass of dispersion.
- Acrylic and styrene monomers, ethanol and D4 content—by GC (HP 5890 series II apparatus FID detector, Hewlett Packard, Palo Alto, CA, USA)

- Mechanical stability—lack or occurrence of separation during rotation in Hettich Universal 32R centrifuge (Westphalian, The Netherlands) at 4000 r.p.m. for 90 min was considered as good stability.
- Average particle size (nm), particle size distribution and zeta potential (mV)—light-scattering method using Malvern Zeta Sizer apparatus.
- Dispersion particles appearance—transmission electron microscope (TEM) Hitachi 2700 (Tokyo, Japan), dispersions were diluted 1000× with water (1 part of dispersion per 1000 parts of water) for taking pictures. High Angle Annular Dark Field (HAADF) mode also called “Z-contrast” was applied for processing the images reproduced in this paper.
- Minimum film-forming temperature (MFFT)—according to ISO 2115 [34] using Coesfeld apparatus equipped with temperature gradient plate. Temperature range: −3–50 °C.
- Glass transition temperature (T_g) of dispersion solids—by differential scanning calorimetry (DSC) (TA Instruments Q2000 apparatus, New Castle, DE, USA), heat–cool–heat regime, 20 °C/min.

2.4. Characterization of Coatings

Coatings were produced from dispersions by applying them on glass (for testing contact angle, hardness, adhesion or water resistance), aluminium plates (for testing elasticity) or on steel plates (for testing impact resistance and cupping) using 120 µm applicator. Drying was carried out for 30 min at 50 °C and then the coatings were seasoned in a climatic chamber at 23 °C and 55% relative humidity (R.H.) for 72 h. Since no continuous coating could be obtained in this procedure for SIL-ACR 1-B and SIL-ACR 2-B, the relevant dispersions were dried at 8 °C for 2 h and then seasoned as above. The resulting coatings were characterized by:

- Contact angle (water)—according to EN 828:2000, using KRÜSS DSA 100E apparatus (KRÜSS GmbH, Hamburg, Germany). The measurements were conducted five times and the mean value was taken.
- Pendulum hardness (Koenig)—according to EN ISO 1522 [35]. The measurements were conducted seven times and the mean value was taken.
- Adhesion—according to EN ISO 2409 [36], the tests were repeated at least three times.
- Elasticity—according to EN ISO 1519 [37], the tests were repeated at least two times.
- Impact resistance (direct and reverse)—according to EN ISO 6272-1 [38], using Erichsen Variable Impact Tester Model 304 (Erichsen, Hemer, Germany). The measurements were conducted at least twice.
- Cupping—according to EN ISO 1520 [39], using Erichsen Cupping Tester (ERICHSEN GmbH & Co. KG, Hemer, Germany). The tests were repeated three times and the mean value was taken.
- Water resistance—glass Petri dishes of 50 mm diameter were filled with distilled water and placed upside-down on the coating, so the coating was covered with 7 mm thick layer of water. Assemblies prepared this way were left for 72 h and appearance of coatings was examined for the bubbles size (S0—no bubbles, S2–S5—small to large size of bubbles) and density (0—no bubbles, 2–5 low to high density of bubbles) according to EN ISO 4628-2 [40]. Observation of changes of coating appearance after 6 days under water were also examined.
- Water vapour permeability—according to ASTM F1249 [41]. TotalPerm 063 (Extra Solution) apparatus was used. Tests were conducted at 23 °C for 0.35 mm thick film. Fomblin perfluorinated grease from Solvay Solexis (Brussels, Belgium) was applied to seal the test vessels. The measurements were repeated at least twice.
- Moreover, coatings applied on PET film were examined for surface structure by X-ray photoelectron spectroscopy (XPS)—ULVAC/PHYSICAL ELECTRONICS PHI5000 VersaProbe apparatus (Physical Electronics, Inc., Chigasaki, Japan).

2.5. Characterization of Films

- Percentage swell, i.e., change of the mass caused by soaking in water or organic solvent—ca. 0.12 g samples of film were weighed and placed in 40 mL H₂O or 40 mL toluene contained in closed glass cups and left for 20 h at 23 °C. Then the samples were taken out, delicately dried with filter paper and weighed. Percentage swell was calculated from the equation: % swell = $(m_1 - m_0) / m_0 \times 100\%$, where m_0 = mass of the sample before test and m_1 = mass of the sample after test. The tests were repeated three times.
- Mechanical properties (tensile strength and elongation at break)—using Instron 3345 testing machine (Instron, Norwood, MA, USA) according to EN-ISO 527-1 [42] at a pulling rate of 50 mm/min on dumbbell-shaped specimens. The measurements were conducted five times and the mean value was used taken.

3. Results and Discussion

3.1. Properties of Dispersions

Properties of hybrid silicone-acrylic (SIL-ACR) and acrylic-silicone (ACR-SIL) dispersions prepared with SIL/ACR *w/w* 1/3 ratio, starting silicone resin dispersions (SIL 1 and SIL 2) and starting acrylic/styrene copolymer dispersions (ACR A and ACR B), are presented in Table 1. All hybrid dispersions were mechanically stable, slightly opalescent white liquids with low viscosity, pH in the range 5.8–6.3 and solids contents close to 42%. Coagulum content was at a very low level –0.04%–0.38%. Blends of starting SIL and ACR dispersions at *w/w* 1/3 ratio were also made, but the resulting dispersions were not mechanically stable and did not produced continuous coatings at room temperature.

3.1.1. Particle Size and Particle Size Distribution

For hybrid dispersions, particle size distribution was monomodal and rather narrow, although in most cases wider than that for starting SIL and ACR dispersions. Zeta potentials were all very low (i.e., very negative) which indicated good dispersion stability that was confirmed by mechanical stability tests.

The average particle size was distinctly higher for hybrid dispersions SIL-ACR than for starting SIL dispersion and almost the same for ACR-SIL than for starting ACR dispersion (see Figure 4) what could indicate formation of shell on starting SIL dispersion core particles during polymerization of ACR monomers and lack of formation of core-shell particle structure in the case of polymerization of SIL monomers in starting ACR dispersion. The comparison of particle size distribution patterns confirmed that assumption for ACR-SIL dispersions—see Figure 5a. As it can be seen in Figure 5b, in synthesis of SIL-ACR dispersions acrylic/styrene copolymer particles smaller than particles of starting SIL dispersion were probably formed along with core-shell SIL-ACR particles.

In general, average particle size was significantly higher for SIL-ACR dispersions than for ACR-SIL dispersions of the same composition of SIL and ACR parts—see Figure 6 where the particle size distribution of one of the SIL-ACR dispersions (SIL-ACR 2-B) and of the corresponding ACR-SIL dispersion (ACR-SIL B-2) is shown. The reason for that was higher particle size of starting SIL dispersions than for starting ACR dispersions.

Table 1. Properties of hybrid silicone-acrylic (SIL-ACR) and ACR-SIL dispersions and of starting SIL and ACR dispersions. In the case of starting ACR dispersions all properties were determined for dispersions neutralized after polymerization while ACR dispersions before neutralization (with pH ca. 3.0) were used in synthesis of ACR-SIL hybrids. N.A. = Not Applicable because dispersion did not produce continuous film at room temperature (R.T.).

Designation of Dispersions	pH	Solids Content %	Coagulum Content %	Viscosity at 23 °C mPa·s	Average Particle Size nm	Particle Size Distribution nm	Polydispersity	Zeta Potential mV	Minimum Film-Forming Temperature (MFFT) °C	T _g (Disp. Solids) °C
SIL 1	6.3	19.3	0.00	2	121.7	104–157	0.121	−50.9	N.A.	−117.33
SIL 2	6.2	18.5	0.00	3	128.6	116–154	0.086	−49.5	N.A.	−119.46
ACR A	6.2	51.1	<0.1	94	105.7	74–119	0.112	−51.0	+11.4	+17.17
ACR B	6.2	51.5	<0.1	98	112.2	108–135	0.066	−56.0	+32.7	+32.36
SIL-ACR 1-A	5.8	42.2	0.06	20	143.8	69–160	0.074	−57.7	+7.3	−126.66 +17.66
ACR-SIL A-1	6.3	43.2	0.38	140	111.7	71–131	0.096	−55.2	−0.5	−130.54 +14.58
SIL-ACR 1-B	6.3	42.3	0.11	24	140.3	69–190	0.072	−59.5	26.2	−129.09 +30.87
ACR-SIL B-1	6.3	42.0	0.21	61	114.4	98–133	0.071	−55.0	16.0	−126.33 +27.98
SIL-ACR 2-A	6.1	41.7	0.04	20	151.2	107–214	0.064	−59.2	−1.0 ¹	−132.94 +17.29
ACR-SIL A-2	6.3	41.6	0.13	55	109.3	98–122	0.085	−47.2	−0.4	+16.13
SIL-ACR 2-B	6.3	41.4	0.05	16	149.9	125–156	0.057	−55.7	+26.0 ¹	−131.46 +32.56
ACR-SIL B-2	6.3	42.2	0.24	56	115.9	104–130	0.069	−53.6	+14.8	+20.04

¹ For these dispersions also maximum film forming temperature was observed. It was +10.5 °C for SIL-ACR 2-A and +36.2 °C for SIL-ACR 2-B.

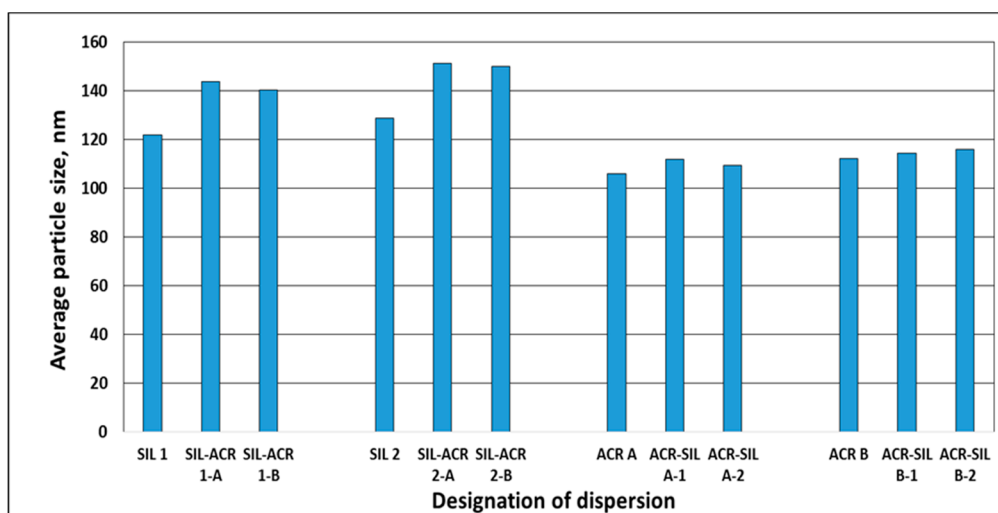


Figure 4. Comparison of average particle size of SIL and ACR dispersions and hybrid SIL-ACR and ACR-SIL dispersions.

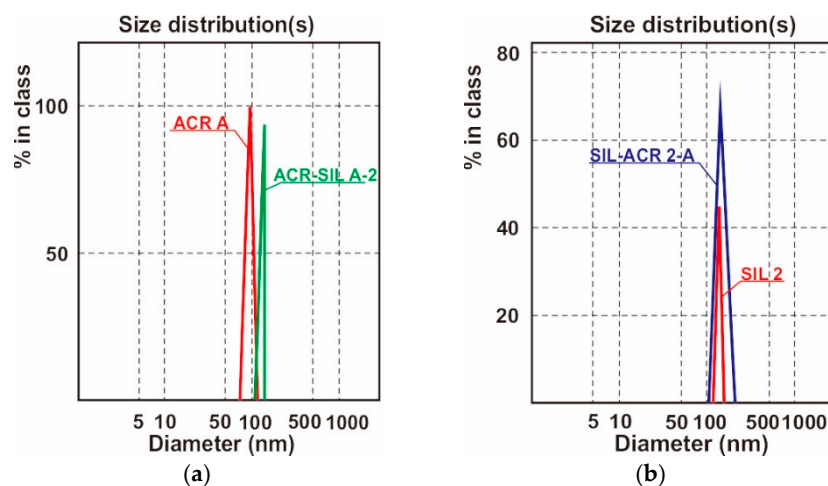


Figure 5. Comparison of particle size distribution patterns of hybrid ACR-SIL A-2 dispersion and starting ACR A dispersion (a) and of hybrid SIL-ACR 2-A dispersion and starting SIL 2 dispersion (b). X-axis is logarithmic.

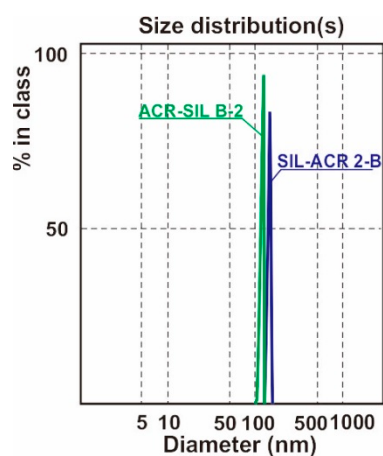


Figure 6. Comparison of particle size distribution patterns for SIL-ACR and ACR-SIL dispersions of the same composition of SIL and ACR parts. X-axis is logarithmic.

3.1.2. Particle Structure

In Figure 7 the structure of hybrid dispersion particles of SIL-ACR and ACR-SIL dispersions determined by TEM is shown. As can be seen in Figure 7a, in the case of SIL-ACR dispersion coalescence of particles proceeded during testing, so the TEM image shows a tiny piece of film rather than the single particle, but it is clear that well defined silicone resin particles (lighter shade) are surrounded by acrylic/styrene copolymer phase (darker shade). Individual particles can be identified better in Figure 7b where lower magnification was used and it can be concluded that a kind of “fruit cake” particle structure where a few “cores” made of one polymer are surrounded by continuous mass of the other polymer was formed during polymerization of ACR monomers in SIL dispersion. In the case of ACR-SIL, dispersion coalescence of particles during testing also proceeded. While both individual particles and aggregates of silicone resin particles and acrylic/styrene copolymer particles were present, it was also possible to identify in TEM images abundant single particles of specific structure shown in Figure 7c. In this structure kinds of spheres made of silicone resin (lighter shade) were embedded in the mass of acrylic/styrene copolymer (darker shade). It can be anticipated that in the course of synthesis of ACR-SIL hybrid dispersions silicone monomers penetrated into acrylic/styrene copolymer particles and after completion of polymerization a kind of sphere of silicone resin was formed because of lack of compatibility of acrylic/styrene copolymer and silicone resin. Such a particle structure called an “embedded sphere” has been found also earlier in polyurethane-acrylic/styrene hybrid dispersions [4].

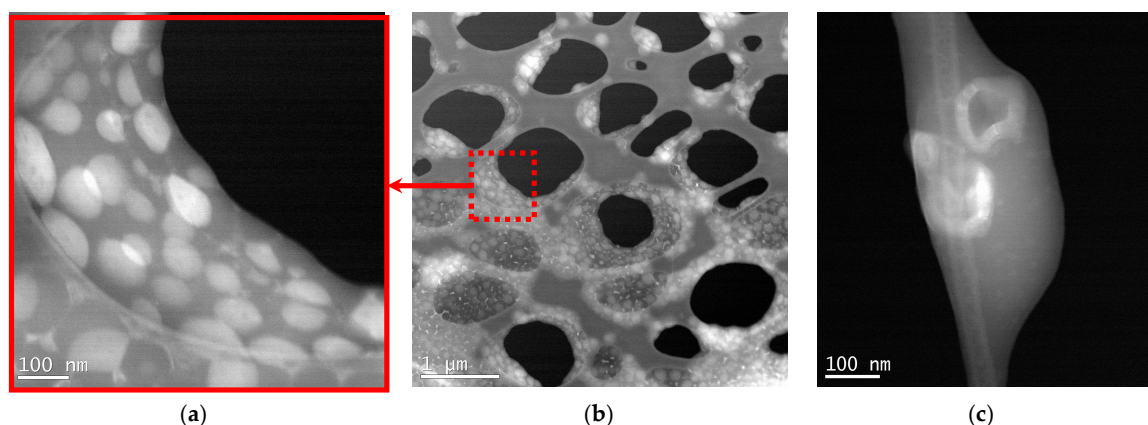


Figure 7. Structure of hybrid dispersion particles settled on the micromesh net as determined by transmission electron microscopy (TEM): (a) SIL-ACR dispersion, higher magnification, (b) SIL-ACR dispersion, lower magnification, (c) ACR-SIL dispersion, higher magnification. Lighter shade represents silicone resin and darker shade—acrylic/styrene copolymer.

Lack of formation of core-shell ACR-SIL hybrid particles in the course of polymerization of silicone monomers in acrylic/styrene copolymer dispersion could have been expected since it was clear from the review of available literature on that subject [11] that only if special approaches were applied to synthesis (e.g., functionalization of acrylic particle surface with silane and hydrolysis of alkoxysilane groups prior to polymerization [22]) the particles with acrylic polymer core and silicone shell could be obtained.

3.1.3. Minimum Film-Forming Temperature (MFFT)

As it can be seen in Figure 8 MFFT values determined for ACR-SIL hybrid dispersions were much lower than for starting ACR dispersion and lower than for SIL-ACR dispersions of the same SIL and ACR parts composition what can be explained by the fact that only a fraction of particles of ACR-SIL dispersion hybrid structure exhibited a hybrid morphology shown in Figure 6b and the presence of separate silicone resin particles resulted in lower MFFT.

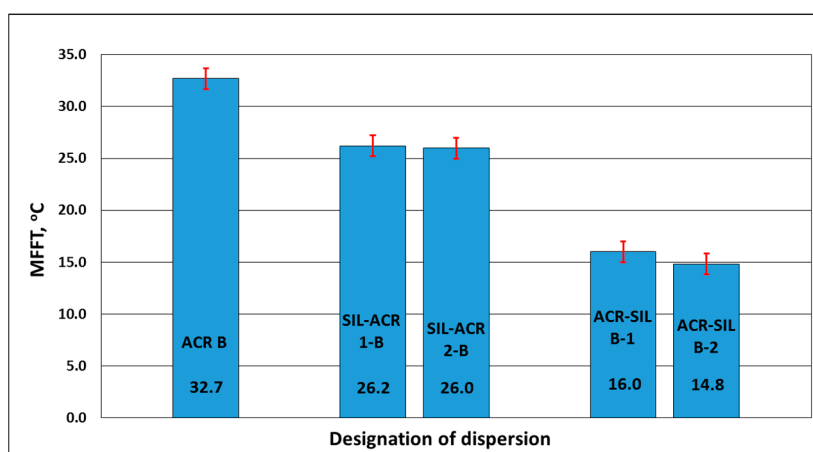


Figure 8. Comparison of MFFT determined for hybrid dispersions SIL-ACR and ACR-SIL. MFFT of starting ACR dispersion used for synthesis of ACR-SIL dispersions is also shown.

3.1.4. Glass Transition Temperature (T_g)

DSC results showed that hybrid dispersion solids usually exhibited two T_g s: one corresponding to SIL part at c.a. -120 °C and the other corresponding to ACR part in the range of ca. 15 – 30 °C, depending on the T_g of starting acrylic/styrene copolymer—see Figure 9 where DSC patterns determined for starting SIL and ACR dispersions and for SIL-ACR and ACR-SIL dispersions having the same composition of ACR and SIL parts are presented.

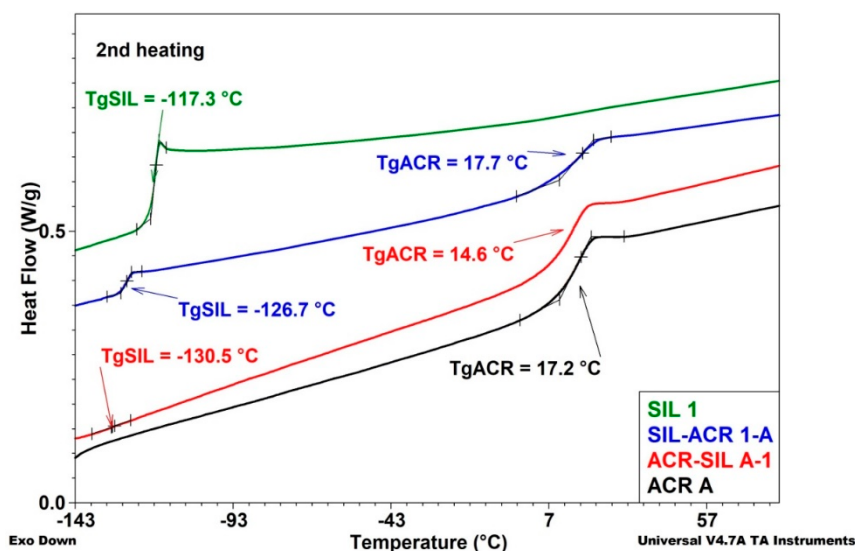


Figure 9. Differential scanning calorimetry (DSC) patterns determined for starting SIL and ACR dispersions and for SIL-ACR and ACR-SIL dispersions having the same composition of ACR and SIL parts.

Only for two dispersions (ACR-SIL A-2 and ACR-SIL B-2) just one T_g was detected at around 16 and 20 °C, respectively, what suggested that in the case of these two dispersions the particle structure was rather uniform and no separate silicone resin particles were formed. This phenomenon can be explained by the fact that in these two dispersions silicone monomers (D4 + ethoxy-functional silane) mixture that was polymerized in acrylic/styrene copolymer dispersion contained much more VTES (more polar) and did not contain MTES (less polar), so penetration into acrylic/styrene copolymer particles was easier and grafting of VTES on acrylic/styrene copolymer and formation of “embedded sphere” structures shown in Figure 7c were much more probable.

It was also interesting that T_{gs} of SIL and ACR parts of all hybrid dispersion solids where two glass transitions were detected were significantly lower than T_{gs} of starting SIL and ACR dispersions solids. Decrease in T_g of ACR part can be explained by plasticizing effect of modification with silicone resin. However, in order to clarify why decrease in T_g of SIL partly occurred, more insight is needed to the processes which took place in the course of both silicone monomers polymerization in acrylic/styrene copolymer dispersion and acrylic/styrene monomers polymerization in silicone resin dispersion. The key assumption (confirmed by the hybrid particle structures) is that in hybrid dispersion particles silicone resin particles are “trapped” within a mass of acrylic/styrene copolymer, so D4 and higher oligodimethylsiloxane cycles (e.g., D5) which are always present in SIL dispersions [43] and are also formed in synthesis of hybrid ACR-SIL dispersions are also “trapped” and therefore cannot be released during drying and may plasticize the silicone resin contained in dispersion solids. That “trapping” of silicone resin in acrylic/styrene copolymer part of hybrid dispersion particles should be more distinct if the SIL part contained more VTES because of possibility of grafting the decrease in T_g should be more distinct for hybrid dispersions ACR-SIL 1-A and ACR-SIL 1-B than for hybrid dispersions ACR-SIL 2-A and ACR-SIL 2-B. Comparison of the relevant T_g values in Table 1 confirmed that this was actually the case.

3.2. Properties of Coatings and Films

Properties of coatings and films obtained from hybrid silicone-acrylic (SIL-ACR) and acrylic-silicone (ACR-SIL) dispersions prepared with SIL/ACR w/w 1/3 ratio, starting silicone resin dispersions (SIL 1 and SIL 2) and starting acrylic/styrene copolymer dispersions (ACR A and ACR B) are presented in Table 2. Some hybrid dispersions and starting silicone resin dispersions did not form mechanically strong continuous coatings or films, but certain properties like e.g., contact angle or % swell could be determined by casting layers which, after drying, formed mechanically weak coatings or films.

It is essential that for all hybrid dispersions the key coating properties that were expected to improve as compared to acrylic/styrene copolymer dispersions (contact angle, water vapor permeability and water resistance) actually did improve significantly. Mechanical properties of coatings (e.g., impact resistance or elasticity) also improved, but hardness decreased what could be expected. The same trend was reflected in film properties—increase in elongation at break was accompanied by a decrease in tensile strength.

3.2.1. Surface Properties

The high contact angle of coatings is important since it means high surface hydrophobicity and, consequently, lower water uptake and lower dirt deposition [5]. As can be seen in Table 2, all coatings obtained from hybrid SIL-ACR and ACR-SIL dispersions showed high contact angles in the range of 80–90° while contact angles recorded for films obtained from starting ACR dispersions were quite low (ca. 30°). It is worth to note that contact angles recorded for coatings produced from ACR-SIL dispersions were generally higher than those recorded for coatings produced from SIL-ACR dispersions (see Figure 10) what indicates that in the former case more silicone migrated to the coating surface.

Migration of silicone to the coating surface observed for coatings containing silicones was described in the earlier papers, e.g., [32,44,45] and was fully confirmed by XPS also for coatings obtained from SIL-ACR and ACR-SIL hybrid dispersions. In Figure 11 the percentage of Si in the layers close to coating surface as determined by XPS for hybrid SIL-ACR and ACR-SIL dispersions is plotted against distance from the surface. It is clear from Figure 11 that in the coatings obtained from hybrid dispersions silicone migrated to coating surface and that migration was different for coatings obtained from ACR-SIL dispersions than for those obtained from SIL-ACR dispersions, most probably due to “trapping” of silicone resin in acrylic/styrene copolymer particles in the latter coating.

Table 2. Properties of coatings and films made from hybrid SIL-ACR and ACR/SIL dispersions and of starting SIL and ACR dispersions. N.A. = Not Applicable because dispersion did not produce continuous coating or/and film at R.T. Although SIL-1 and SIL-2 dispersions did not produce continuous a mechanically strong coatings, it was possible to measure their contact angles on very mechanically weak coats that were cast on glass Petri dishes.

Designation of Dispersions	Contact Angle (H ₂ O) (°)	Water Vapour Permeability g/m ² /24h	Water Resistance after 72 h	Impact Resistance (direct) J	Impact Resistance (reverse) J	Cupping mm	Elasticity (Rod Diameter 2 mm)	Hardness (Koenig)	Adhesion to Glass	Swell in H ₂ O %	Swell in Toluene %	Tensile Strength MPa	Elongation at Break %
SIL 1	111				N.A.					18	202		N.A.
SIL 2	104				N.A.					10	387		N.A.
ACR A	30	28.1	>5(S5) 5(S2)	2.0	19.6	10.7	passed	0.082	5	14	1156	4.2	1000
ACR B	35	15.6	Medium whitening 5(S2)	2.0	0	10.7	failed	0.458	5	15	1547	12.0	340
SIL-ACR 1-A	83	56.5	Medium whitening 0(S0)	9.8	19.6	11.6	passed	0.040	3	26	591	2.1	773
ACR-SIL A-1	95	45	Light whitening 5(S2)	15.7	19.6	11.0	passed	0.022	2	21	1050	0.8	1851
SIL-ACR 1-B	81	64.5	Light whitening 0(S0)	0	0	10.9	passed	0.085	5	11	561	4.3	11
ACR-SIL B-1	92	34.6	Medium whitening	5.9	19.6	10.9	passed	0.050	5	26	905	3.1	1015
SIL-ACR 2-A	77				N.A.					20	605		
ACR-SIL A-2	92	39.4	0(S0) Medium whitening	13.7	19.6	10.5	passed	0.034	5	16	1112	0.9	1516
SIL-ACR 2-B	85				N.A.					9	665		N.A.
ACR-SIL B-2	82	28.0	0(S0) Medium whitening	3.9	19.6	11.0	passed	0.058	5	31	991	3.2	947

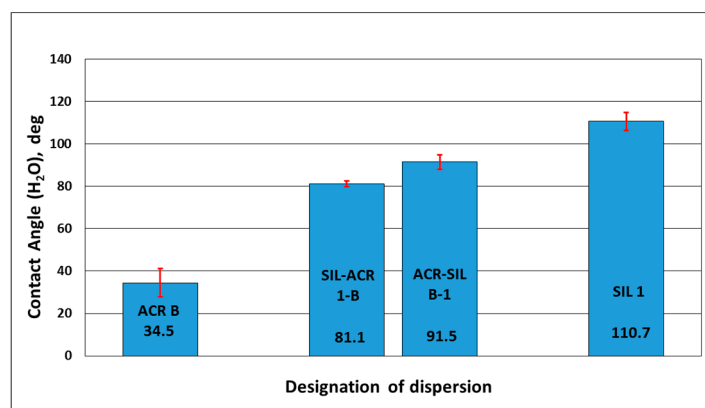


Figure 10. Comparison of contact angle values determined for coatings obtained from starting SIL and ACR dispersions and corresponding hybrid SIL-ACR and ACR-SIL dispersions having the same composition of ACR and SIL parts. Contact angle determined for starting acrylic/styrene copolymer dispersion (ACR B) is also shown.

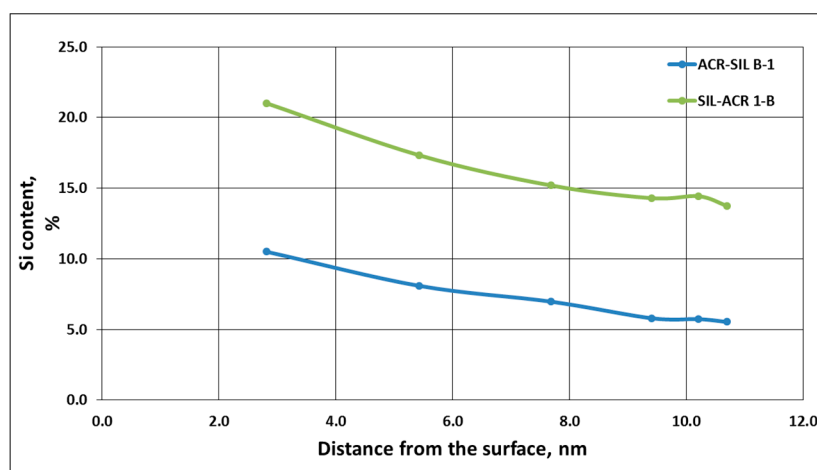


Figure 11. Decrease in Si content with distance from coating surface determined by XPS for coatings obtained from SIL-ACR and ACR-SIL dispersions.

3.2.2. Water Resistance

Good water resistance of architectural paints is crucial since it ensures longer life of the paint and better comfort of the building walls (lack of water uptake) if combined with high water vapour permeability. Therefore, determination of the water resistance of coatings produced from dispersions which are intended to be applied as binders for architectural paints seems to be very important test. In our investigations we measured water resistance of coatings obtained from starting ACR dispersions and from SIL-ACR and ACR-SIL dispersions using our own method partly described in Section 2.4 and the results were assessed based on EN ISO 4628-2 [40]. All coatings made from hybrid dispersions exhibited better water resistance than those produced from starting ACR dispersions and it was significantly better for coatings obtained from ACR-SIL dispersions than from SIL-ACR dispersions—see Figure 12 where photos of coatings produced from different dispersions and left under water for 6 days are shown.

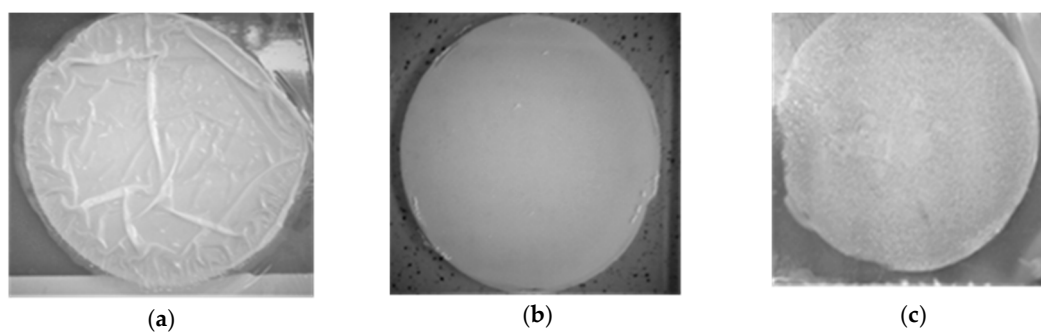


Figure 12. Comparison of water resistance of starting acrylic/styrene copolymer dispersion. ACR A (a), acrylic-silicone dispersion (ACR-SIL A-1) (b) and corresponding silicone-acrylic dispersion SIL-ACR (c). Samples were kept under water for 6 days. ACR A—deterioration of coating occurred, ACR-SIL A-1—coating did not change except for light whitening, SIL-ACR 1-A—coating changed significantly—numerous small bubbles.

3.2.3. Swell in Water and in Toluene

As can be concluded from Table 2 percent of swell in water was very similar for all films (despite of differences in water resistance of coatings) and was quite low (ca. 20%) while swell in toluene that can be considered as a measure of crosslinking density (higher swell means lower crosslinking density) was much higher for films made from ACR dispersions than for films made from SIL dispersions, and also much higher for films made from hybrid ACR-SIL dispersions than for films made from SIL-ACR dispersions—see the relevant comparison in Figure 13.

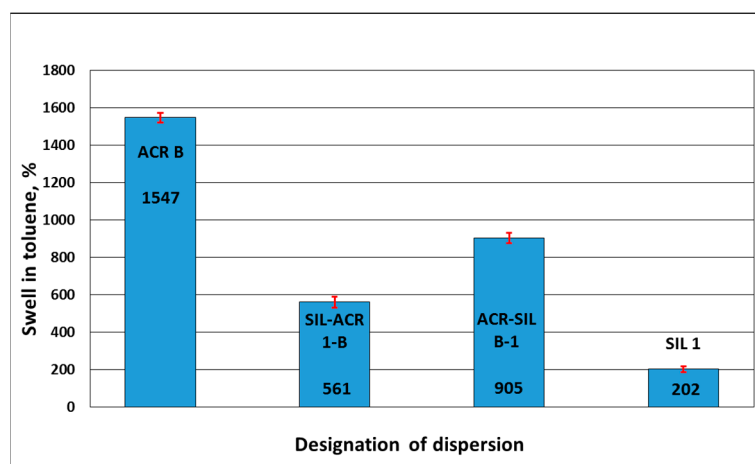


Figure 13. Comparison of % swell in toluene determined for starting silicone resin dispersion (SIL-1), starting acrylic/styrene copolymer dispersion (ACR B) and hybrid dispersions ACR-SIL B-1 and SIL-ACR 1-B having the same composition of SIL and ACR parts.

The difference between crosslinking density of films (i.e., also for coatings) made from ACR-SIL and SIL-ACR dispersions having the same composition of ACR and SIL parts can be explained by a higher possibility of grafting of acrylic/styrene monomers on silicone resin than of grafting VTES on acrylic/styrene copolymer. Another reason can be a higher possibility of trapping of partly crosslinked silicone resin inside particles made of acrylic/styrene copolymer in the case of films made from SIL-ACR dispersions than in the case of films made from ACR-SIL dispersions—see the discussion of hybrid dispersions particle structures contained in Section 3.1.2.

3.2.4. Water Vapour Permeability

As has already been pointed out in Section 3.2.2, good architectural paint should exhibit not only good water resistance, but also good water vapour permeability. This positive combination of properties can be achieved in practice only for paints based on silicone-acrylic binders because silicone polymers are characterized by good permeability of gases due to high mobility of poly(dimethylsiloxane) chains. It was proved in our study that coatings produced from hybrid SIL-ACR and ACR-SIL dispersions showed higher water vapour permeability than those produced from starting ACR dispersions—see Figure 14.

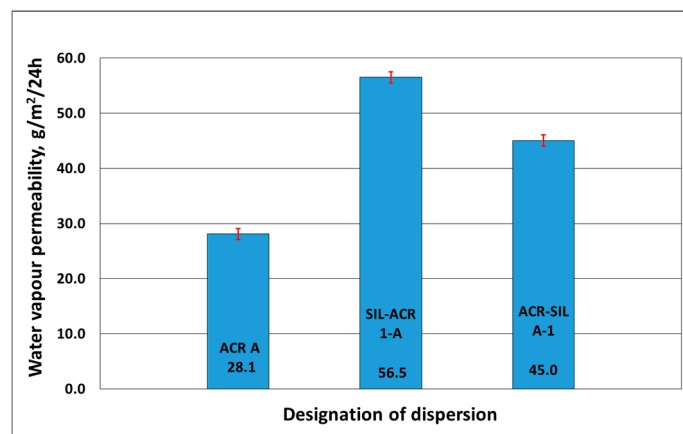


Figure 14. Comparison of water vapour permeability determined for starting acrylic/styrene copolymer dispersion (ACR A) and hybrid dispersions ACR-SIL A-1 and SIL-ACR 1-A having the same composition of SIL and ACR parts.

It can be noted from the results presented in Figure 14 that water vapour permeability was better for coatings obtained from SIL-ACR dispersions than from ACR-SIL dispersions, probably because of differences in coating structure that resulted from differences in dispersion particle structure.

3.2.5. Mechanical Properties

If the results of testing the mechanical properties of coatings and films produced from hybrid ACR-SIL and SIL-ACR dispersions presented in Table 2 are compared with mechanical properties of coatings produced from starting ACR dispersions, it is clear that modification with silicone led generally to less brittle coatings, especially in the case of starting dispersion ACR A. The most spectacular difference was in the (direct) impact resistance of coatings—see Figure 15.

For coatings and films produced from starting dispersion ACR B and hybrid coatings and films where ACR B composition of monomers was applied in synthesis of the relevant dispersions, the results of mechanical tests were much less convincing, presumably because T_g of ACR B was quite high (over 30 °C). Cupping test results were good for all coatings and in direct elasticity measurements, only coatings produced from starting dispersion ACR B failed. Elongation at break increased for some films made from hybrid dispersions as compared to films made from starting ACR dispersions and decreased for some others (specifically for these produced from hybrid dispersions with particles having ACR B composition of ACR part) and tensile strength decreased for all films where this could be expected taking into account plasticizing effect of silicone resin. Much higher elongation at break and much lower tensile strength observed for films made from ACR-SIL dispersions than from SIL-ACR dispersions can be explained by a different supramolecular structure of films that results from different morphology of hybrid dispersion particles (see Figure 7) that coalesce to produce these films in the process of air-drying of dispersions.

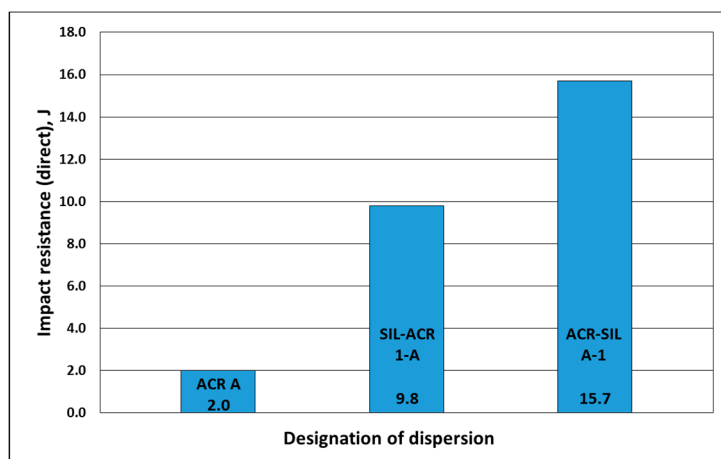


Figure 15. Comparison of impact resistance (direct) determined for coatings obtained from starting acrylic/styrene copolymer dispersion (ACR A) and hybrid dispersions ACR-SIL A-1 and SIL-ACR 1-A having the same composition of SIL and ACR parts.

4. Conclusions

Simultaneous synthesis of aqueous silicone-acrylic and acrylic-silicone hybrid dispersions (SIL-ACR and ACR-SIL) by (1) emulsion polymerization of acrylic/styrene monomers (BA, ST, KA and MA) mixtures of different composition (ACR A and ACR B) in aqueous dispersions of silicone resins of different composition (SIL 1 and SIL 2) and (2) emulsion polymerization of silicone monomers (D4, VTES and MTES) mixtures of different composition (SIL 1 and SIL 2) in aqueous dispersions of acrylic/styrene copolymers (ACR A and ACR B) was successfully conducted. Hybrid dispersions had good mechanical stability, low minimum film-forming temperature and particle size in the range of 100–150 nm, narrow particle size distribution, and contained very little of coagulate. TEM investigation of hybrid dispersions particle structure revealed that particles of SIL-ACR dispersions exhibited “fruit cake” structure while particles of ACR-SIL dispersions showed “embedded sphere” structure. For most of the dispersions two separate T_{gs} of dispersion solids (one for SIL part and the other for ACR part) that were detected by DSC were lower than T_{gs} of corresponding starting SIL and ACR dispersions while single T_g was detected for two of them. These differences were explained by differences in dispersion particle structure.

Most of the hybrid dispersions formed mechanically strong continuous coatings and films. As compared to coatings obtained from starting ACR dispersions, those obtained from hybrid dispersions showed much higher contact angles, much better water resistance and water vapour permeability and exhibited much better impact resistance. Different coating properties were observed when coatings were produced from SIL-ACR and ACR-SIL dispersions having the same composition of ACR and SIL parts, which most probably resulted from different structure of dispersions particles. Films produced from hybrid dispersions were less brittle than those produced from starting ACR dispersions. Determinations of % swell in toluene measured for films produced from hybrid dispersions revealed the difference between crosslinking density of films (i.e., also for coatings) made from ACR-SIL and SIL-ACR dispersions having the same composition of ACR and SIL parts, which was explained by higher possibility of grafting of acrylic/styrene monomers on silicone resin than of grafting VTES on acrylic/styrene copolymer. The authors believe that the selected hybrid dispersions described in this paper can be applied as binders in the formulation of architectural paints that will be characterized by high water resistance and high surface hydrophobicity combined with high water vapour permeability.

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