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Self-Crosslinking Dispersions Based on Core-Shell Nanoparticles

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Aqueous dispersions of amino functionalized latex particles, which can undergo crosslinking reactions during film formation, are described. Precursor polyvinyl formamide-polystyrene butadiene (P-VFA-SB)-core-shell latex particles were prepared by a seeded emulsion polymerization. In this process, various amounts of P-VFA chains were attached to the surface of the SB latex particles by a grafting-onto process. The P-VFA-SB-core-shell latex particles showed excellent film-forming properties, such as high transparency and filmhardness. As these films were completely redispersible in water, a self-crosslinking system was developed. Partial hydrolysis of the formamide groups of the P-VFA chains allowed for the introduction of amino functions on the particles. The addition of diacrylates crosslinked the particles during film formation by a Michael addition reaction resulting in transparent, water insoluble films with good mechanical stability.

Keywords: self-crosslinking dispersions; core shell; grafting onto; emulsion

1 Introduction

Dispersions of particles with a core-shell morphology are used in a variety of applications (1) such as paints, coatings, active electronic and optical elements (2). The synthesis of core-shell polymer dispersions is usually a two-step emulsion polymerization via seeded latices with two separate polymerization steps (3). Different ways of addition of the second monomer, such as a continuous addition (drop-wise method) and batch process (swelling method) have been used to form the shell (4). Due to ecological demands, these processes are mainly performed in aqueous dispersions (5–12). Ambient cure waterborne systems have been widely investigated due to the superior properties of the materials in high performance applications such as storage stability and exceptional film properties e.g. hardness, scratch and also water and alcohol resistance (6).

In recent years endeavors to create self-crosslinking coatings based on aqueous systems have increased. Most are based on core-shell structures that contain reactive groups on the surface. The core-shell structure provides unique film forming characteristics and increased mechanical performance of the films obtained from the dispersion. Functional groups on the surface can afford a latex particle with unique

properties such as improved colloidal stability, modified rheological behavior, as well as better adhesion to a given substrate (7, 8). For example, Lee et al. reported particles, prepared by emulsion polymerization, containing oxazoline and carboxylic reactive groups. In these systems, film-forming and homogeneous crosslinking were observed at moderate temperatures (9). In a different approach, self-crosslinking of aqueous latex dispersions functionalized with epoxy and amino groups has been investigated (8). These emulsions are used as binders in ambient cure primers for aircraft and for industrial maintenance coating (8). The main disadvantage of these systems are the allergic potential of the functional groups on the surface (13). In another approach, Feng et al. reported the formation and crosslinking of latex films by the reaction of acetoacetoxy groups with diamines under ambient conditions. However, the continuous hydrolysis of the acetoacetoxy function, as a reverse Claisen condensation, limits industrial applications (10).

Research on self crosslinking latices has focused on alkoxy-silane functional acrylic latices to increase the weather and water resistance of polyacrylic and poly(acrylic-co-styrene) emulsion coatings (11, 12). In this concept, latex films containing alkoxy-silane functional groups were crosslinked under ambient conditions (pH > 7) by siloxane formation during the drying process (11, 12). However, these systems require complicated syntheses. The development of a suitable water-based self-crosslinking dispersion is still a challenge.

The present work reports the preparation and characterization of a new generation of core-shell particles based on a poly(styrene-co-butadiene) core and a polyvinylformamide

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shell by emulsion polymerization. The film-forming properties of the obtained dispersions are investigated e.g. by mechanical measurements and DSC analysis. As the films are redispersible in water, the formamide groups are partially hydrolyzed to amino groups, and then the nanoparticles cross-linked via Michael addition. This results in a very hard, non-redispersible latex film with a very high transparency.

2 Experimental

Deionized water was used in all experiments. N-Vinylformamide (VFA) from BASF-AG was vacuum distilled prior to use [60°C (10⁻² bar)] and stored at -20°C. 2,2'-Azobis-isobutyric acid amidindichloride V-50 (Fluka), Lithium chloride (Fluka), Tetraethylglycolediacylate (Sigma-Aldrich), sodium hydroxide (WTL Laborbedarf GmbH) and Polyvinylamine (BASF-AG), sec-Butylamine (Aldrich) and D₂O (Deutero GmbH) were used without further purification. ¹H-NMR-studies were recorded on a Bruker DPX 250; the strain-stress curves were measured by a Instron 6022.

2.1 Characterization of the SB-latices

Two styrene-co-butadiene-dispersions (BASF-AG, Ludwigshafen) with a solids content of 51.3 wt% (SB_I-Latex) and 50.3 wt% (SB_{II}-Latex) were used as seeded latices in the emulsion polymerization. Both latex dispersions were characterized by dynamic light scattering and elemental analysis (see Table 1). Photon correlation spectroscopy performed on a Malvern Zetasizer 4000 yielded monodisperse distributions with 161 nm and 160 nm as the z-average value for the particle size.

2.2 Grafting of VFA on SB-latex Particles

2.2.1 Batch Polymerization (Method I)

The mixtures to prepare the grafted SB-VFA-latices are shown in Table 2. Lithium chloride was dissolved in deionized water. VFA and the SB-Latex dispersion were added to the salt solution. The dispersion was heated to 75°C and

degassed by nitrogen for 45 min. Injection of a solution of V-50 started the polymerization. The resulting dispersions (Scheme 1) were analyzed by dynamic light scattering (Malvern Zetasizer 4000). The dispersions were purified by membrane filtration (cut off limit of the membrane 50000 g/mol).

2.2.2 SB-VFA-latex Particles by the Continuous Process (method II)

The lithium chloride was dissolved in deionized water and the SB-latex dispersion was added to the salt solution. The latex dispersion was heated to 75°C. VFA and V-50 as initiator was dissolved in deionized water. In both solutions, oxygen was removed by bubbling nitrogen through the mixtures for 45 min. The monomer/initiator solution was continuously added with a defined dosing speed to the latex dispersion. The composition of different by prepared SB-VFA-latex particles is shown in Table 3.

2.2.3 Preparation of non-crosslinked Films with SB-VFA-dispersions

For the preparation of the non-crosslinked films, the SB-VFA dispersions were poured on glass plates and dried at room temperature for 2 h and finally under vacuum for 6 h.

2.2.4 Procedure of Crosslinked Films/one Dispersion System

30% of the VFA units on the P-VFA-SB- Latex particles were hydrolyzed by adding the corresponding amount of powdered sodium hydroxide (Table 4). The obtained dispersion was purified by membrane filtration. The solids content was gravimetrically determined to 16.5 wt%. To perform the cross-linking reaction, different amounts of TEGDA were added to the hydrolyzed SB-VFA dispersion. The mixtures were homogenized in a high speed stirrer. To obtain the crosslinked films the mixtures were poured on glass plates and dried at 60°C and under vacuum for 4 h.

2.3 Two Dispersion System

2.3.1 Surface Modification of SB-Particles with Tetraethyleneglycol Diacrylate (TEGDA)

Sodium hydroxide was powdered and dried under vacuum. An exact amount of sodium hydroxide was dissolved in water and slowly given to a mixture of the SB-VFA-dispersion and the corresponding amount of TEGDA (Table 5). The mixtures were heated up to 50°C and stirred for 20 h to complete the addition reaction.

2.3.2 Crosslinking of the Films/system Based on Two-dispersions

P-VFA grafted SB-VFA Dispersions were used as Dispersion A in the film-forming processes. Defined amounts of powdered sodium hydroxide were dissolved in 0.5 g water and added to the surface modified SB-VFA-TEGDA

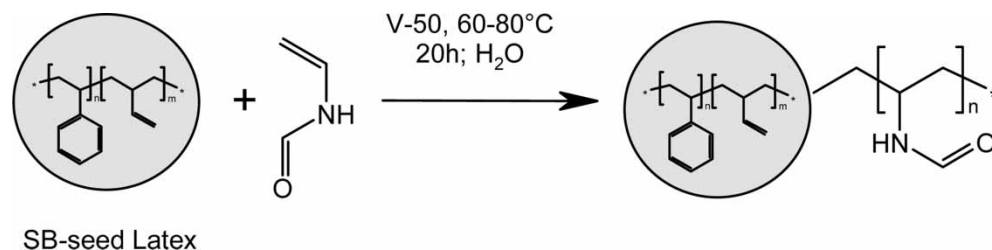
Table 1. SB-latex-dispersions; composition and analytical results

	SB _I -Latex	SB _{II} -Latex
Styrene	76%	66%
Butadiene	20%	30%
Ionic. emulsifier	4%	4%
wt% _{polymer}	50.51	50.7
\bar{M}/nm	161	160.5
PDI	0.03	0.01
%C	88.04	86.41
%H	8.93	8.95
%N	/	0.28

Table 2. Seeded emulsion polymerizations according to method I and results of dynamic light scattering

Experiment	VFA/g	SB-Latex		V-50/ mmol	LiCl/ mmol	Solids content wt%	M_z /nm	PDI	VFA/ wt%	VFA/wt% by elemental analysis
		ID	/g							
P-VFA-SB _I -1	0	I	4.6	0.4	1.2	13.5	160	0.05	0.0	0.96
P-VFA-SB _I -2	0.9	I	4.8	0.4	1.2	15.8	180	0.12	15.9	16.59
P-VFA-SB _I -3	1.6	I	4.9	0.4	1.2	17.6	250	0.13	24.2	24.4
P-VFA-SB _I -4	1.9	I	4.9	0.4	1.2	18.6	260	0.17	27.8	27.6
P-VFA-SB _I -5	3.0	I	5.1	0.4	1.2	21.3	220	0.12	36.6	36.9
P-VFA-SB _I -6	3.4	I	5.2	0.4	1.2	21.4	240	0.28	39.3	39.0
P-VFA-SB _I -Mixture-1	0.5	I	2.9	—	1.2	15.7	— ^a	—	14.9	18.4
P-VFA-SB _I -Mixture-2	1.0	I	3.4	—	1.2	18.1	— ^a	—	23.0	25.5
P-VFA-SB _I -Mixture-3	1.5	I	3.8	—	1.2	19.1	— ^a	—	28.7	27.4
P-VFA-SB _I -Mixture-4	2.6	I	4.9	—	1.2	21.3	— ^a	—	35.3	35.6
P-VFA-SB _I -Mixture-5	3.0	I	5.21	—	1.3	21.8	—	—	36.6	40.2
P-VFA-SB _{II} -7	4.2	II	14.5	1.8	4	20.0	220	0.12	22.4	21.6
P-VFA-SB _{II} -10	10.4	II	29.2	1.4	17	15.9	240	0.28	26.2	28.2

^aDispersions showed agglomerations.



Sch. 1. General synthesis of grafted SB-VFA-latexes.

dispersion (Dispersion B). For the film-forming reactions, both dispersions were mixed and homogenized (Table 6). Within 30 min, the mixtures were poured on glass plates and dried at room temperature and finally under vacuum for 4 h.

2.3.3 Polymerization of VFA with Various Initiator Concentrations

VFA was dissolved in water and heated up to 80°C. Oxygen was removed by bubbling nitrogen for 45 min through the mixture. V-50 as initiator was dissolved in deionized water and injected into the monomer solution. The viscosity of the polymer solution was determined by an Ubbelohde viscosimeter at 25°C (Table 7).

3 Results and Discussion

The aim of this work is to create new latex particles with improved film-forming properties. The mechanical stability of latex films is mainly governed by the interaction between the different polymerchains in the film (3). If the particles are very stiff, e.g. in highly crosslinked polystyrene beads, the connection between them is very weak as an entanglement between the polymer chains is not possible. This can be improved by surrounding the beads with a flexible shell, typically butylacrylate (2). Such a dispersion is still redispersable in water and the films are very flexible with low scratch resistance, so a further enhancement of the interaction between the particles is required. This will be addressed by a physical crosslinking of particles via hydrogen-bonding of surface attached amide functions and also by chemical crosslinking. As such a system could be industrially applicable, commercially available polybutadiene-polystyrene latex particles were chosen as starting material for the synthesis of new core-shell structures by grafting of polyvinylformamide to the surface.

3.1 Grafting of Vinylformamide to Poly-(styrene-co-butadiene) Particles

For the synthesis of the core-shell particles, with a poly-(styrene-co-butadiene) (SB) core and a grafted polyvinylformamide shell, the emulsion polymerization techniques

known as continuous dropwise method and swelling/batch method were used (4). For the batch process, different amounts of SB-particles and vinylformamide (VFA) were mixed and homogenized. After a swelling period of 5 h, the polymerization was initiated by injection of the initiator and heating to 70°C. In the continuous process, VFA and the initiator solution were added with different dosing speeds to a dispersion of poly-(styrene-co-butadiene) particles at 70°C and directly polymerized.

3.2 Characterization of the Grafted Latex Particles

In order to prove the grafting process and the formation of an additional shell, the size distribution of the original SB-latexes (SB_I and SB_{II}, see Tables 1 and 3 Experimental section) and of the grafted P-VFA-SB-core-shell latexes (PVFA-SB-9 dispersion) were measured.

Figure 1 shows a comparison of the hydrodynamic radius of the starting SB-core particles and the P-VFA-SB_{II}-9-Latexes obtained via a continuous polymerization process. The increase of the particle size from 160 to 220 nm indicates that grafting had occurred. These results were confirmed by Scanning Electron Microscopy (SEM). Comparing the images of the starting SB_I particles (Figure 2) with the purified P-VFA-SB_I-7 core-shell latex particles (Figure 3) demonstrates an increase in the particle diameter, up to 240 nm.

P-VFA-SB dispersions before and after purification by membrane filtration (cut off limit of the membrane: 50000 g/mol) showed a nitrogen recovery rate between 90% and 95%, even after dialysis. As dissolved P-VFA chains in solution would be removed by the filtration process, this proved that the P-VFA content remained quantitatively on the surface of the SB latex particles to form the expected core-shell structure. The high P-VFA content indicates that either the yield of grafting was very high or strong adsorption on the surface of grafted SB beads had occurred.

To distinguish between adsorbed and grafted-P-VFA on the SB particles, purification by ultracentrifugation (25000 rpm) was performed. After sedimentation of the beads, the serum containing the non-grafted P-VFA was separated and the solid freeze-dried. The nitrogen content in the solid was determined by elemental analysis to calculate the amount of grafted P-VFA. The crude material was subsequently redispersed again in water by ultrasonification

Table 3. Seeded emulsion polymerizations according to method II

Experiment	VFA/ g	SB-latex/ g	V-50/ mmol	LiCl/ mol%	Dosing speed/ ml * h ⁻¹	M _z /nm	PDI	Solids content/ wt%	VFA/ wt% calc.	SB/wt% calc.	VFA/wt% by elemental analysis
P-VFA-SB _{II} -8	9,5	29,1	1.8	6.0	70 ^a	305	0.35	20.3	24.6	75.4	24,6
P-VFA-SB _{II} -9	10	29,1	1.4	11.6	70 ^a	290	0.40	15.8	25.6	74.4	27,70
P-VFA-SB _{II} -11	10	29,1	1.4	11.7	30.4	290	0.40	15.8	25.6	74.4	27,4
P-VFA-SB _{II} -12	10,4	29,1	1.4	12.1	10.1	280	0.23	16.9	26.2	73.8	26,7
P-VFA-SB _{II} -13	10,2	29,1	1.4	12.0	50.7	375	0.7	16.9	25.9	74.1	27,6
P-VFA-SB _{II} -14	10,2	29,2	0.1	18.2	30.4	295	0.3	15.9	25.9	74.1	25,9
P-VFA-SB _{II} -15	20,6	58,6	0.2	12.6	30.4	475	0.56	15.8	26.0	73.9	27,1
P-VFA-SB _{II} -16	20,4	58,3	0.3	12.3	30.4	609	0.74	15.8	25.9	74.1	26,9

^aCalculated dosing speed.

Table 4. One dispersion system partially hydrolyzed P-VFA-SB_{II}-8-core-shell system crosslinked by TEGDA

P-VFA-SB _{II} -8*	P-VFA-SB _{II} -8 particles/mg	mmol P-VFA in particles	mmol TEGDA	Ratio TEGDA/P-VFA/%	Ratio TEGDA/PVAm/%	Dried/°C
30% hydrolyzed	1650	5.72	0.077	1.4	4,5	60
30% hydrolyzed	1650	5.72	0.300	5.2	17,5	60
30% hydrolyzed	1650	5.72	0.442	7.7	25,8	60

Table 5. Dispersions used in the two-dispersion system

Dispersion A	P-VFA-SB _{II} -10	P-VFA-SB _{II} -14	P-VFA-SB _{II} -15
wt% P-VFA in particles	26.2	25.9	26.1
wt% SB Latex in particles	73.8	74.1	73.9
solid content of dispersion/wt%	15.9	15.9	15.8
calculated degree of PVFA hydrolysis	100%	100%	100%
Dispersion B			
<i>TEGDA modified dispersion</i>	10-TEGDA	14-TEGDA	15-TEGDA
wt% P-VFA in particles	13.8	12.3	12.3
wt% SB Latex in particles	38.7	35.2	34.9
wt% TEGDA in particles	47.5	52.5	52.8
solids content of dispersion/wt%	21.8	23.5	27

and the purification process repeated until the nitrogen content of the solid remained constant.

In both the batch and continuous polymerization processes, the nitrogen content dramatically decreased during the first five cleaning procedures and became constant with an average P-VFA content of 15 to 20 wt% of the initial amount (Figure 4). The batch and continuous polymerization techniques provided nearly the same amount of grafted P-VFA chains. This indicated that

most of the P-VFA is non-covalently attached to the surface. In comparison to the grafting of P-VFA on pure polystyrene, where only 2 wt% of the obtained P-VFA are covalently bonded, the yield is high (14). This suggests that the grafting process mainly proceeds by a copolymerization of VFA with the free double bonds in the polybutadiene moieties in the SB particles. As the non-bonded P-VFA could not be removed by dialysis, the high affinity of P-VFA to the SB-latex particles was

Table 6. Film formation by the two dispersion system

	Amount particle A/mg	mmol P-VFA in particle A	Amount particles B/g (TEGDA compound)	mmol TEGDA in particle B	Ratio TEGDA/P-VFA _{initial} /%	Ratio TEGDA/PVAm/%	Dried/°C
P-VFA-SB _{II} -10							
2.2% hydrolyzed	797	2.94	46	0.07	2.5	108	RT
4.5% hydrolyzed	805	2.97	87	0.14	4.6	105	RT
7% hydrolyzed	796	2.93	112	0.18	6.0	88	RT
10% hydrolyzed	795	2.93	156	0.24	8.3	82	RT
20% hydrolyzed	796	2.93	375	0.59	20.1	100	RT
43% hydrolyzed	795	2.93	780	1.23	41.8	98	RT
86% hydrolyzed	797	2.94	1560	2.45	83.4	97	RT
P-VFA-SB _{II} -15							
2.5% hydrolyzed	1583	5.81	88	0.15	2.6	103	RT & 60°C
5% hydrolyzed	1581	5.81	165	0.29	5.0	100	RT & 60°C
7.5% hydrolyzed	1581	5.81	253	0.44	7.6	101	RT & 60°C
10% hydrolyzed	1584	5.82	334	0.58	10.0	100	RT & 60°C

Table 7. Polymerization of VFA with various initiator concentrations

	VFA/g	VFA/mol/l	Solvent/g	V-50/ mg	V-50/ mmol/l	Solids Content wt%	Viscosity/ mm ² /s
P-VFA-1	2.50	1.53	22.51	380	61.14	10	180
P-VFA-2	2.53	1.55	22.51	190	30.47	10	250
P-VFA-3	2.51	1.53	22.51	76	12.18	10	640
P-VFA-4	2.51	1.54	22.50	38	6.16	10	1300
P-VFA-5	2.50	1.53	22.56	19	3.03	10	4375

demonstrated. One possible explanation might be that the chains that are covalently attached to the surface act as anchor groups for the free P-VFA chains and the adsorption process is assisted via hydrogen bonding.

3.3 Preparation and Testing of Non-crosslinked P-VFA-SB Films

To investigate the film-forming properties of VFA-SB core-shell latices, a known amount of the VFA-dispersions is placed on glass plates and dried at room temperature for 2 h and then 6 h under vacuum. This drying process guaranteed a slow evaporation of the solvent to avoid the formation of bubbles in the film, and allowed for the preparation of homogeneous films. The variation of P-VFA content in the grafted dispersions influenced the transparency and hardness of the films (Figure 5). SB-core-P-VFA-shell dispersions (P-VFA-SB_I-1 to 2) with less than 24 wt% of P-VFA, afforded inhomogeneous and turbid films. These films were brittle and could be easily removed from the surface. When the P-VFA content exceeded 24wt% (P-VFA-SB_I-3 to 4), the films became transparent, and the hardness increased with the amount of incorporated P-VFA. This effect can be explained by

the strong hydrogen bonding interaction between the amide hydrogen and the formyl group (Figure 6).

Excellent film-forming properties were only observed in the core-shell systems, whereas films of mixtures of SB Latices and homo P-VFA (obtained by BASF, Mn = 12000 g/mol) exhibited a very low transparency and hardness. Only the use of P-VFA concentrations of more than 35 wt% in the mixture allowed for the preparation of films with a similar transparency as observed for the core-shell systems. This indicates that without the attachment of the P-VFA chains to the particles, a strong phase separation between the hydrophilic and hydrophobic chains occurred resulting in phase separation in the films.

3.3.1 Mechanical Properties

The influence of the grafted P-VFA chains on the mechanical properties of the films are measured by recording stress-strain curves of the polymer films at room temperature (Figures 7 and 8). To control the mechanical stability of the films, the chain length of the grafted P-VFA-chains was varied. Model experiments were used to show that the molecular weights of P-VFA increase with lower initiator concentration, as indicated by higher inherent viscosities (see experimental part). To increase the chain length of P-VFA, 0.07 mol% (P-VFA-SB_{II}-15) and 0.1 mol% (P-VFA-SB_{II}-16) of the

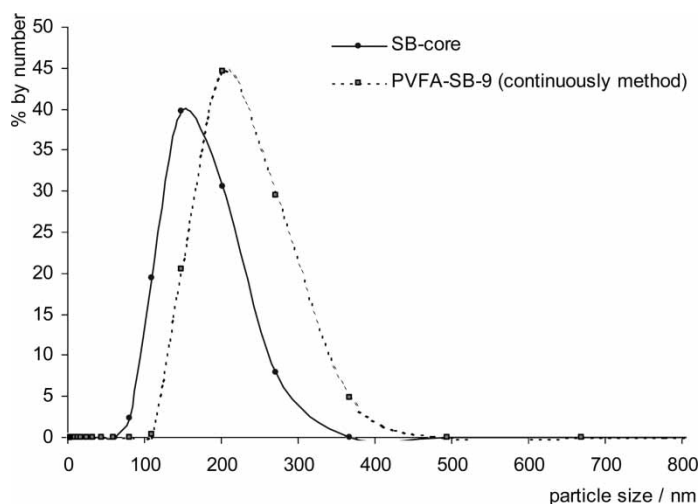


Fig. 1. Particle size distribution of VFA- grafted and original SB_{II}-Latices measured by dynamic light scattering (Θ angle = 90° at 25°C).

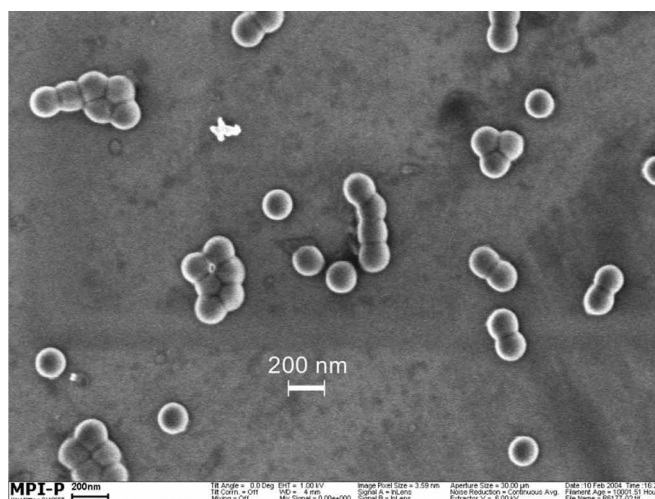


Fig. 2. SEM photomicrograph of SB_I-seed particles.

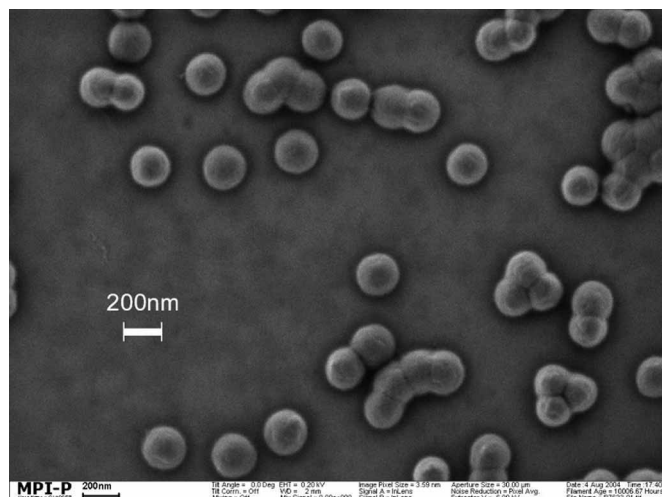


Fig. 3. SEM photomicrograph of Grafted P-VFA-SB₁₋₇ core-shell particles.

initiator were added during the grafting process as opposed to 1 mol% initiator, as used in P-VFA-SB₁₋₅. The P-VFA contents in P-VFA-SB₁₁₋₁₆ dispersions were a constant 26 wt%, with a solids content of 15.8 wt%. All measurements of the films of the grafted particles demonstrated a typical rubber elasticity behavior, as initially the stress increased linearly with the strain (Figure 7).

This effect is attributed to a better entanglement of the long P-VFA chains, resulting in an enhanced interaction between the particles. A more profound effect on the mechanical properties of the films was observed when the content of P-VFA in the core-shell-particles increased from 26 to 39 wt%. A viscoelastic deformation process was observed at 35 MPa

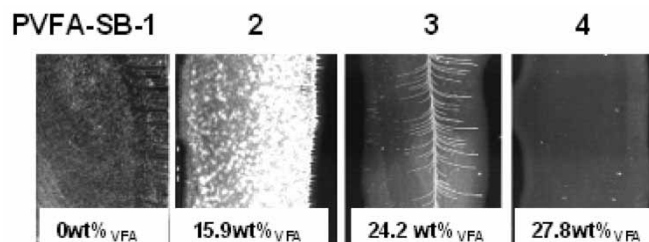


Fig. 5. P-VFA-SB films (P-VFA-SB₁₋₁ to 4) with increasing P-VFA content and transparency from the left to the right dried at RT and finally under vacuum at 60°C.

for an elongation of $\lambda = 1.125$. In comparison to other core-shell structures, e.g. butylacrylate-styrene based dispersions where only a tensile strength of 1–5 MPa was observed (6), and also to the previous systems with lower P-VFA content, a very high mechanical stability was found. This again reflects the strong intermolecular interaction of the polymer chains due to the hydrogen bonds between the formamide groups in the P-VFA-SB core-shell lattices. The high mechanical stability makes the material promising for the use in abrasion resistant coatings.

When comparing the results of the different systems, two effects have to be considered. The mechanical stability of the films can be directly correlated to the amount of grafted P-VFA. By increasing the VFA content from 24 wt% to almost 40 wt% an order of magnitude higher mechanical stability is achieved. The elongation at break of the films was much lower, showing the improved hardness of the films. By increasing the chain length the mechanical stability goes up. As explanation in both cases, an improved interaction between the P-VFA shells can be assumed, either

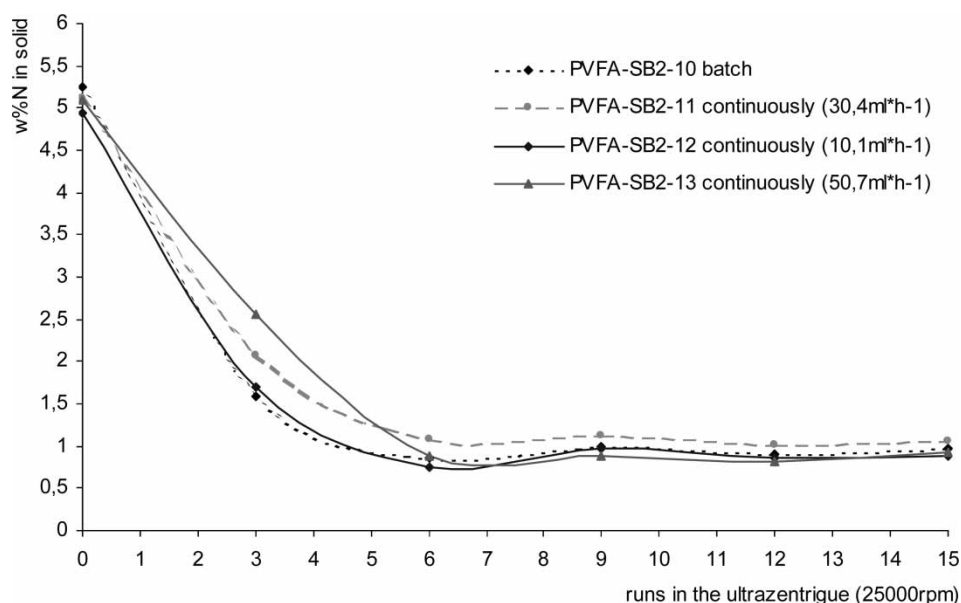


Fig. 4. Nitrogen content in the dispersions after ultracentrifuge (25000 rpm).

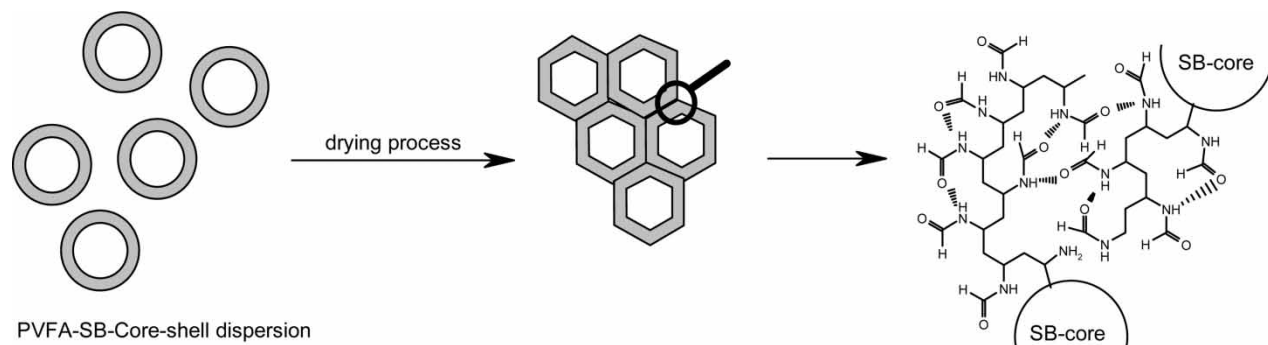


Fig. 6. Schematic illustration of the film-forming process of PVFA-SB-core-shell particles.

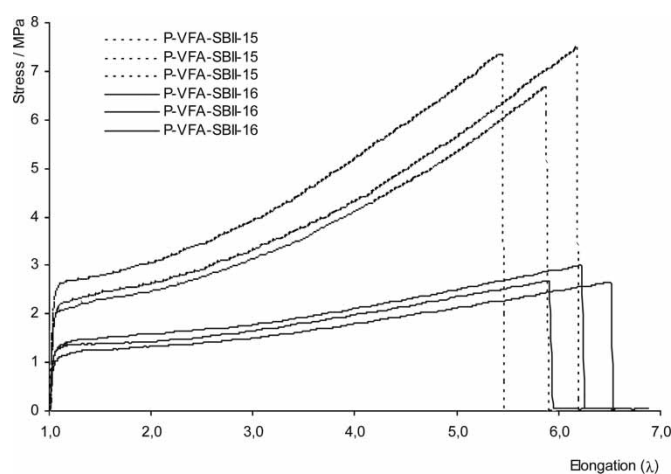


Fig. 7. Stress-strain curves of P-VFA-SB-15/16 dispersions (non-crosslinked), measured at tensile direction with 10 mm/min at room temperature in a range from 0 to 100 N.

by a higher content or by longer chains, resulting in better entanglement. However, a major drawback of the films was observed when testing the water resistance of the films by immersing the films in water for 12 h, as each film was redispersible in water. This limits the usefulness of P-VFA-SB latex particles to non aqueous applications. To solve the problem of redispersion in water, chemical crosslinking of the beads during film formation was investigated.

3.4 Crosslinked P-VFA-SB Films (One Dispersion System)

To develop a system for the crosslinking of P-VFA-SB nanoparticles, several requirements have to be considered. The crosslinking process should not occur during the storage of the dispersion, but relatively fast during film formation. The crosslinking process should be possible at room temperature, as additional heating of the films should be avoided. The process should also form a stable network that does not permit redispersion. In particular, in the presence of polar

solvents (H_2O , alcohol) the films should be inert or swell only slightly.

In light of these restrictions, a new crosslinking system for P-VFA-SB core-shell latex particles is presented. It is based on a Michael addition using diacrylates as biselectrophiles. Such an approach requires free amino groups on the surface of the nanoparticles, which can easily be generated by partial hydrolysis of the P-VFA chains under basic conditions. The addition of tetraethyleneglycol diacrylate (TEGDA) to the dispersion should result in a crosslinking reaction between the amino-functionalized P-VFA-SB latices (Scheme 2), and TEGDA during film formation.

To study the applicability of the proposed concept, a model reaction of 1-aminobutane and TEGDA as “crosslinking” agent, with D_2O as the solvent was first performed in a NMR tube. The amine concentration for the mixture was calculated with 10% excess to assure a complete conversion of TEGDA. After addition of the amine, the 1H -NMR spectrum demonstrated that the signals of the vinyl group of TEGDA at 6.2 ppm disappeared and a new resonance at 2.9 ppm, attributed to the newly formed N- CH_2 group, appeared after 10 min. This illustrated that the Michael addition between the diacrylate and an aliphatic amine proceeded fast at room temperature and therefore is suitable as the designed crosslinking reaction during a film-forming process.

To transfer this concept to the P-VFA functionalized latex particles, a dispersion with 20 wt% solids content and 25 wt% of grafted P-VFA per particle, synthesized by the batch polymerization method (P-VFA-SB_{II}-8), was partially hydrolyzed (30% of the P-VFA content) by addition of a defined amount powdered sodium hydroxide according to literature procedures (15–17). The exact amount of free amino groups could not be determined by 1H -NMR spectroscopy, as the spectra were broad due to the solids content. Elemental analysis could not provide exact information about the content of free amino groups, due to the limited accuracy of this method. It is known from the literature that the hydrolysis of the P-VFA can be controlled by addition of the required amount of sodium hydroxide (15). The content of amino groups is estimated by the amount of added NaOH. To

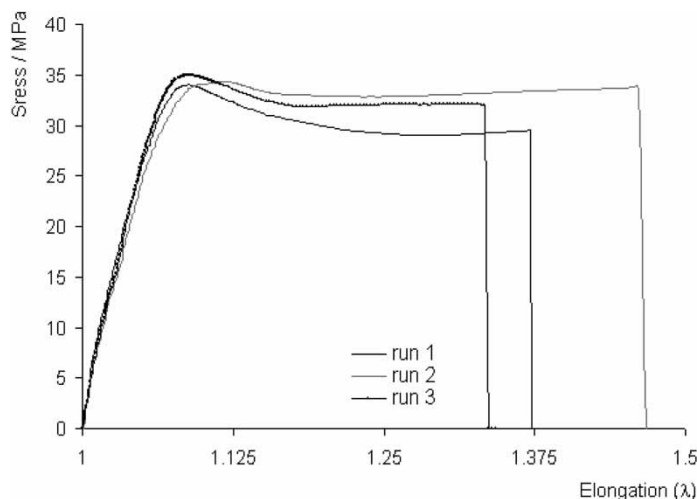


Fig. 8. Stress-strain curves of P-VFA-SB_I-5 latices containing 39 wt% P-VFA. Measured at tensile direction with 10 nm/min at room temperature in a range from 0 to 100 N.

remove sodium formiate from the dispersions the hydrolyzed dispersion was purified by membrane filtration (Cut off limit of the membrane: 50000 g/mol). To the partially hydrolyzed P-VFA-SB_{II}-8 dispersion, an equivalent amount of TEGDA was added prior to film formation.

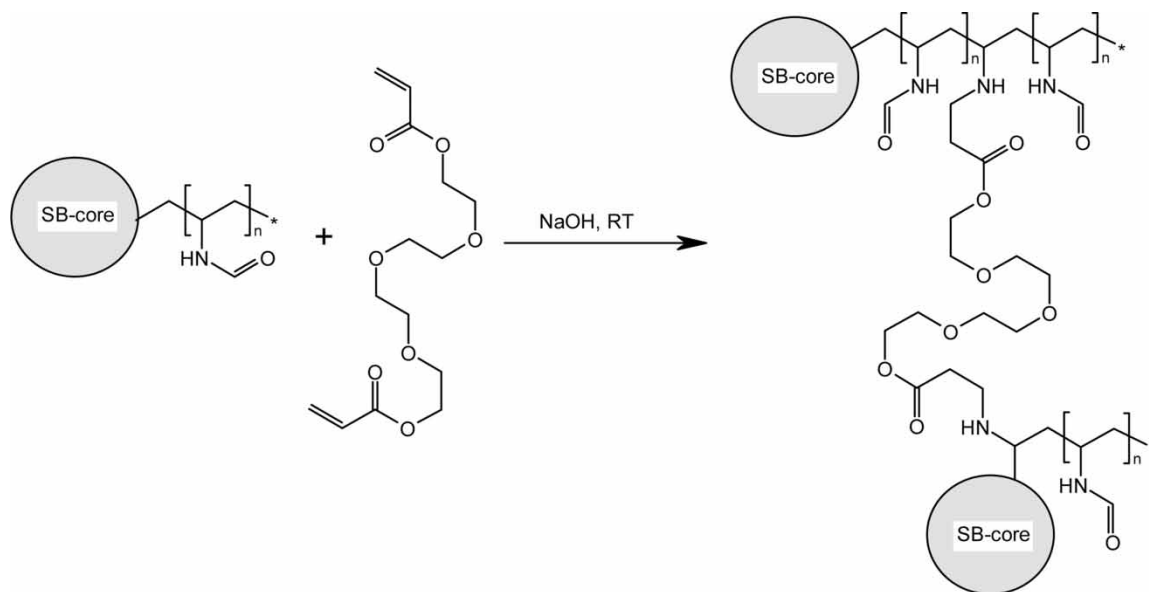
The degree of crosslinking, calculated by the ratio of TEGDA versus P-VFA (Table 8), was varied from 0% (Blind sample) to 7.5%, with addition of varying amounts of TEGDA to the P-VFA-SB_{II}-8 dispersion. Highly transparent films of this dispersion were prepared on glass plates and slowly dried at room temperature to avoid the formation of bubbles. To complete the evaporation of the water the drying process was finalized by applying a vacuum for 4 h at 60°C.

The water resistance of the films was tested, by treating them in water overnight. The blind sample film (0% cross-linked) was partially redispersed after one day and completely redispersed after five additional days. In contrast, all other samples containing the TEGDA crosslinker did not redisperse, but became turbid due to swelling. This indicated that the crosslinking reaction was performed successfully. However investigations of the mechanical stability showed that the wet films were destroyed by touching and that the scratch resistance of the films decreased with increasing crosslinker content. Furthermore, dispersions mixed with TEGDA were not stable, as a few days after preparation a partial precipitation was observed. The limited mechanical stability indicated that the crosslinking density is very low. It is assumed that the crosslinker mainly reacted within a single chain and not between different chains of different particles. Furthermore, unreacted TEGDA might have acted as plasticizer in the latex films.

3.5 Crosslinked P-VFA-SB-films (Two Dispersion System)

As the mechanical stability and the storage lifetime of the P-VFA-SB-Core-shell system crosslinked by Michael addition with TEGDA are unsatisfying, a two dispersion system was developed. Dispersion-A of this system was a standard P-VFA-SB core-shell dispersion as described above after the grafting polymerization process. Dispersion-B, was the completely hydrolyzed P-VFA-SB core-shell latex surface modified with TEGDA (Scheme 3).

The unhydrolyzed particles were mixed with excess TEGDA and slowly hydrolyzed. This guaranteed that during the hydrolysis, an excess of crosslinker is always present and favoring the mono addition of the diacrylate. The surface modified P-VFA-SB latex dispersions were



Sch. 2. Self crosslinking reaction by a Michael-addition.

Table 8. Systems of partially hydrolyzed P-VFA-SB_{II}-8-core-shell dispersion crosslinked by TEGDA

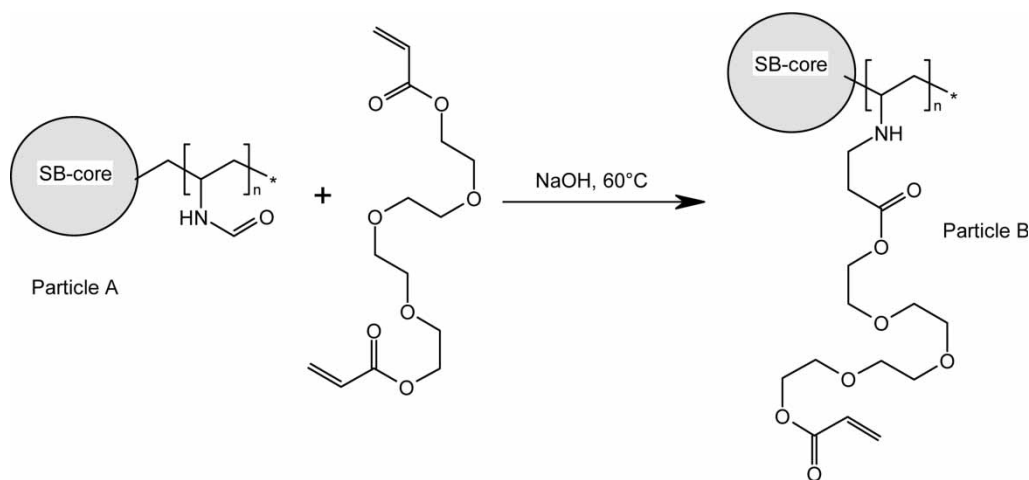
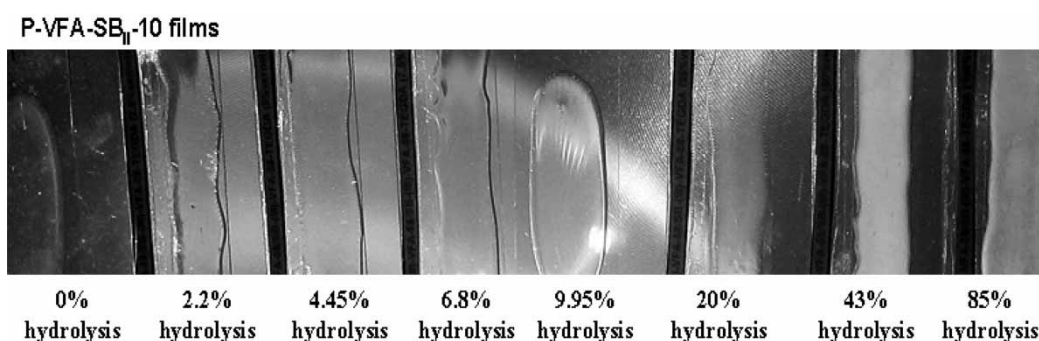
P-VFA-SB _{II} -8 ^a	P-VFA-SB _{II} -8 particles/mg	Initial mmol P-VFA in the particles/g	mmol TEGDA/g particles	Ratio TEGDA/P-VFA/%	Ratio TEGDA/PVAm/%
30% hydrolyzed ^a	1650	3.47	0.047	1.4	4,5
30% hydrolyzed ^a	1650	3.47	0.182	5.2	17,5
30% hydrolyzed ^a	1650	3.47	0.268	7.7	25,8

^aContents calculated by the amount of NaOH used for hydrolysis.

stable over long periods and could be used as a crosslinker agent for Dispersion-A.

For film formation a calculated amount of sodium hydroxide was added to Dispersion-B. By mixing the two dispersions, the formamide in Dispersion-A was partially hydrolyzed due to the NaOH in Dispersion-B. The amino groups react with the TEGDA surface modified P-VFA-SB dispersions to crosslink the system by a Michael addition during the drying process. Films with different degrees of crosslinking were synthesized by mixing defined amounts of the two dispersions.

Up to 10% hydrolysis the films were transparent (Figure 9). If the degree of hydrolyzed formamide groups in Dispersion-A exceeded 20%, the films became cloudy. Furthermore, the hardness of the films decreased with increasing degree of hydrolysis. It is assumed that at higher degrees of (P-VFA-SB_I-1 to 2) a phase separation of the two types of particles occurred, which resulted in inhomogeneous films. All films were insoluble in water, and redispersion was not observed. The addition of 2% of the crosslinking particles resulted in water stable films. All films lost their transparency when treated with water, but became clear after drying.

**Sch. 3.** P-VFA-SB-Latex surface modification with TEGDA.**Fig. 9.** Partially hydrolyzed P-VFA-SB_{II}-10 films crosslinked with TEGDA surface modified P-VFA-SB latices (two dispersion system), dried at RT. (2 h) and under vacuum (4 h).

The mechanical stability of the films obtained from this two-dispersion system was improved in comparison to the previous system. The films were self-supporting and could easily be removed from the glass plates.

Remarkably, the mechanical stability of the films was higher when a lower content of the crosslinker (Dispersion-B) was used. Comparing systems containing 2.5 wt% and 10 wt% of crosslinking particles, the 2.5 wt% film required a higher stress for the same elongation. The glass transition temperature of the crosslinked films decreased with increasing the crosslinker content (Table 9). From these results, it was concluded that the P-FA-SB-latex particles modified with TEGDA in the films acted as plasticizer agents. By heating the films up to 60°C, a further improvement of the mechanical stability was observed in all cases. This was attributed to a higher degree of crosslinking between the nanoparticles, facilitated by the higher mobility of the grafted chains at elevated temperature. In all cases the stress-strain (elongation) measurements (Figure 10) of the samples resulted in a rubber elastic behavior, typical for crosslinked materials.

In contrast to the bisfunctional TEGDA, the use of multifunctional crosslinkers, such as the TEGDA functionalized latex particles at low concentrations, resulted in non-redispersible latex films. A water-based self-crosslinking system was thus obtained, which does not require heating for the curing process. Water stable films with good mechanical stability can be prepared at room temperature.

4 Conclusions

The use of SB-latex particles containing reactive double bonds allowed for the easy grafting of polar monomers to create the target core-shell structures. Polyvinylformamide-shell-(polystyrene-co-butadiene)-core latices particles were thus prepared and their film-forming properties investigated. Depending on the P-VFA content, P-VFA-SB-core-shell latex produces films with excellent transparency and hardness. Increasing the P-VFA content in the P-VFA-SB-core-shell latex particles improved the mechanical stability of the films. This was attributed to strong hydrogen bonding between the P-VFA chains on the surface of the particles. However, this type of film exhibited no water resistance and was completely redispersible. To overcome this

Table 9. DSC and TGA results of P-VFA-SB_{II}-15 films

P-VFA-SB _{II} -15	Glass transition temperature/°C	Pyrolysis/°C
unhydrolyzed	95	425
2.5% hydrolyzed	17	420
5% hydrolyzed	14.5	410
7.5% hydrolyzed	10.5	420
10% hydrolyzed	18	415

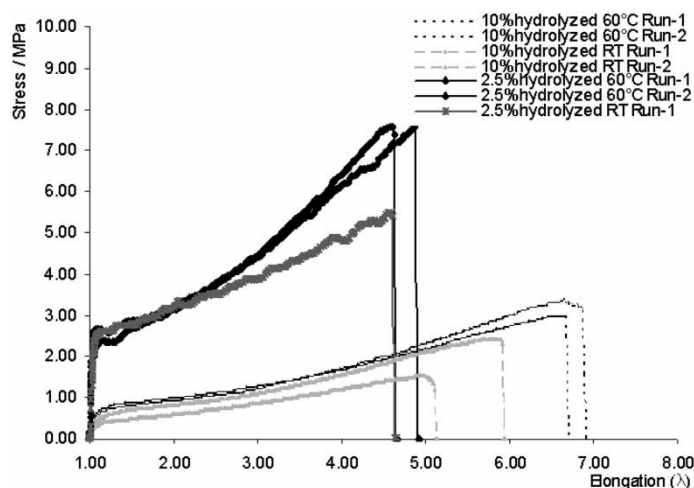


Figure 10. Stress strain curves of crosslinked P-VFA-SB_{II}-15-core-shell latices films (two compound system). Measured at tensile direction with 10 nm/min at room temperature in a range of 100 N.

problem, which would hamper the use of this material in industrial applications, a procedure for crosslinking P-VFA-SB core-shell latex particles during film formation was developed. The crosslinking reaction utilizing the Michael addition of a partially hydrolyzed P-VFA with tetraethyleneglycol diacrylate was introduced. In this case the effect of crosslinking on the film properties was weak due to intra-particle Michael addition and the TEGDA became a plasticizer in the films. To improve the film properties a multifunctional crosslinker based on a latex particle was developed. Mixtures of partially hydrolyzed P-VFA-SB-core-shell latex particles and a modified P-VFA-SB-core-shell latex containing acrylate functions on the surface as crosslinker yielded water resistant and mechanically stable films. The Michael addition thus proved to be a versatile way for creating crosslinked films of water-based dispersions. The crosslinking reaction did not require the addition of an activator or thermal treatment, and room temperature water-stable films were accessible. This approach offers the possibility, by varying the ratio of the components, to tune the mechanical and optical properties over a wide range and to create stable networks from readily low cost commercially available materials.

5 Acknowledgement

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6 References

1. Černáková, L., Chrástová, V. and Volfová, P. (2005) *J. Macromol. Sci., Part A, Pure and Appl. Chem.*, **42**(4), 427–439.

2. Nachrichten aus der Chemie u. *Technik*; Vol. 49, 3, 2000.
3. Schellenberg, C., Tauer, K. and Antonietti, M. (2000) *Macromol Symp.*, **151**(1), 465–471.
4. Okubo, M., Yamada, A. and Matsumoto, T. (1980) *J. Polym. Sci.: Part A, Polym. Chem.*, **18**, 3219.
5. Overbeek, A., Brückmann, F., Martin, E., Steenwinkel, P. and Annable, T. (2003) *Progress in Organic Coatings*, **48**(2–4), 125–139.
6. Esser, R.J., Devona, J.E. and Setzke, D.E. (1999) *Progress in Organic Coatings*, **36**(1–2), 45–52.
7. Pichot, C. (1990) *Makromol. Chem., Macromol. Symp.*, **35/36**, 327.
8. Gardon, J.L. (1997) ACS Symposium Series, **663**, 27.
9. Lee, D.I. (2005) *Polymer*, **46**(4), 1287–1293.
10. Feng, J., Pham, H., Macdonald, P. and Winnik, M.A. (1998) *J. Coat. Tech.*, **70**(881), 57–68.
11. Castelvetro, V., De Vita, C., Giannini, G. and Malvaldi, M. (2005) *Macromol. Symp.*, **226**(1), 289–302.
12. Guo, T.Y., Xi, C., Hao, G.J., Song, M. and Zhang, B.H. (2005) *Adv. Polymer Techn.*, **24**(4), 288–295.
13. Cahill, J., Keegel, T., Dharmage, S., Nugriaty, D. and Nixon, R. (2005) *Contact Dermatitis*, **52**(3), 147–153.
14. Naegele, D. and Raether, B. BASF AG private communication.
15. Gu, L., Zhu, S. and Hrymak, A.N. (2002) *J. Appl. Polym. Sci.*, **86**(13), 3412–3419.
16. Yamamoto, K., Imamura, Y., Nagatomo, E., Serizawa, T., Muraoka, Y. and Akashi, M. (2003) *J. Appl. Polym. Sci.*, **89**(5), 1277–1283.
17. Badesso, R.J., Nordquist, A.F., Pinschmidt, R.K. and Sagl, D.J. (1996) *Advances in Chemistry Series*, **248**, 489–504.