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Silicone-containing hybrid polymer dispersions designed for coating applications

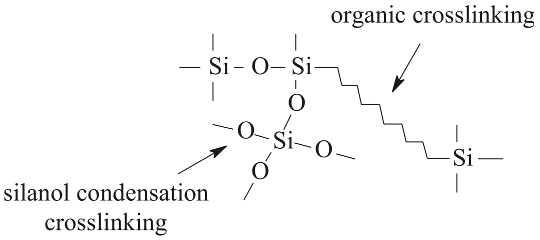
Summary — The results of studies on novel aqueous silicone-containing hybrid polymer dispersions of specific architecture designed for coatings are presented. Dispersions were synthesized either *via* polymerization of acrylic and styrene monomers in aqueous poly(siloxaneurethaneurea) anionic dispersions prepared from the mixture of polysiloxanediol, saturated polyol and unsaturated polyol and cycloaliphatic diisocyanate or *via* polymerization of silicone monomers in commercially available acrylic copolymer dispersions. The effect of structural parameters of the hybrid polymers with constituted dispersion particles on the properties of dispersions, films and coatings was studied and it was found that they were significantly influenced by the share and kind of silicone component. More detailed studies of surface properties of the coatings using wettability determinations (DCA, SFE), ESCA, and AFM techniques revealed self-assembling of the surface layers depending on the chemical composition of the polymers constituting the hybrid system. The results show, that the macro-scale properties of hybrid materials (combination of organic polymers and silicones) can be tailored to the demands of particular application through designing of the specific micro- or even nano-scale architecture of the hybrid system.
Key words: hybrid polymers, polysiloxanes, polyurethane, acrylate copolymers, aqueous dispersions, coating compositions.

POLIMEROWE DYSPERSJE HYBRYDOWE ZAWIERAJĄCE SILIKONY, PRZEZNACZONE DO ZASTOSOWANIA JAKO MATERIAŁY NA POWŁOKI

Streszczenie — Przedstawione w artykule badania dotyczą wodnych dyspersji nowych, hybrydowych polimerów zawierających fragmenty krzemoorganiczne; specyficzną budowę tych produktów dostosowano do ich zastosowania w kompozycjach powłokowych. Otrzymano je bądź w wyniku polimeryzacji mieszaniny metakrylanu metylu, akrylanu butylu i styrenu w wodnej anionowej dyspersji poli(siloksanouretanomocznika) (otrzymanego z polisiloksanodiolu, nasyconego poliolu, nienasyconego poliolu i cykloalifatycznego diizocyjanianu), bądź też na drodze emulsyjnej polimeryzacji monomerów krzemoorganicznych (oktametylocyklotetrasiloksanu, metylotrietoksysilanu, winylometylocyklosiloksanów) w dostępnej na rynku handlowym dyspersji kopolimerów akrylowych. Dyspersje otrzymywane tą drugą metodą zawierały ponadto niesilikonowe modyfikatory polimerowe (wosk polietylenowy, politetrafluoroetylen). Scharakteryzowano szereg właściwości uzyskanych dyspersji, m.in. wymiary cząstek, wartość pH, zawartość substancji stałych (tabele 1 i 3). Wyniki badań właściwości zarówno różnych dyspersji, jak i uzyskiwanych z nich powłok (tabela 2, rys. 1—4) wskazują, że właściwości te (np. twardość, odporność na rozpuszczalniki) w sposób istotny zależą od rodzaju i udziału składnika silikonowego.

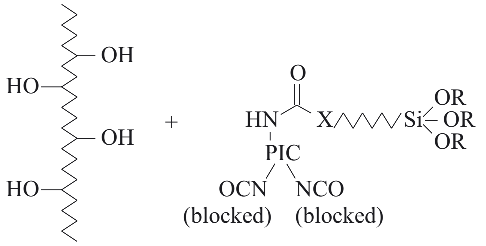
Bardziej szczegółowe badania właściwości powierzchni powłok z zastosowaniem metod umożliwiających określenie ich zwilżalności (dynamiczny kąt zwilżania — DCA, swobodna energia powierzchni — SFE, tabela 4), a także metod ESCA/XPS i AFM ujawniły samoorganizowanie się warstw powierzchniowych w sposób zależny od budowy chemicznej polimerów tworzących układ hybrydowy. Przedstawione wyniki świadczą o tym, że właściwości materiałów hybrydowych opartych na silikonach i polimerach organicznych można dopasować do wymagań występujących w konkretnym zastosowaniu dzięki doborowi specyficznej struktury układu hybrydowego w skali mikrometrycznej, a nawet nanometrycznej.
Słowa kluczowe: polimery hybrydowe, polisiloksany, poliuretany, kopolimery akrylanowe, dyspersje wodne, kompozycje powłokowe.

Silicone-containing hybrid polymer systems have been attracting attention of researchers for last couple of years since silicones can provide a set of unique properties to the hybrid material, including improved low temperature elasticity, heat resistance, specific surface properties and excellent water resistance combined with gas and water vapour permeability [1]. Novelty materials of this kind have been introduced to the market and are now being used widely in the industrial applications, for instance coatings. Good examples are Ormocer® and Ceramer® materials already utilized in industrial practice [2, 3]. The general principle applied in those materials, which is presented in Scheme A, involves two types of crosslinking — one through silanol groups and another through organic groups.



Scheme A. Example of silicone-containing hybrid polymer system

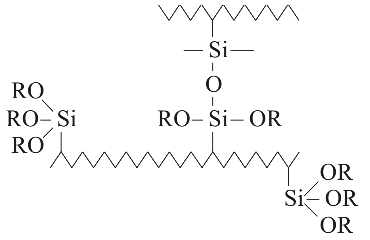
Practical implementation of that specific concept of silicone-containing hybrid system in the field of coatings can be seen in Scheme B where the chemical composition of two-component polyurethane coating system combined with silicone is presented [4].



Scheme B. Example of a hybrid coating system involving organic and silicone fragments [4]

The macro-scale properties of hybrid material, which represent combination of organic polymers and silicones, can be tailored to the demands of particular application through designing of the specific micro- or even nano-scale architecture of the hybrid system. This concerns, in particular, aqueous hybrid dispersions containing silicones, where "hybrid" shall mean hybrid dispersion particles composed of organic polymer and silicone, not mixture of one kind of dispersion particles composed of organic polymer and another kind of dispersion particles composed of silicone. Only then the advantages of hybrid composition could be fully utilised to get a material where positive features of both silicone and organic polymer were combined.

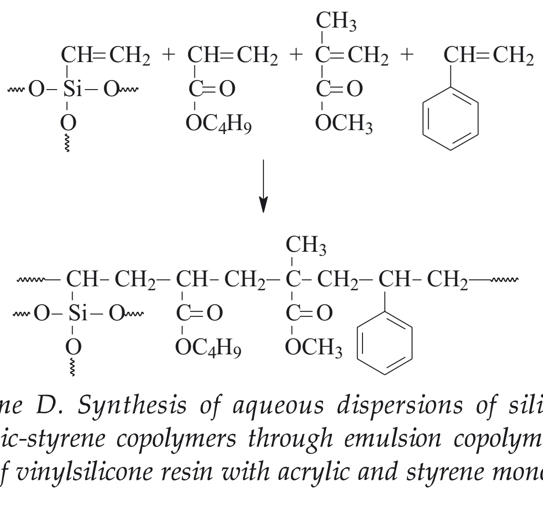
Obviously, this goal may be achieved in various ways, one of possible approaches is represented in Scheme C showing the chemical structure of a potential aqueous dispersion coating binder which comprises an organic (acrylic) polymer containing alkoxysilane side groups and being therefore capable for crosslinking with siloxane units [5]. In this case, each dispersion particle would contain both siloxane and organic part and thus would meet criteria for being a true "hybrid" system.



Scheme C. Chemical structure of acrylic polymer capable for crosslinking through alkoxysilane groups that can be used as coating binder in the form of aqueous dispersion [5]

Similar effect was achieved in the earlier studies carried out in the Industrial Chemistry Research Institute (ICRI) when especially synthesized silicone resin containing alkoxysilane and vinyl groups was copolymerized (see Scheme D) with acrylic and styrene monomers in a radical emulsion polymerization process yielding fine aqueous dispersions of silicone-acrylic-styrene copolymers potentially useful as binders for coatings [6, 7].

Synthesis of aqueous anionic dispersions of poly(siloxaneurethaneureas) from polysiloxane diols and diisocyanates using prepolymer-ionomer method was also



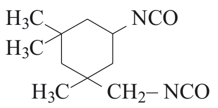
Scheme D. Synthesis of aqueous dispersions of silicone-acrylic-styrene copolymers through emulsion copolymerization of vinylsilicone resin with acrylic and styrene monomers [6, 7] developed in ICRI [7]. Such dispersions may also be considered "true hybrid" since both soft domains constituting of polysiloxane segments and hard domains constituting of urethane and urea segments are contained in each dispersion particle. Coatings produced from those dispersions showed very good properties [8].

Recently, studies on two novel types of aqueous silicone-containing hybrid polymer dispersions of specific architecture designed for coatings were carried out in ICRI. Dispersions were synthesized either *via* polymerization of acrylic and styrene monomers in aqueous poly(siloxaneurethaneurea) anionic dispersions prepared from the mixture of polysiloxanediol, saturated polyol, unsaturated polyol and cycloaliphatic diisocyanate [9, 10] (Type 1) or *via* polymerization of silicone monomers in commercially available acrylic polymer dispersions [11] (Type 2). Selected results of these studies will be presented below.

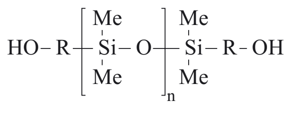
EXPERIMENTAL

Synthesis of Type 1 silicone-containing hybrid dispersions (SHD-1)

Synthesis of SHD-1 was carried out from aqueous poly(siloxaneurethaneurea) anionic dispersions (PSUD) *via* radical polymerization according to a process described in [12] and [13] using mixture of monomers: methyl methacrylate (MM from Firma Chemiczna Dwory SA, Poland) + butyl acrylate (BA, supplied by the same company) + styrene (S, from Fluka AG) containing 34 wt. % of MM, 25 wt. % of BA and 41 wt. % of S and potassium persulfate as initiator.



(I)
IPDI



$$HO-R-\left[\overset{Me}{\underset{Me}{Si}}-O\right]_n-\overset{Me}{\underset{Me}{Si}}-R-OH$$

(II)
Tegomer 2111
$R = -(CH_2)_6-$
$n = 10$

PSUD were synthesized in the three step reaction as described in [8] from cycloaliphatic diisocyanate (isophoronediisocyanate — IPDI from Huels — structure I) and the mixture of polysiloxanediol (Tegomer 2111 from Goldschmidt — structure II), saturated polyol (polytetramethylene glycol — PTMG 2000 from BASF) and unsaturated polyol (hydroxyl value = 276 and acid value = 1.8) containing different proportions of the latter three components. Dimethylolpropionic acid (from Fluka) was used as source of carboxylic groups.

Synthesis of Type 2 silicone-containing hybrid dispersions (SHD-2)

The following silicone-containing hybrid dispersions (SHD-2) were synthesised *via* emulsion polymerization of organosilicon compounds in commercially available acrylic copolymer dispersion (ACD):

— SHD-2A — silicone/acrylic/polyolefine polymer system containing SiOH reactive groups,

— SHD-2B — silicone/acrylic/polytetrafluoroethylene (PTFE) polymer system containing SiOH reactive groups,

— SHD-2C — silicone/acrylic/polyolefine (PO) polymer system containing Si-CH=CH_2 reactive groups,

— SHD-2D — silicone/acrylic/PTFE polymer system containing Si-CH=CH_2 reactive groups.

Hybrid dispersions SHD-2 type A and B were synthesised by emulsion polymerization of octamethylcyclotetrasiloxane (GE-Bayer) and methyltriethoxysilane (Linegal) in ACD (Rhodopas 910, Rhodia) by using dodecylbenzoic acid (Chemical Works, Rokita SA) as catalyst and emulsifier, as described in [11] followed by addition of polyolefin (high melting polyethylene wax) dispersion (POD) Permanol HDF with pH = 8.5—9.5 (Clariant) to obtain SHD-2 A or PTFE dispersion with pH = 4.5 (PTFED) (Nitrogen Chemical Works — Tarnów) to obtain SHD-2B.

Hybrid dispersions SHD-2 type C and D were synthesised by emulsion polymerization of vinylmethylcyclosiloxanes (GE-Bayer) and methyltriethoxysilane (Linegal) in ACD by using a catalyst based on KOH (POCh, Polish Chemical Reagents — Gliwice) and nonionic and anionic type emulsifiers as described in [11] followed by addition of POD to obtain SHD-2C or PTFED to obtain SHD-2D. The area of optimal recipes of dispersion systems was determined based on designed factorial experiments.

Preparation of coatings from hybrid dispersions

Coatings were obtained from PSUD and SHD-1 by casting *ca.* 10 cm^3 of dispersion onto a glass plate degreased with 1/1 toluene/ethyl alcohol mixture using 120 μ applicator and drying at room temperature over 72 hours. Some coatings obtained from PSUD or SHD-1 were subjected to additional oxidative curing. For testing the effect of additional oxidative curing, 3 % of Additol VXW940 dryer from USB (per dispersion solids) was used.

Silicone-containing coating materials based on SHD-2A — D were obtained by crosslinking of functional polysiloxanes synthesized in dispersion systems. SHD-2 type A and B were crosslinked by condensation of silanol functional groups. Aqueous solution of zinc organometallic compound Siltex CL4 (Chemical Plant "Polish Silicones" SA) was applied as condensation catalyst. SHD-2 — type C and D were crosslinked *via* hydrosilylation of vinyl functional groups using platinum catalyst in vinylcyclosiloxanes PC085 (Linegal) emulsified in water.

Commercial silicone resin emulsion Sarsil ME 25 (Chemical Plant "Polish Silicones") was used as a starting material to obtain pure silicone resin coating (SRC) by drying within 24 h at 20 °C. SRC was tested as a control sample, not containing organic modifier. Commercially available silicone-PTFE emulsion Antigraf 01 (Chemical Plant "Polish Silicones") was used as a starting material to obtain silicone-PTFE coating (SHF) by crosslinking in the presence of Antigraf CL catalyst. SFIF was tested as a control sample, not containing acrylic component.

Testing of dispersions

Solids content, pH, viscosity, minimum film forming temperature (MFFT), particle size and particle size distribution were determined for PSUD, SHD-1 and SHD-2. Solids contents and pH were tested according to standard EN tests. Viscosity was determined at 25 °C using Hoeppler Rheoviscometer according to PN-68/C-04419. Particle size, particle size distribution and zeta potential analysis were determined using a Malvern Zeta Sizer 4 apparatus. MFFT was measured on a MFT Thermostair apparatus (Coesfeld). For SHD-2 mechanical stability of dispersions was determined by using centrifuge Universal 16R (Hettich) 3600 rpm at 25 °C. Stability of dispersion was checked after every 15 min of the centrifuge test. Freezing resistance was determined by storing of dispersion sample at -15 °C over 18 h and checking the stability of dispersion.

Testing of coatings

Drying time, hardness (Persoz), water and solvent (methylethyl ketone — MEK) resistance, adhesion and surface properties were determined for coatings obtained from PSUD and SHD-1.

Drying time was tested according to PN-79/C-81519 where drying progress is defined as follows: "1^{o}" means that the coating is "sand dry" (no adhesion of sand to the coating) and "3^{o}" means that the coating is "hard dry" (no adhesion of paper to the coating under specified load).

Hardness (Persoz) was determined according to PN-79/C-81530.

Water resistance was tested according to PN-76/81521 (24 h immersion in water). According to that standard, increased numbers 1—4 mean increased size of bubbles and increased letters A—D mean increase number of bubbles.

For testing solvent resistance, the coating was rubbed with a cloth wetted with MEK and after 80 rubs the appearance of the coating ("+" or "–" meaning "resistant" or "not resistant") was recorded.

Adhesion to steel was tested according to PN-80/C-81531 (double-blade method). Numbers 1—4 mean decreasing adhesion to steel. DSC determinations were made according to ASTM D 3418-82.

Surface properties of coatings were investigated using two independent methods: electron spectroscopy for chemical analysis (ESCA/XPS) using a ESCALAB-210, Fisons Instruments apparatus, and dynamic contact angle (DC A) using a Processor Tensiometer K12, Kruss apparatus.

Drying time and solvent (MEK) resistance and surface properties were determined also for coatings obtained from SHD-2 dispersions using the same methodology.

Morphology and roughness of coating surface was examined using AFM method (TMX 2000 Discoverer SPM, Topo Metrix).

Freezing resistance was examined for treated and untreated samples of limestone subjected to the following freeze-thaw test: immersion in water for 6 h and freezing at 20 °C for 18 h. After each cycle, physical changes of the samples were examined.

Soiling test was performed by using soiling composition of glazier sand and silica mixture containing 10 wt. % of carbon black and having the particle size range 0.1 mm to 2.5 μm. In this test increasing numbers correspond to decreasing soiling resistance. Detailed description of the procedure was published earlier [14].

RESULTS AND DISCUSSION

SHD-1 type of silicone-containing hybrid dispersions and coatings

In our preliminary studies on SHD-1 and corresponding PSUD and coatings based on those dispersions published earlier [9, 10] the effect of the components of the hybrid (polysiloxane segments content in silicone-urethane-urea part of the polymer, ratio of acrylic/styrene part of the polymer to silicone-urethane part) and also the effect of double bonds content in silicone-urethane part was investigated. It was found that all those factors influence the properties of coatings significantly and especially interesting were relationships between double bonds content (originating from unsaturated polyol) and acrylic/styrene part content what suggested that grafting with participation of double bonds took place during polymerization of acrylic/styrene monomers in PSUD. This phenomenon will be further discussed below based on data obtained in another set of experiments where PSUD and corresponding SHD-1 were subjected to additional oxidative curing with a special dryer.

Detailed studies of the effect of polysiloxane segments, double bonds content in silicone-urethane part of the hybrid and acrylic/styrene part to silicone/urethane part ratio on the properties of PSUD, SHD-1 and coatings produced from them were later conducted in ICRI using a designed factorial experiment with those three factors applied as three independent variables. Some selected results of that designed factorial experiment were presented at the FATIPEC Congress in 2004 [12] and will be published soon [13]. In this paper detailed discussion

Table 1. Properties of PSUD and corresponding SHD-1 dispersions that were used for preparation of coatings tested for the effect of additional curing*)

Dispersion	Dispersion properties					
	solids content wt. %	pH	viscosity mPas	average particle size, nm	particle distribution, nm	MFFT, °C
PSUD-0, UP (–)	30.64	7.7—8.0	54	57.6	26.6—123	-0.5
PSUD-1, UP (+)	30.63	7.7—8.0	66	99.9	55.6—183	-0.5
PSUD-2, UP (++)	29.68	7.4—7.7	72	110.5	40.7—222.9	-0.5
SHD-1-0 (based on PSUD-0)	31.18	6.5—6.8	44	55.2	77.3—256.9	-0,5
SHD-1-1 (based on PSUD-1)	30.18	6.5—6.8	48	173.9	81.5—317.7	-0,5
SHD-1-2 (based on PSUD-2)	30.24	6.5—16.8	30	163.0	74.4—296.5	-0,5

*) SHD-1 were made using 33 wt. parts of monomers mixture per 100 wt. parts of dispersion solids. No unsaturated polyol (UP) was used in synthesis of PSUD-0 [designation: UP (–)] while PSUD-1 and PSUD-2 contained double bonds in polymer chain (less double bonds in PSUD-1 [designation UP (+) and more double bonds in PSUD-2 [designation UP (++)].

Table 2. Effect of additional curing with a dryer (oxidative curing) on the selected properties of coatings produced from both PSUD and SHD-1 dispersions listed in Table 1

Dispersion (designation from Table 1)	Drying time at R.T., min		Resistance to solvents (80 MEK rubs)		Hardness, Persoz		Water resistance		Adhesion to steel	
			Curing conditions							
	1	3	72 h, R.T.	72 h, R.T. + dryer	72 h, R.T.	72 h, R.T. + dryer	72 h, R.T.	72 h, R.T. + dryer	72 h, R.T.	72 h, R.T. + dryer
PSUD-0, UP (–)	45	45	—	—	—	0.27	—	1A, w**) remains after 1 h	1	1
PSUD-1, UP (+)	40	45	—	+ m*)	—	0.49	—	3C, w remains after 1 h	1	1
PSUD-2, UP (++)	35	45	—	+ m	—	0.67	—	1D, w remains after 1 h	1	1
SHD-1-0 (based on PSUD-0)	40	50	—	—	—	0.16	—	3C, w remains after 1 h	1	1
SHD-1-1 (based on PSUD-1)	40	50	—	+ m	—	0.49	—	3C, w remains after 1 h	1	1
SHD-1-2 (based on PSUD-2)	35	40	—	+ m	—	0.63	—	1C, w remains after 1 h	1	2

*) m = matt, **) w = whitening.

of the effect of silicone part of the hybrid poly(siloxaneurethaneurea-acrylic/styrene) polymer that constitutes the dispersion particles in SHD-1 on the properties of dispersions and coatings will be also provided below.

Effect of additional curing on the properties of coatings

Properties of SHD-1 and corresponding PSUD (starting materials for SHD-1) that were used for preparation of coatings tested for the effect of additional curing are presented in Table 1. So, no unsaturated polyol was used in synthesis of PSUD-0 while PSUD-1 and PSUD-2 contained double bonds in polymer chain (more double bonds in PSUD-2).

The results shown in Table 1 clearly proved that silicone-containing hybrid dispersions (SHD-1) characterized by very good properties (pH close to 7, low viscosity, low average particle size, low MFFT — similar to MFFT values of standard polyurethane dispersions) could be obtained by polymerization of acrylic/styrene monomers in aqueous poly(siloxaneurethaneurea) anionic dispersions. Interesting observation is that the particle size of SHD-1 is generally higher than that of PSUD and particle size distribution in SHD-1 is as good as in PSUD what suggests formation of hybrid particles.

Effects of additional curing with a dryer (oxidative curing) on selected properties of coatings produced from both PSUD and SHD-1 dispersions listed in Table 1 are presented in Table 2. The results shown in Table 2 proved that additional oxidative curing led to improved resistance of coatings to water and solvents (positive MEK rubs test). In the same time no significant difference between the properties of coatings obtained from SHD-1 and corresponding PSUD was observed. This indicates that some of double bonds still remained in the polymer chain after polymerization of monomers that was supposed to proceed through grafting of monomers on poly(siloxaneurethaneurea) chain of PSUD. For coatings produced from SHD-1 that were subjected to oxidative curing, hardness was significantly increasing with increasing double bond content in the starting PSUD polymer what further confirmed that assumption. Similar results were obtained when coatings were subjected to additional UV curing (but they could not be included here due to the limitations of paper volume).

Effect of silicone part of SHD-1 on the properties of coatings

In the preliminary investigations quoted earlier [9] it was found that the content of silicone part in PSUD affected the properties of coatings (in particular hardness) in a very complex way. Below, discussion of some results obtained in the studies on the effect of silicone part in SHD-1 on the coating hardness through a designed factorial experiment (that has been already mentioned previously) will be presented. In Fig. 1 and 2 the effect of silicone part content at different levels of unsaturated polyol (UP) content in the mixture of polyols used for synthesis on the coating hardness is presented. These results were obtained for SHD-1 synthesized from corresponding PSUD using 30 parts or 60 parts of acrylic/styrene monomers per 100 parts of dispersion solids.

It can be noticed from both Fig. 1 and Fig. 2 that the effect of silicone content in dispersion solids (expressed in those figures by polysiloxanediol content in the mixture of polyols used for dispersion synthesis) on coating hardness depends very much on UP content in the respective polyol mixture. While at low UP levels decrease in coating hardness with increase in silicone content is observed (what can be expected because of the flexibility of polysiloxane chain), the situation changes dramatically at high UP levels. At those high UP levels, rise in silicone content is hardness-increasing factor, and this phenomenon is quite difficult to explain. The only possible explanation seems to be dramatic change in coating microstructure resulting from the change in phase segregation occurring in this complex system. At high levels of unsaturation in the polymer what facilitates crosslinking, silicone chains may be locked in the crosslinked polymer structure and their migration to the coating surface may be more difficult. Detailed investigations of coating structure will be needed to confirm this assumption.

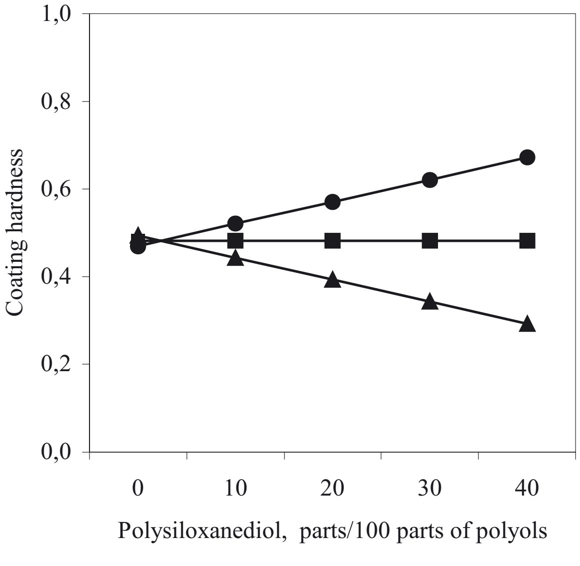


Fig. 1. Effect of silicone part content in the SHD-1 hybrid polymer on the coating hardness at various levels of unsaturated polyol content in the mixture of polyols used for synthesis of starting PSUD. Results presented in this figure were obtained for SHD-1 synthesized using 30 wt. parts of acrylic/styrene monomers per 100 wt. parts of dispersion solids (UP = unsaturated polyol) drying at RT, 72 h, without additional curing; UP (wt. parts/100 wt. parts of polyols): ▲ *— 0,* ■ *— 10,* ● *— 20*

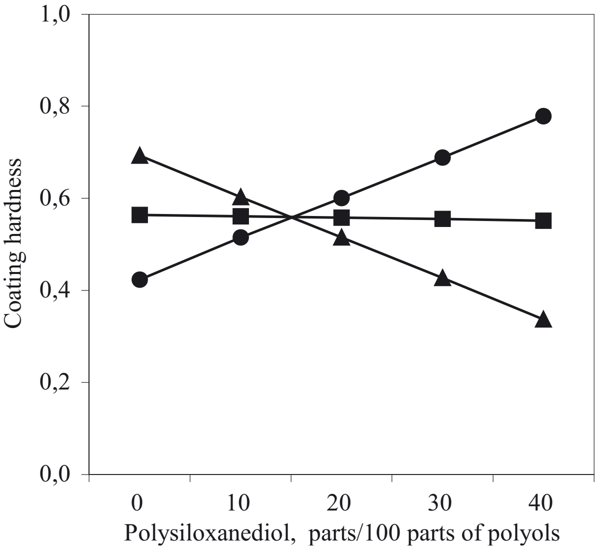


Fig. 2. Effect of silicone part content in the SHD-1 hybrid polymer on the coating hardness at various levels of unsaturated polyol content in the mixture of polyols used for synthesis of starting PSUD. Results presented in this figure were obtained for SHD-1 synthesized using 60 wt. parts of acrylic/styrene monomers per 100 wt. parts of dispersion solids. UP = unsaturated polyol; meaning of symbols see Fig. 1, drying as in Fig. 1

It should also be noticed that acrylic/styrene part of the polymer can definitely play some role in the process of formation of coating microstructure and thus can influence the relationship between silicone and UP that was discussed above. It becomes clear when direct comparison of the results obtained for SHD-1 of low content of acrylic/styrene part ((Fig. 1) and SHD-1 of high content of acrylic/styrene part (Fig. 2) is made. In general, coating hardness is higher when acrylic/styrene part content is higher, but quite complex relationship between silicone part and acrylic/styrene part of the hybrid can be observed. This may result from the fact that both silicone-urethane part and acrylic/styrene part of the hybrid are located in the same hybrid dispersion particles and therefore their direct interaction at a nanoscale level is possible. Good confirmation for this assumption comes from DSC investigations [12] since two glass transitions observed for starting PSUD (one about -70 °C and the other about +70 °C—+90 °C) change only slightly in corresponding SHD-1 what suggests that dispersion particles may have rather "gradient" or "fruit cake" morphology, that helps interactions between parts of the hybrid, than "core-shell" morphology where parts of the hybrid are separated.

Quite interesting data were provided by investigations of surface properties of coatings produced from SHD-1 and starting PSUD. It was found that while dynamic contact angle values were quite similar for coatings produced from SHD-1 and from starting PSUD, detailed measurements of Si/N ratio on the surface made by ESCA (showing the extent of polysiloxane chains migration) revealed much more Si on the surface for SHD-1. This finding indicated much lower compatibility of the whole hybrid system in case of SHD-1 than in the case of PSUD. Nevertheless, the values of Si/N (as measured at a distance of *ca.* 4 nm from the surface) for PSUD (0.742) and corresponding SHD-1 (1.786) were much higher than the value calculated from the hybrid polymer composition (0.529). Similar effect, namely the selective concentration of silicone on the surface of cured coatings, was observed by authors of [15] in the case of epoxy-acrylic/polyorganosiloxane system. More detailed information on surface properties of the SHD-1 and PSUD coatings will be published soon [13].

The results of detailed investigations of another hybrid polymer dispersion system (SHD-2) that can be considered potentially useful for coating applications presented below will provide some other interesting data on the role of acrylic part of silicone-containing hybrid polymer constituting dispersion particles in the process of formation of coating microstructure.

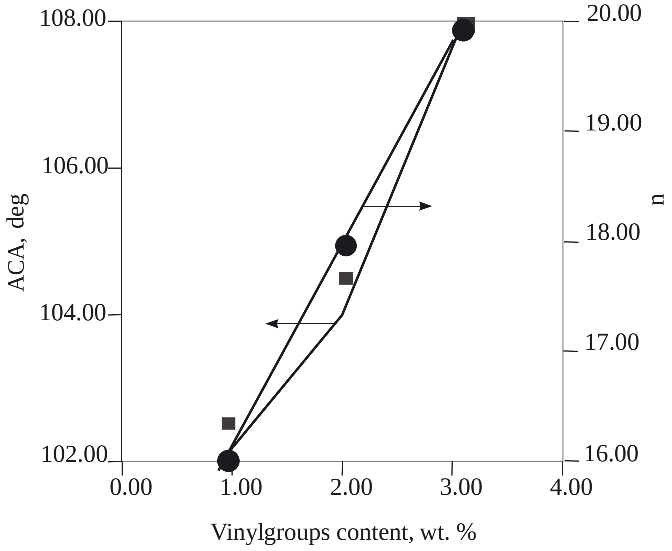


Fig. 3. Effect of functional vinyl groups content on freezing cycles number (n, ●) and dynamic contact angle (ACA, ■) of coatings prepared from SHD-2

SHD-2 type of silicone-containing hybrid dispersions and coatings

The properties of selected samples of SHD-2 are presented in Table 3. Based on these results it is clear that the properties of SHD-2 dispersion systems synthesised by emulsion polymerization of silicones in commercially available acrylic copolymer dispersions (ACD) are acceptable from the point of view of their potential applications in the area of protection of porous building materials. As it can be noticed from the results described below, the effect of crosslinking density depending on the functional groups content and crosslinking process parameters on the surface properties of coating materials prepared from SHD-2 is evident.

Effect of the functional groups content on dynamic contact angle (DCA) of coatings and freezing resistance of limestone treated with SHD-2 was studied for the system containing Si-CH=CH$_2$ functional groups (Fig. 3). The increased content of functional groups is responsible for the increased values of DCA and freezing cycles number what is connected with higher crosslinking density giving better immobilization of the surface nanolayer structure leading to the observed hydrophobic properties and better weathering resistance.

Wettability of coatings received from SHD-2 was studied based on DCA measurements and surface free energy (SFE) calculations performed using computer programme available in the software package supplied

Table 3. Properties of selected samples of SHD-2 dispersions

Sample	Organic modifier content, wt. %	pH	Average particle size, nm	Particle size distribution	Zeta potential mV	Dispersion stability, min	MFFT
SHD-2A 12	11.5	6.5	82	68—109	-37.5	90	-0.5
SHD-2B 15	11.5	6.5	85	72—98	-41.6	105	-1.0
SHD-2C 3	8.5	6.7	108	92—135	-21.2	75	-1.0
SHD-2C 11	8.5	6.7	83	75—105	-24.1	90	-0.5
SHD-2D 4	9.5	6.7	78	60—149	-25.6	90	+0.5
SHD-2D 10	9.5	6.7	84	82—91	-41.8	105	-1.0

by the apparatus manufacturer. The values of measured and calculated wettability parameters are presented in Table 4. The highest values of advancing and receding contact angles (ACA and RCA) were observed for coatings containing polyolefin (PO, polyethylene wax) as non-silicone containing organic modifier (NSCOM, SHD-2A). Moreover, the DCA hysteresis calculated for this sample based on ACA and RCA values was significantly lower as compared with values obtained for other tested samples (SHD-2B, SHD-2C) as well as for silicon-PTFE coating (SHF) and pure silicone coating (SRC). It indicates that the surface roughness of SHD-2A is lower as compared with other samples.

Table 4. Wettability parameters of coatings obtained from SHD-2, SHF and SRC dispersions (for detailed explanation see text)

Parameter	Sample				
	SHF	SHD-2A	SHD-2B	SHD-2C	SRC
NSCOM content and type, wt. %	20 PTFE	8.5 PO	6.5 PTFE	6.5 PO	0
Dynamic contact angle:					
ACA (water), deg	103.0	109.0	97.0	108.0	92.1
RCA (water), deg	88.9	105.8	87.5	100.2	83.9
DCA hysteresis, deg	14.1	3.2	9.5	7.8	8.2
Surface free energy (SFE)					
— total, mN/m	19.90	19.10	21.8	19.80	22.00
— polar, mN/m	8.75	7.64	12.96	10.89	17.16
— dispersion, mN/m	11.15	11.46	8.84	8.91	4.84
— dispersion/ polar component ratio	1.27	1.50	0.68	0.82	0.28

Surface morphology of the coatings prepared from SHD-2 was investigated by the AFM technique. Changing of the grain shape from cylindrical for pure silicone resin (sample SRC) to regular spherical for sample SHF containing 20 wt. % of PTFE as NSCOM and to regular grain structure for sample SHD-2A containing 8.5 wt. % of PO as NSCOM was noted. The size of structural elements in SHD-2 was significantly lower then that of pure silicone resin and PTFE [16]. It suggests that silicone and acrylic copolymer containing polymer matrices present in SHD-2 form a new differently structured hybrid polymer system as compared with that based on silicone resin and PTFE.

The chemical composition of surface nanolayer of silicone-containing polymer matrices was determined at various sampling depths, *i.e.* at 2.1 nm, 6.1 nm and 12.0 nm, using the ESCA/XPS method. The difference between the content of F and C atoms in the surface nanolayer and in the bulk was observed. The regular morphology of SHD-2A coating surface can be considered as a key point in achieving the best wettability parameters measured for this sample.

The best result of soiling test was determined also for the same sample — SHD-2A. This result is in very good coincidence with the parameters responsible for the surface properties: ACA ratio of dispersion/polar component of SFE, surface roughness R_a and enrichment of the surface nanolayer with F + C atoms. Figure 4 illustrates for instance good coincidence of anitisoil properties with ACA. The effects of SFE dispersion/polar component ratio of SFE and R_a value on soiling test results for tested samples were more significant than the effect of the enrichment of the surface layer with F and C atoms. Moreover, the water vapour permeability of treated limestone samples was not decreased as compared with non treated samples. Weathering resistance based on freezing cycles was better as compared with the samples treated with pure silicone resin. It can suggest that the role of uniform, tightly packed surface morphology of coatings formed by silicone-containing polymer matrix is more important for macro-scale surface properties than chemical composition of the surface nanolayer. It seems that this effect can be ascribed to the formation of so-called composite surface [17, 18]. Low contact angle hysteresis for such composite surfaces can be achieved only when texture of the surface is very regular. The effect of surface chemical composition on DCA values is significantly lower.

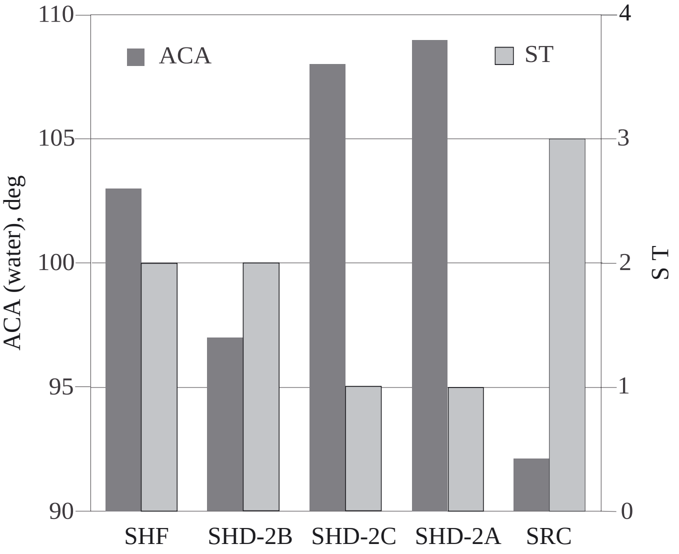


Fig. 4. Effect of surface properties on antisoiling properties of coatings obtained from SHD-2 on the example ACA vs. soiling test (ST)

CONCLUSIONS

The results presented in this paper clearly proved that novel silicone-containing hybrid dispersion systems were developed that could be used to produce coatings of very interesting properties. Type I hybrid dispersions (SHD-1) synthesized *via* polymerization of acrylic/styrene monomers in poly(siloxaneurethaneurea) dispersions designed to be used for coatings on metal or wood formed coatings of properties depending on content of unsaturated bonds in the silicone-urethane part of the hybrid. Additional oxidative curing led to excellent hardness and solvent resistance of coatings. Silicone content in the hybrid was found to affect the coating properties in a complex way what could be attributed to drastic change in coating microstructure at certain silicone content resulting from dramatic change in compatibility of the whole hybrid system. Further investigations of surface properties of the coatings using dynamic contact angle (DCA) determinations and ESCA/XPS proved that a complex relationship existed between acrylic/styrene part of the hybrid and silicone part of the hybrid and that the introduction of new component (acrylic/styrene part) to already complex hybrid polymer poly(siloxaneurethaneurea) resulted in diminishing compatibility of the system.

The advantages of coatings designed for porous building materials obtained from Type II hybrid dispersions (SHD-2) prepared *via* polymerization of silicone monomers in acrylic copolymer dispersions observed in this study over those produced from acrylic copolymer dispersions were the consequence of their ability to crosslink *in situ* after treatment of substrate. Due to the fact that the crosslinking reactions through several reactive groups are possible, the design of coating system tailored for various substrates can be proposed. Moreover, the inclusion of non-silicone containing organic modifier (PTFE or polyolefine for example) in silicon-containing hybrid system is very important from the point of view of proper protection of building materials. The selection of an organic modifier may be critical to the surface properties of these coatings as well as to water vapour permeability being the key parameter in protection of building materials.

The results of this study suggested that future work on silicone-containing hybrid polymer dispersions should be focused on design of architecture of other types of silicone-containing hybrid systems characterized by more homogeneous distribution of organic and silicone part of the system in hybrid polymer matrix what would be advantageous from the coating application point of view. More detailed studies on relationships between the chemical composition of the polymers constituting the hybrid system and micro (or rather nano-scale) architecture of hybrid dispersion particles and of the coatings formed by such hybrid dispersions, and on the effect of such relationships on the macro-scale properties of the coatings are also needed.

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