

Maleic Anhydride Based Copolymer Dispersions for Surface Modification of Polar Substrates

I. D. Gunbas,¹ M. E. L. Wouters,² M. M. R. M. Hendrix,³ R. A. T. M. van Benthem,^{3,4}
C. E. Koning,¹ B. A. J. Noordover¹

¹Laboratory of Polymer Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

²TNO, 5600 HE Eindhoven, The Netherlands

³Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

⁴DSM Ahead, 6160 MD Geleen, The Netherlands

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ABSTRACT: In this article, we report the modification of poly(styrene-*alt*-maleic anhydride) (PSMA) with monofunctional amine-terminated poly(dimethyl siloxane) (PDMS-NH₂) by thermal imidization, followed by the preparation and characterization of a surfactant-free artificial latex thereof and application of this latex onto cotton fabric. The imidization reaction was monitored by NMR and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. 1,2-Cyclohexyldicarboxylic anhydride was chosen as a model compound for the PSMA copolymer; this allowed a more detailed characterization by NMR and ATR-FTIR spectroscopy. After the PSMA/PDMS-NH₂ imidization reached completion, a fraction of the anhydrides were ammonolyzed. In this way, a self-emulsifying latex with an average particle diameter of approximately 145 nm and a ζ potential of -56 mV was obtained. It was found that the PDMS-modified PSMA latex in which 30

mol% of the initial amount of anhydride groups were previously imidized by using PDMS-NH₂ and a fraction of the anhydrides were ammonolyzed with 0.3 eq. of NH₃ (PSMA30) was stable in the pH range 4–10. The water contact angle values of the latex-coated cotton textile fabric indicated a hydrophobized surface, with a static contact angle of $135.7^\circ \pm 1.2^\circ$. The washing studies with a standard soap solution of the cotton samples with or without crosslinker showed that the crosslinked PSMA30 offered a good coating durability to the cotton. This waterborne resin based on surfactant-free latices displayed promising properties for coating applications and seemed to be very suitable for the hydrophobization of polar surfaces. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1745–1757, 2012

Key words: coatings; copolymers; latices; polysiloxanes; surface modification

INTRODUCTION

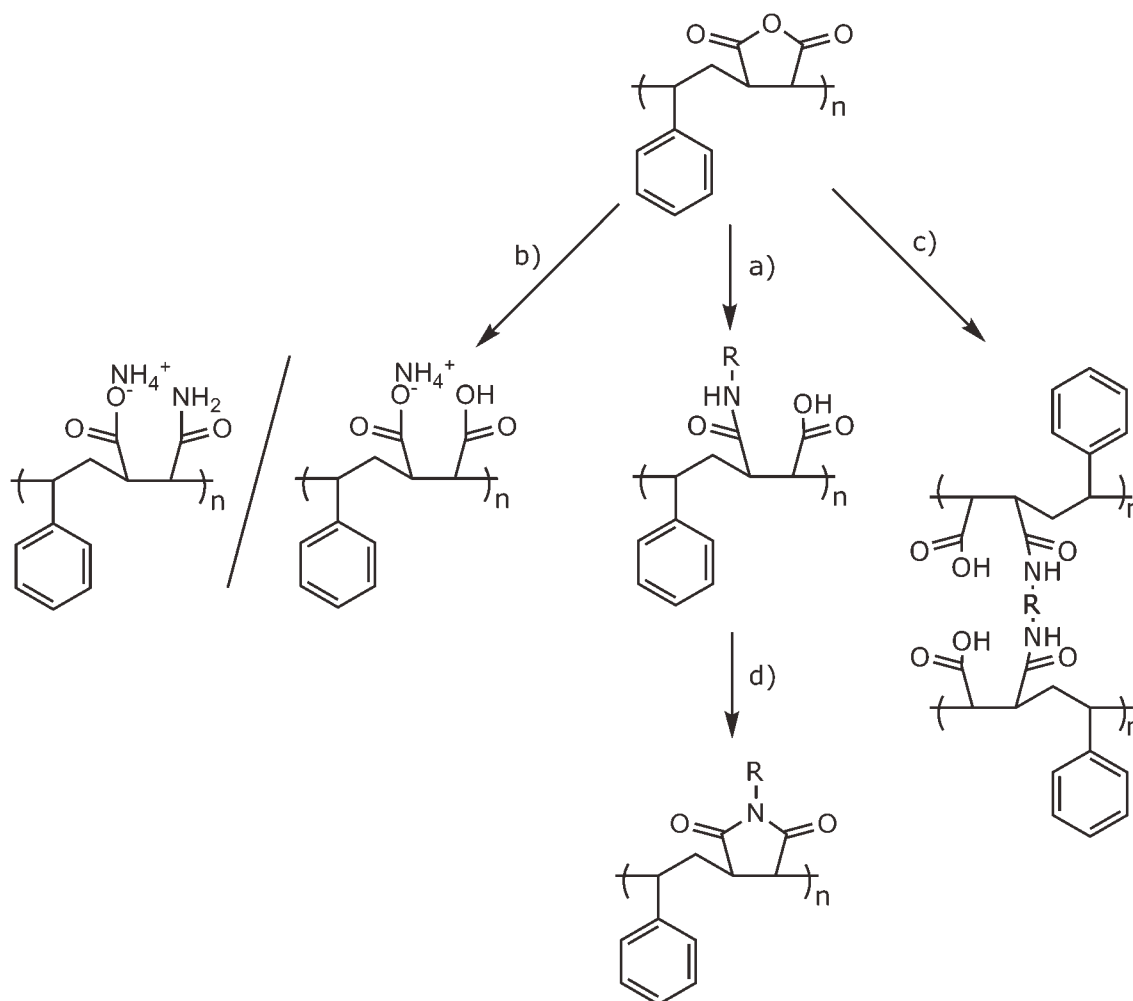
For many applications of polymeric materials, their surface properties are very important. The chemical modification of polymer surfaces can be applied to control the adhesion, wettability, and biocompatibility as important surface properties of interest for a variety of applications. Flame treatment, corona discharge treatment, plasma modification, and surface grafting are some of the practical approaches to polymer surface modification.^{1–3} Unfortunately, these techniques do not result in chemically well-defined and lasting/stable surfaces, which in view of the demanding requirements, should be carefully designed and prepared.

Poly(styrene-*alt*-maleic anhydride)s (PSMAs) have excellent properties, including a high thermal stability, tunable solubility, and adjustable compatibility when blending with styrenic polymers and polar polymers is desired.^{4–6} The large number of anhydride groups in the alternating PSMA copolymer offers the possibility for interaction with polar groups, such as -OH and -NH₂, present on all kinds of polar surfaces; this is expected to give good adhesion to the surface of interest. Moreover, the carboxylic acids from hydrolyzed anhydrides may be neutralized or ammonolyzed with ammonia; this results in a self-emulsifying polymer in water. The anhydride groups also offer the possibility to make such alternating PSMA copolymers much more hydrophobic by modification with nonpolar, amine-terminated molecules;^{7–10} this would make the material less sensitive to hydrolysis. After partial chemical modification, the remaining anhydride groups can, in addition to providing adhesion to polar surfaces, be used for crosslinking with, for example, diamines,^{11,12} to make the coating solvent-resistant. Soer and coworkers^{13,14} described the modification of PSMA with *n*-heptylamine, its ammonolysis, and its crosslinking reactions with diamines or dihydrazides (Scheme 1).

Additional Supporting Information may be found in the online version of this article.

Correspondence to: B. A. J. Noordover (b.a.j.noordover@tue.nl).

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Scheme 1 Schematic representation of the different possible reactions involving the cyclic anhydride units of the alternating PSMA copolymer:¹³ (a) primary amine, (b) $\text{NH}_3/\text{H}_2\text{O}$, (c) diamine (or dihydrazide), and (d) heat.

Our approach was to tune the surface properties or, more specifically, increase the surface hydrophobicity by coating polar substrates with water-based, alternating maleic anhydride copolymers chemically modified with monofunctional, amine-terminated poly(dimethyl siloxane) (PDMS- NH_2) instead of *n*-heptylamine.

Poly(dimethyl siloxane) (PDMS) is an important inorganic polymer, as PDMS and PDMS-based materials are attractive for a variety of industrial applications because of their unique properties, including good thermal stability in air and a wide temperature range of usability.¹⁵ It has a high chain flexibility, excellent thermal and oxidative stabilities, high gas permeability, and biocompatibility, and in various fields, it is extensively used as a functional polymeric material.^{16–18} PDMS was used in textile water-repellency treatment because of its low surface energy and its high hydrophobicity.^{19–21} However, PDMS has poor adhesion to the textile surfaces²² and, accordingly, can easily be removed by cleaning or washing procedures. Many researchers have reported the introduction of PDMS into polymer materials to improve their flexibility

and to provide a linkage of PDMS to the textile surface.^{23–28} Also, several kinds of copolyimides containing PDMS in their polymer backbone (polysiloxane-*block*-polyimides) have been reported.^{29,30}

Our aim was to graft PDMS onto the polymer main chain of PSMA by imidization. This grafting resulted in a novel randomly partially modified PSMA copolymer with hydrophobic properties, which could be used to make a self-emulsifying latex by partial ammonolysis of the remaining anhydride groups with ammonia. The resulting self-emulsifying latex still had functional groups available for adhesion to polar substrates and for cross-linking, so it could be used as a curable, waterborne coating resin. With such coatings, materials such as wood and cotton could be made hydrophobic.

EXPERIMENTAL

Chemicals

All materials were purchased from Sigma-Aldrich Co. (St. Louis, MO, US) and were used as received,

unless noted otherwise. Solvents were purchased from Biosolve (Valkenswaard, The Netherlands) and were used without further purification. SMA1000F, which was synthesized by standard free-radical techniques (PSMA; styrene/maleic anhydride (MAN) molar ratio: 1 : 1), was kindly provided by Sartomer (Paris, France) (number-average molecular weight = 2650 g/mol). PDMS-NH₂ was purchased from Gelest (Boston, US) (number-average molecular weight = 800–1100 g/mol). Ammonia solution (25 wt % in water) was purchased from Merck (Darmstadt, Germany). Deuterated chloroform was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, US) 1,2-Cyclohexyldicarboxylic anhydride (CDA) was purchased from Acros (Geel, Belgium) and was dried at 120°C before use. Cotton fabric was purchased from a local fabric store. Adipic dihydrazide (ADH) was kindly supplied by DSM NeoResins (Zwolle, The Netherlands) and was used without purification.

Imidization of PSMA and CDA

To convert a random fraction of the anhydride groups (30 mol %) of PSMA into imides, a two-step reaction was performed. The first step was the addition of an amine to a PSMA solution to obtain the corresponding polyamic acids. The second step led to the ring closure of the amic acid groups to form the corresponding imide groups. A tetrahydrofuran solution (40 mL) containing 7.5 g of PDMS-NH₂ was added dropwise to a solution of 5 g of PSMA in tetrahydrofuran at room temperature. This was left to stir for 30 min at room temperature; this was followed by the removal of the solvent at 40°C in a rotary evaporator. The dry material was then put into a vacuum oven at 150°C for 20 h to convert the amic acids into imide residues; this yielded 12.3 g of partially imidized PSMA (PSMA30).

The imidization reaction was also performed with a model compound. CDA (1 mmol) was weighed into a 25-mL, standard round-bottom flask. PDMS-NH₂ (1 mol equiv) was added rapidly (1 mmol). CDA changed into a tacky mass, which rapidly reacted exothermically to give the solid amic acid. Heat was required to obtain the homogenized amic acid product. The mixture was stirred and heated gently to approximately 150°C for 4 h. The flask was connected directly to the vacuum distillation head and was heated further for complete removal of all imidization water and low boiling components under 1–2 mmHg of pressure.

Self-emulsification

First, 0.76 g of ammonia (25 wt % in water) was added to 25 mL of acetone at room temperature. The ammonia solution was then added dropwise to a so-

lution of 7.5 g of PSMA30 (30 mol % of the initial amount of anhydride groups was previously imidized with PDMS-NH₂) dissolved in 125 mL of acetone at room temperature and left to stir for 0.5 h. This mixture was then added dropwise to 75 mL of water under vigorous stirring and the application of a nitrogen flow to evaporate the acetone. This resulted in dispersions with a solid content of 10 wt %. As the stirring speed influenced the particle size of the latex, the same stirring speed (400 rpm) was used in all of the experiments. Higher solid contents (up to 30 wt %) could easily be reached by the evaporation of water, without changes in the other properties of the latex, such as the particle size distribution and stability. For the crosslinking, ADH, a water-soluble crosslinker, was added to these latices at room temperature. Dynamic light scattering experiments and ζ -potential measurements were performed with a Malvern Zeta-Sizer Nano ZS (Worcestershire, UK) at 20°C. The particle size and the distribution thereof were determined according to ISO 13321 (1996). The concentration of the latex samples was 0.1 wt %, unless stated otherwise. All samples were measured three times to obtain an average value. The pH-dependence measurements of size and ζ potential were performed by the addition of a 0.071 mol/L HNO₃ aqueous solution to the latex with a Malvern MPT-2 Autotitrator, with at the pH of the dispersions started as prepared. The pH value was lowered by 0.5 before the next ζ potential and particle size determination until it reached pH 2, and the base titration was performed by the addition of 0.1 mol/L aqueous NaOH solution to the latex, with the pH increased in steps of 0.5 until a pH of 10 was reached. The ζ potential was calculated from the electrophoretic mobility (μ) with the Smoluchowski equation:

$$\zeta = \eta\mu/\varepsilon$$

where $\kappa a \gg 1$ and where η is the solution viscosity, ε is the dielectric constant of the medium, and κ and a are the Debye-Hückel parameter and the particle radius, respectively.

Characterization of the imidized model compound and the partially imidized PSMA

¹H-NMR measurements were performed at room temperature in CDCl₃ on a Varian Mercury 400 or Varian Gemini 300 spectrometer (Santa Clara, US). Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Bio-Rad Excalibur FTS3000MX infrared spectrometer (Philadelphia, US) (60 scans per spectrum, resolution = 4 cm⁻¹) with an attenuated total reflection (ATR) diamond unit (Golden Gate). The measurement was performed by the application of a DMSO-*d*₆ solution

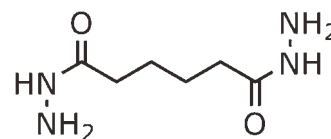
of the material, which was described in the Experimental part, on the ATR diamond. A full spectrum was taken every minute to monitor the amic acid formation at room temperature or every 30 min for monitoring the imide formation at 150°C. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA instrument (Etten-Leur, The Netherlands) in a nitrogen atmosphere. Samples were heated from 50 to 800°C with a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was carried out on a TA Instruments Advanced Q1000 calorimeter. The samples were heated from -150 to 180°C at a rate of 10°C/min followed by an isothermal step for 5 min. A cooling cycle to -150°C at a rate of 10°C/min was performed before a second heating run to 180°C at 10°C/min. The glass-transition temperature (T_g) was determined from the second heating run. Elemental analysis was performed on a CN analyzer (TruSpec CHN analyzer, Michigan, US).

Quantitative monitoring of the imidization with ATR-FTIR spectroscopy

The peak areas of the imide carbonyl peak at 1710 cm^{-1} were taken as a measure of the extent of the reaction. The peak at 2860 cm^{-1} , originating from the C-H stretching of CDA, was taken as a reference for the model compound measurements, whereas the signal arising from the aromatic ring of the styrenic unit at 700 cm^{-1} was used as an internal standard for calculating the percentage imidization of PSMA.

Surface coating of the cotton fabrics

Pieces of cotton 4 × 4 cm^2 were cleaned with water and ethanol to remove possible impurities and then dried in an oven at 50°C. The cotton fabric was coated with (1) a PSMA latex in which a fraction of the anhydrides were ammonolyzed with 0.3 equiv of NH_3 and (2) a PSMA30 latex in which 30 mol % of the anhydrides were imidized with PDMS-NH₂ and a fraction of the anhydrides were ammonolyzed with 0.3 equiv of NH_3 . Coating was performed by immersion of the fabric in the latices for 15 min at room temperature followed by drying at 120°C for 10 min. The same procedure was repeated for the PSMA and PSMA30 latices, which contained a crosslinker, ADH (Scheme 2). The amount of crosslinker, ADH, added to latices was 20 mol % with respect to the initial amount of anhydride groups present in the polymer (the amine functionality of the crosslinker was 2). The contact angles were measured with deionized water on a Dataphysics OCA 30 instrument (Filderstadt, Germany) at room temperature (~ 21°C). All contact angles were determined 60 s after a water droplet of



Scheme 2 Chemical structure of ADH.

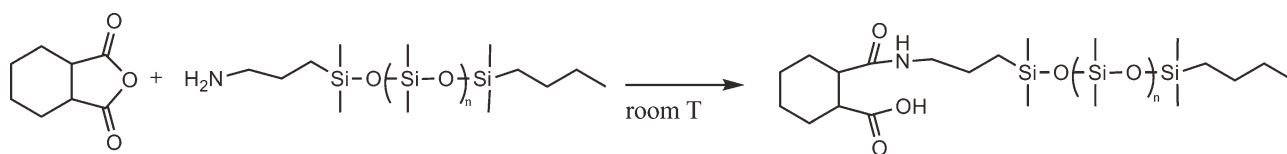
5 μL was placed on the cotton substrate. The contact angles were taken as an average of three to four different measurements at different positions on the same sample. Moreover, the contact angle measurements were done on the bottom and on the top of the coated cotton samples, and the same contact angle values were obtained on both sides in all cases. Scanning electron microscopy (SEM) images of the cotton samples were taken with an FEI Quanta 3D FEG (Eindhoven, The Netherlands). Atomic force microscopy (AFM) experiments on the uncoated and coated cotton pieces were performed on a NT/MDT Solver P47HT (Eindhoven, The Netherlands), with a scanning rate of 0.2 Hz, in semicontact mode under atmospheric conditions with high-resolution, noncontact, gold-coated silicon cantilevers from the NSG11 series (NTI-Europe, Eindhoven, The Netherlands) with a spring constant of 2.5–10 N/m and a typical resonance frequency of 150 kHz.

Washing procedure

For the washing procedure, the ECE soap A (non-phosphate reference detergent without optical brightener) was used. Some glass beads were added to a round-bottom flask to mimic the mechanical interaction of a washing machine. Approximately 50 mL of soap solution (4 g/L, pH 10.7) was used to wash the cotton fabric, and separate round-bottom flasks were used for each type of coating formulation, namely, PSMA and PSMA30 with and without crosslinker. After a piece of a cotton sample was placed in a round-bottom flask with the soap solution, the solution was stirred to allow the soap to interact with the fabric over a time of 20 min. The same procedure was repeated with clean water three times (the rinsing step) for a period of 15 min per rinsing step, and fresh water was added in each rinsing step. After the pieces of cotton were rinsed with fresh water, they were placed in an oven at 120°C for 10 min for drying. Then, the static contact angles measurements and SEM analysis were performed.

RESULTS AND DISCUSSION

The imidization reaction, which is the reaction between an anhydride and an amine to obtain an imide, has been described extensively in literature.^{31,32} A similar approach to obtain an imide was used in this article and is shown in Schemes 3 and 4. Imide



Scheme 3 Ring-opening reaction of CDA with PDMS-NH₂.

formation of the model compound consisted of two steps, as described in the literature and theory.³² The first step was the formation of the so-called amic acid at room temperature immediately after the addition of the amine to the anhydride. The second step was the conversion of the amic acid into the corresponding imide with elimination of water at 150°C. To confirm this reaction by both NMR and ATR-FTIR spectroscopy, the model compound CDA was used. The reason we chose the model compound for NMR and ATR-FTIR characterization was that the overlapping of peaks in both the ¹H-NMR and ¹³C-NMR spectra for PSMA and the imidized PSMA copolymers prevented a straightforward quantitative analysis.^{33–35}

Imidization of CDA with PDMS-NH₂

The conversion of an anhydride into an amic acid was performed with the model compound CDA with PDMS-NH₂ in bulk, as described in the Experimental section. This reaction is given in Scheme 3. The ¹H-NMR spectrum of PDMS-NH₂ is given in Figure 1(a).

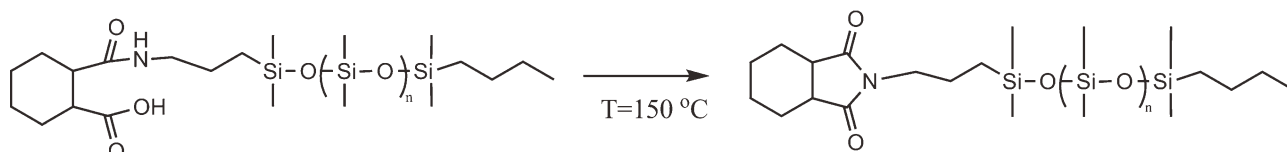
As shown in the ¹H-NMR spectrum of PDMS-NH₂ [Fig. 1(a)], the protons arising from the methyl carbon (H_a) gave rise to a triplet at 0.90 ppm, whereas the protons of the methylene carbon (H_c) attached to silicon resonate at 0.55 ppm. Of particular interest in the ¹H-NMR spectrum were the protons associated with the methyl group attached to silicon (H_d): they showed a large upfield peak at 0.1 ppm. Although methylene protons (H_b) were observed at 1.30 ppm, the resonances associated with H_e protons appeared at 1.45 ppm. The signals assigned to H_e protons, adjacent to the amine, were found at 2.65 ppm. In addition, the observed peaks at 2.20 and 3.70 ppm could be ascribed to a residual ethoxide peak originating from the synthesis of the material. The ¹H-NMR spectrum of the amic acid product obtained after 45 min of reaction at room temperature is given in Figure 1(b). The formation of the corresponding ring-opened product was evidenced by the appearance of a new peak at 3.25 ppm, which was attributed to the meth-

ylene (H_e) signal next to the amide. After the reaction at room temperature, the fully ring-opened CDA with PDMS-NH₂ was obtained. After the ring-opening reaction at room temperature, the reaction mixture was heated to 150°C. The ring closure or the imidization reaction of the amic acid based on CDA and PDMS-NH₂ is given in Scheme 4. The ¹H-NMR spectrum of the reaction product obtained after 240 min at 150°C is given in Figure 1(c).

The occurrence of the imidization was proven by the appearance of a new peak at 3.45 ppm, which was ascribed to H_e protons, connected to the carbon atom adjacent to the imide. Moreover, the complete disappearance of the methylene peaks at 3.25 ppm next to the amide in the amic acid [cf. Figs. 1(b,c)] further confirmed the full conversion of the amic acid to the corresponding imide. The Supporting Information shows the detailed description of ¹H-NMR spectra of the amic acid and the imide based on CDA and PDMS-NH₂.

Also, with ¹H-NMR, the imidization reaction of the amic acid based on CDA and PDMS-NH₂ at 150°C was verified with ATR-FTIR spectroscopy in bulk (Fig. 2). In Figure 2, the ATR-FTIR spectra of CDA, the CDA ring-opened with PDMS-NH₂, and the CDA imidized with PDMS-NH₂ are compared in the region 1900–1600 cm⁻¹.

The ring opening of the anhydride at room temperature led to the disappearance of the anhydride signals at 1780 and 1850 cm⁻¹ [Fig. 2(a)]. Furthermore, one new peak emerged, which belonged to the carbonyl stretching of the carboxamide [1660 cm⁻¹; see Fig. 2(b)]. An increase in the temperature to 150°C led to the formation of one large peak at 1705 cm⁻¹ and one smaller peak around 1775 cm⁻¹; both originated from the two identical carbonyl groups of the imide [Fig. 2(c)].³⁶ In this model study, the conversion of the anhydride into imide was complete after 240 min because then the anhydride or amic acid signals were no longer observed after the heat treatment at 150°C; this was in agreement with the results obtained by ¹H-NMR.



Scheme 4 Ring-closure reaction of the amic acid based on CDA and PDMS-NH₂.

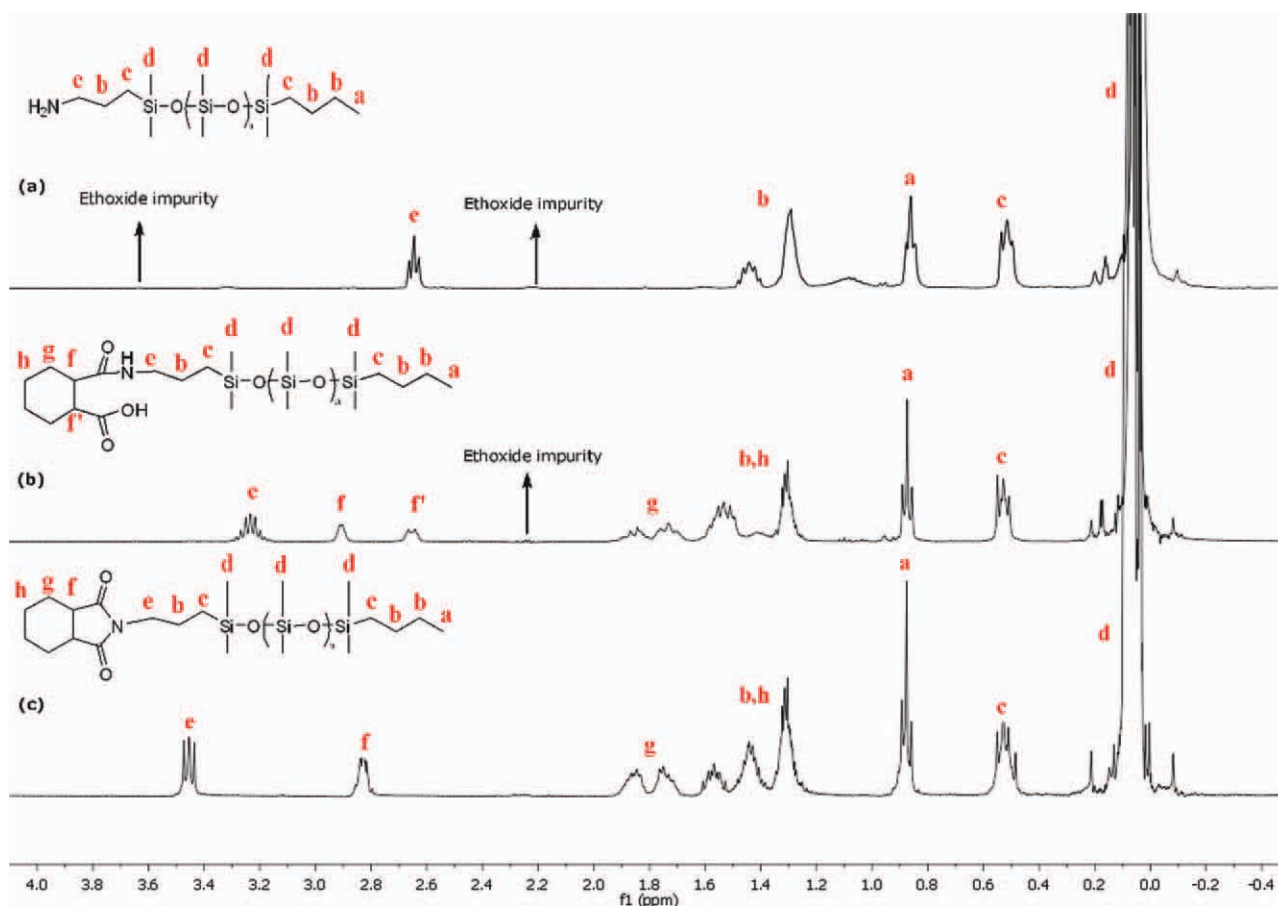


Figure 1 ¹H-NMR spectra of (a) PDMS-NH₂ in CDCl₃, (b) CDA ring-opened with PDMS-NH₂ in CDCl₃ recorded after 45 min of stirring in bulk at room temperature, and (c) the reaction product of the amic acid based on CDA and PDMS-NH₂ in CDCl₃ after 4 h at 150°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

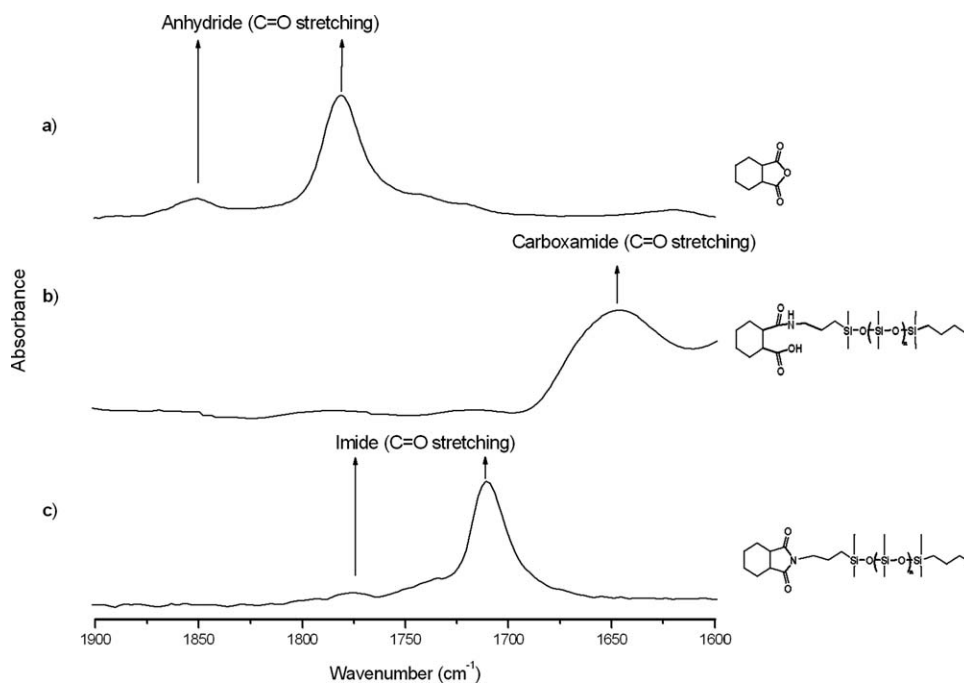


Figure 2 ATR-FTIR spectra of (a) CDA, (b) the formation of the ring-opened CDA at room temperature, and (c) the ring-closed imide (CDI) after heating at 150°C for 240 min.

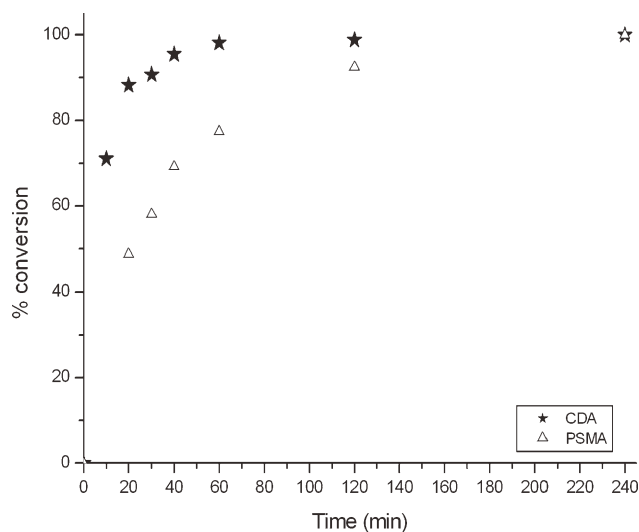


Figure 3 Conversion of the amic acid based on CDA and PDMS-NH₂ and PSMA and PDMS-NH₂ to imide by ATR-FTIR spectroscopy during 240 min of reaction time at 150°C.

The conversion of the amic acid based on CDA and PDMS-NH₂ to the ring-closed imide (CDI) was monitored in time by ATR-FTIR spectroscopy and was calculated with the following equation:

$$\text{Conversion(\%)} = (A_{1710\text{ cm}^{-1}}/A_{2860\text{ cm}^{-1}})s_t / (A_{1710\text{ cm}^{-1}}/A_{2860\text{ cm}^{-1}})s_{\infty} \quad (1)$$

where $A_{1710\text{ cm}^{-1}}$ is the peak area of the imide peak at 1710 cm⁻¹, $A_{2860\text{ cm}^{-1}}$ is the peak area of the reference peak at 2860 cm⁻¹, s_t is the sample at a particular stage of imidization, and s_{∞} is the sample cured at 150°C, which showed 100% imidization (proven by NMR, as discussed before).

Figure 3 shows the conversion of the amic acid from CDA and PDMS-NH₂ to the ring-closed imide (CDI); the Supporting Information shows the peak area values of the peaks at 1710 and 2860 cm⁻¹ and the corresponding ratios). As can be seen in Figure 3, the conversion or the peak area ratio, which is the peak area ratio of the peaks at 1710 cm⁻¹ (the imide C=O stretching) and at 2860 cm⁻¹ (the internal standard originating from the C-H stretching of CDA), increased as the reaction proceeded during the first 60 min, and it leveled off during the rest of the reaction. During the first 60 min of the reaction, the imide product formation was faster than during the following time, according to the ATR-FTIR results. We concluded that after 60 min of reaction time at 150°C, the imidization reaction was almost complete (Fig. 3).

Imidization of PSMA

As mentioned before, ¹H-NMR is not a suitable technique for analyzing the degree of imidization of

PSMA because of the overlapping peaks of PSMA and imidized PSMA. However, the model study with CDA showed that the NMR and ATR-FTIR data were in full agreement; this convinced us that the imidization of PSMA could be monitored in a reliable way by ATR-FTIR spectroscopy only. The imidization of the anhydride groups in the polymeric PSMA samples was investigated in a similar way, and comparable results were obtained under similar conditions, as judged from the ATR-FTIR spectra of PSMA, PSMA30, and completely imidized poly(styrene-*alt*-maleic anhydride) (PSMI), which are all given in Figure 4. The reason we used only 30 mol % anhydride groups for imidization is that the remaining anhydride groups were used for ammonolysis, adhesion, and optionally, crosslinking. Figure 3 shows the conversion of the amic acid from PSMA and PDMS-NH₂ to the ring-closed imide (PSMI). The conversion or the peak area ratio, which was the peak area ratio of the peaks at 1710 cm⁻¹ (the imide C=O stretching) and 700 cm⁻¹ (the signal arising from the aromatic ring of the styrenic unit at 700 cm⁻¹), increased as the reaction proceeded and reached completion after 240 min at 150°C, as can be seen in Figure 3.

The typical absorptions of PSMA could be found at 1860 cm⁻¹ (C-O-C), 1780 cm⁻¹ (C=O), and 1220 cm⁻¹ [C-O-C stretching; Fig. 4(a)]. As can be seen in Figure 4(c), the appearance of the characteristic absorption peaks of the imide groups at 1780 cm⁻¹ (C=O symmetric stretching), 1705 cm⁻¹ (C=O asymmetric stretching), and 1400 cm⁻¹ (C-N

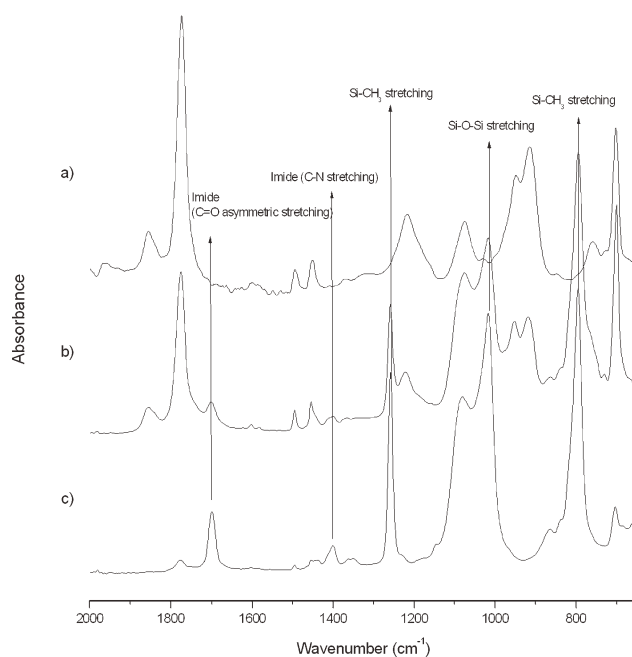


Figure 4 ATR-FTIR spectra of (a) PSMA, (b) PSMA with 30 mol % of the anhydride groups imidized with PDMS-NH₂ (after 20 h, 150°C), and (c) PSMI fully imidized with PDMS-NH₂ (after 20 h at 150°C).

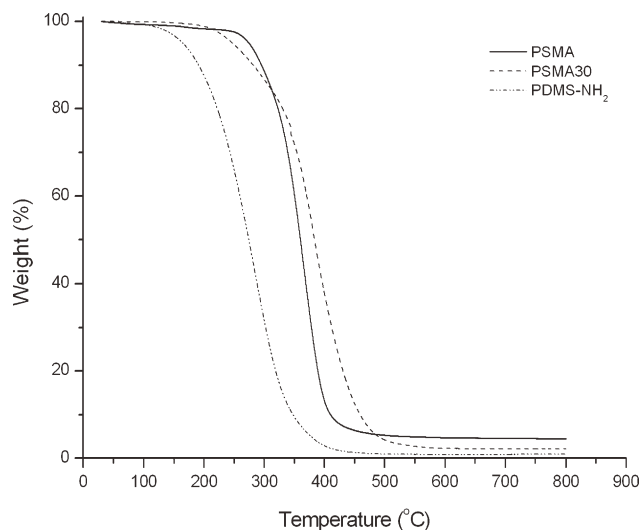


Figure 5 TGA plots of PSMA and PDMS-grafted PSMA.

stretching)³⁶ indicated the formation of the imide product after the corresponding amic acid product based on PSMA and PDMS-NH₂ were heated at 150°C for 20 h. No double peaks were recorded at 1780 and 1860 cm⁻¹, as shown Figure 4(c). Thus, ATR-FTIR analyses suggested that the imidization reaction of PSMA with PDMS-NH₂ was successful. Also, the presence of PDMS was confirmed by the Si-CH₃ (795 and 1260 cm⁻¹) and Si-O-Si (1016 cm⁻¹) stretching modes. For the PSMA, of which 30 mol % of the anhydride groups was targeted to be imidized with PDMS-NH₂, the real percentage imidization was calculated with the following equation:

$$\text{Conversion}(\%) = \frac{(A_{1710 \text{ or } 1400 \text{ cm}^{-1}}/A_{700 \text{ cm}^{-1}})s_t}{(A_{1710 \text{ or } 1400 \text{ cm}^{-1}}/A_{700 \text{ cm}^{-1}})s_\infty} \times 100 \quad (2)$$

where $A_{1710 \text{ cm}^{-1} \text{ or } 1400 \text{ cm}^{-1}}$ is the peak area of the imide peak at 1710 or 1400 cm⁻¹, $A_{700 \text{ cm}^{-1}}$ is the peak area of the reference peak at 700 cm⁻¹ (the signal arising from the aromatic ring of the styrenic unit at 700 cm⁻¹), s_t is the sample at a particular stage of imidization, and s_∞ is the sample cured at 150°C, which showed 100% imidization after 20 h of reaction.

Use of the peaks at 1710 and 1400 cm⁻¹ for the calculation of the percentage imidization gave similar results, namely, 28.4 and 29.8 mol %, respectively. These calculated values were close to each other, and both of them were very close to the theoretical percentage imidization (30 mol % on the basis of the added amount of PDMS-NH₂). This result shows that the use of the previous equations for the calculation of the percentage imidization was reliable. Moreover, the elemental analysis data agreed quite well with calculated values for the proposed structures of the polyimides:

ANAL. Calcd for PSMA30: C, 51.6%; H, 7.6%; N, 0.70%. Found: C, 50.7%; H, 7.5%; N, 0.64%. Calcd for PSMI: C, 43.6%; H, 8.6%; N, 1.04%. Found: C, 42.4%; H, 8.4%; N, 0.95%.

After the percentage of imidization was calculated, the effect of partial imidization on the thermal stability and T_g of PSMA was investigated by TGA and DSC for the sample PSMA30, which had approximately 30 mol % of the available anhydride groups imidized. The TGA thermograms recorded in a nitrogen atmosphere are shown in Figure 5. The 5% weight loss temperature of PDMS-NH₂ was found to be 162.7°C, and the 5% weight loss temperature of PSMA was 271°C. For PSMA30, containing PDMS attached to the PSMA backbone, the 5% weight loss temperature was detected at 246°C. PSMA30, thus, showed a slightly lower thermal stability than pure PSMA; this may have been due to the presence of the more thermally labile PDMS side chains.

The amount of PDMS-NH₂ grafted onto the polymer backbone had an effect on T_g of the polymer. T_g of the pure, nonimidized PSMA was approximately 150°C, whereas for PSMA30, which was modified with PDMS-NH₂, two T_g 's were detected (see Fig. 6). This indicated the presence of two phases, namely, a PDMS-rich phase and a PSMA30-rich phase. T_g of the PDMS-rich phase was around -129°C. T_g of the PSMA30-rich phase was found to be around 162°C. The observed phase separation was favorable for the modification of a polar surface with a hydrophobic top layer because the polar anhydride groups interacted with a polar surface, and the apolar PDMS migrated to the surface, which enhanced hydrophobicity of the top layer. Depending on the domain sizes of the phase-separated material, the coating was either transparent or

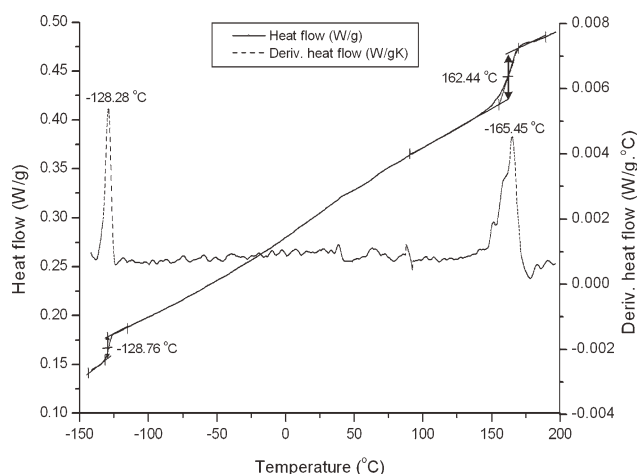
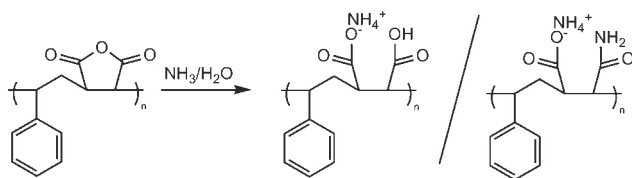


Figure 6 DSC thermogram for PSMA30 showing the heat flow and temperature derivative of heat flow as a function of the temperature for the second heating. The glass transitions of the PDMS-rich and the PSMA30-rich phase are indicated.



Scheme 5 Ammonolysis of PSMA.

opaque. A 20–25 μm thick coating of crosslinked-PSMA30 on a glass substrate was found to be transparent; this indicated small domain sizes.

Properties of the artificial latex from PSMA30

A PSMA copolymer of which 30 mol % of the available anhydride groups was imidized with PDMS-NH₂ (PSMA30) was used to prepare a latex. The produced imide was hydrophobic as a result of the hydrophobic grafted PDMS tails, and the imide groups were expected to be much more stable against hydrolysis than the anhydride. Therefore, the PDMS grafts formed the core of the particles upon addition of the copolymer to water. The imidized PSMA30 copolymer was first ammonolyzed by the addition of NH₃ (aqueous) to the polymer solution in acetone to increase the hydrophilicity of the polymer and to make it self-emulsifying; this was followed by the dropwise addition of the partially ammonolyzed polymer solution to water under vigorous stirring. This led to the formation of the latex. A fraction of the anhydrides was ammonolyzed with 0.3 equiv of NH₃ before the latex formation was performed to achieve electrostatic stabilization. Partial ammonolysis of the anhydride with ammonia led to an amide and a carboxylic acid group,⁸ which in aqueous medium would introduce ionic charges (Scheme 5). The residual 40 mol % of the anhydride groups remained available for optional crosslinking and/or adhesion to polar surfaces. The particle size and the size distribution of the obtained latex were studied with dynamic light scattering directly after preparation. The z-average and volume mean sizes of the particles were 144.8 and 150.7 nm, respectively. The polydispersity index was found to be 0.156.

Electrostatic stability of the artificial latex

The ζ -potential measurements were performed to study the stability of the PSMA-based latex particles. As mentioned before, the particles were stabilized by electrostatic interactions, caused by the ring opening of the anhydride units along the polymer main chain by NH₃ (Scheme 5). The ammonolysis led to negatively charged carboxylate groups along the polymer backbone when the polymer was added to water; this resulted in a negative ζ potential.

One of the parameters that affected the latex stability was the pH value. At low pH values, the anionic groups were neutralized; this led to a decreased electrostatic stabilization. Therefore, the pH dependence of the particle size and the ζ potential of the PSMA30-based latex were investigated by the method explained in the Experimental section. The results are shown in Figure 7.

For the latex, the initial pH was slightly above 7 (this gave the earlier mentioned particle size of ca. 145 nm), and the initial ζ potential at that pH was approximately -56 mV. The particle size distribution of the latex was not affected too much by changes in the pH of the latex in the range 4–10, and it was found that the particle size remained in the range 120–145 nm within this mentioned pH range. Furthermore, it was observed that the ζ potential of the latex increased (with the absolute value decreasing) when the pH was lowered below 4. This indicated that a significant amount of the carboxylate groups was neutralized below pH 4; this led to decreased electrostatic repulsions, as previously mentioned by Soer et al.¹³ However, a ζ potential of -30 mV was still sufficient to stabilize the particles. To conclude, the self-emulsifying latex was stable in the pH range 4–10 without the use of additional surfactants and stabilizers.

Surface structure and wettability of the as-received and coated cotton fabrics

As determined by SEM, the as-received cotton sample had a tightly woven, fibrous structure, as shown in Figure 8(a), and the surface structure of the cotton coated with PSMA30 is given in Figure 8(b).

The SEM images showed a clear change in the surface structure of the cotton fabric after

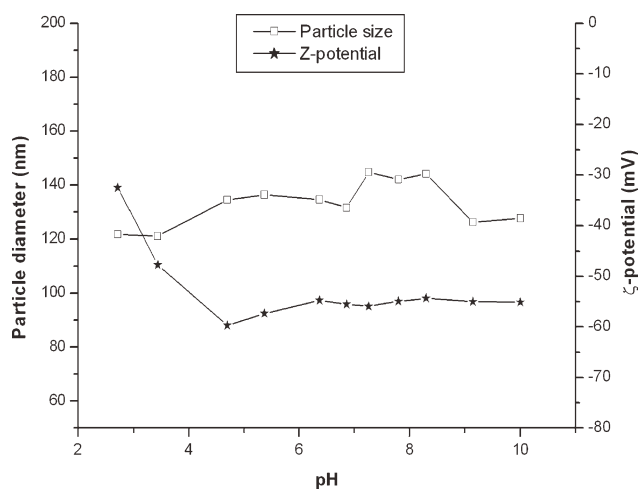


Figure 7 ζ potential of PSMA30-based latex, having 30 mol % anhydrides imidized with PDMS-NH₂, where a fraction of the anhydrides were ammonolyzed with 0.3 equiv of NH₃.

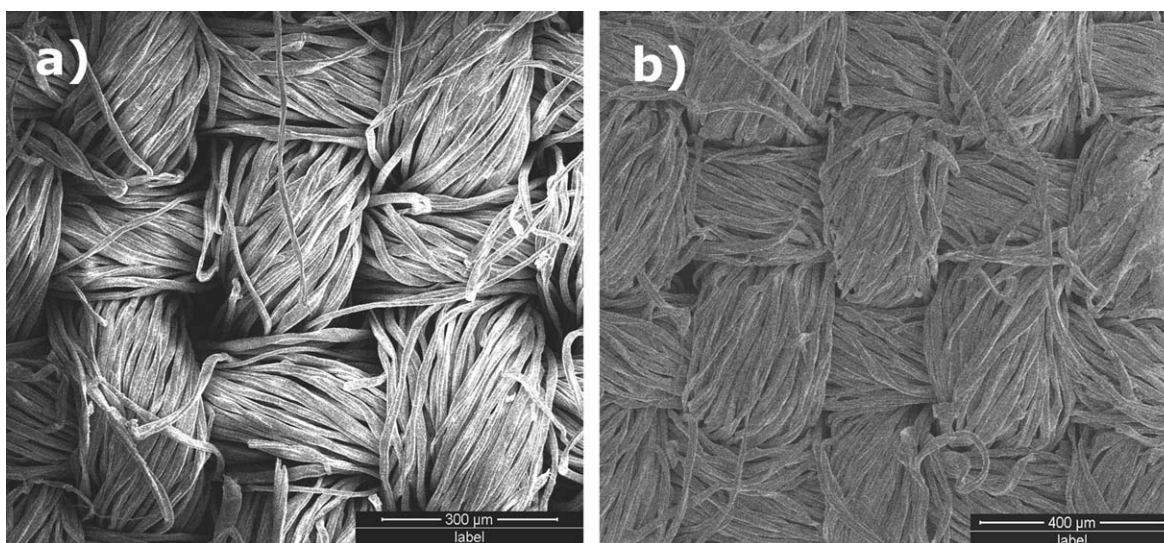


Figure 8 SEM images of the (a) as-received cotton fabric used in this study and (b) cotton fabric coated with PSMA30.

application of the PSMA30 coating. As can be seen in Figure 8(b), the fibers were coated individually as was the total surface of the cotton. Moreover, the typical longitudinal fibril structure was observed in the control sample [see Fig. 9(a)]. In contrast, such a structure was not visible in the treated samples. The surface of the fiber appeared to be coated with PSMA or PSMA30 [Fig. 9(b,c)], which enhanced the water repellency.

The surface wettability of the cotton fabric coated with the PSMA latex, where a fraction of the anhydrides were ammonolyzed with 0.3 equiv of NH_3 , and the PSMA30 latex, with 30 mol % of the initial anhydrides imidized with PDMS- NH_2 and where a fraction of the anhydrides were ammonolyzed with 0.3 equiv of NH_3 , was examined by water contact angle measurements. The PSMA and the PSMA30 latices with or without crosslinking were applied onto the cotton fabric, as described in the Experimental section (surface coating of cotton fabrics). It is a well known fact that cotton fabrics are very hydrophilic materials. When water droplets are placed on the surface of cotton fabrics, they spread instantly, and the contact angle is less than 10° . All of the static contact angles were measured, as described in the Experimental section. It should be noted that the measurement of contact angles was not straightforward because of fibers sticking out of the cotton sample; this led to difficulties in determining the baseline of the water droplet, which may have, in turn, led to a possible underestimation of the contact angle data.³⁷ Additionally, it was also difficult to obtain accurate values for advancing and receding water contact angles^{37,38} because the protruding fibers had some elasticity and could, thus, exert forces on the water droplet.³⁹ Therefore, only

the static contact angle for a 5- μL water droplet is reported here.

The static contact angle of the cotton fabric coated with PSMA was found to be $84.5 \pm 2.0^\circ$ [Fig. 9(b)]. Clearly, the presence of the PSMA on the cotton fibers added some hydrophobicity to the substrate (please remember that on pure, untreated cotton, the contact angle could not even be determined because of the very rapid wetting). The cotton fabric coated with PSMA30 latex became significantly more hydrophobic, with a static water contact angle of $135.7 \pm 1.2^\circ$, as shown in Figure 9(c). The PDMS tended to concentrate at the polymer/air interface and obviously gave the cotton a hydrophobic surface. The static contact angle results showed that the hydrophobicity of the cotton could be improved significantly with PSMA30 as a waterborne coating.

Preliminary quantitative analysis on the basis of the AFM images indicated that the root mean square roughness of the pure cotton and coated cotton were in the range 10–20 nm. For example, the root mean square roughness for the coated cotton fabric was 10.3 nm within an area of $1.4 \times 1.4 \mu\text{m}^2$ (Fig. 10). In this case, where we had a hydrophobic surface, the intrinsic surface roughness of the cotton led to an increased water repellency. However, as the surface roughness of the cotton before and after coating did not change significantly, we did not expect this to have a very large effect on the observed contact angle. The observed difference between the contact angles of the pure cotton (full spreading of water) and the coated samples ($135.7 \pm 1.2^\circ$ for PSMA30) was mainly due to the hydrophobic character of the applied coating.

In addition, the PSMA- and PSMA30-coated cotton samples with or without crosslinker were washed as

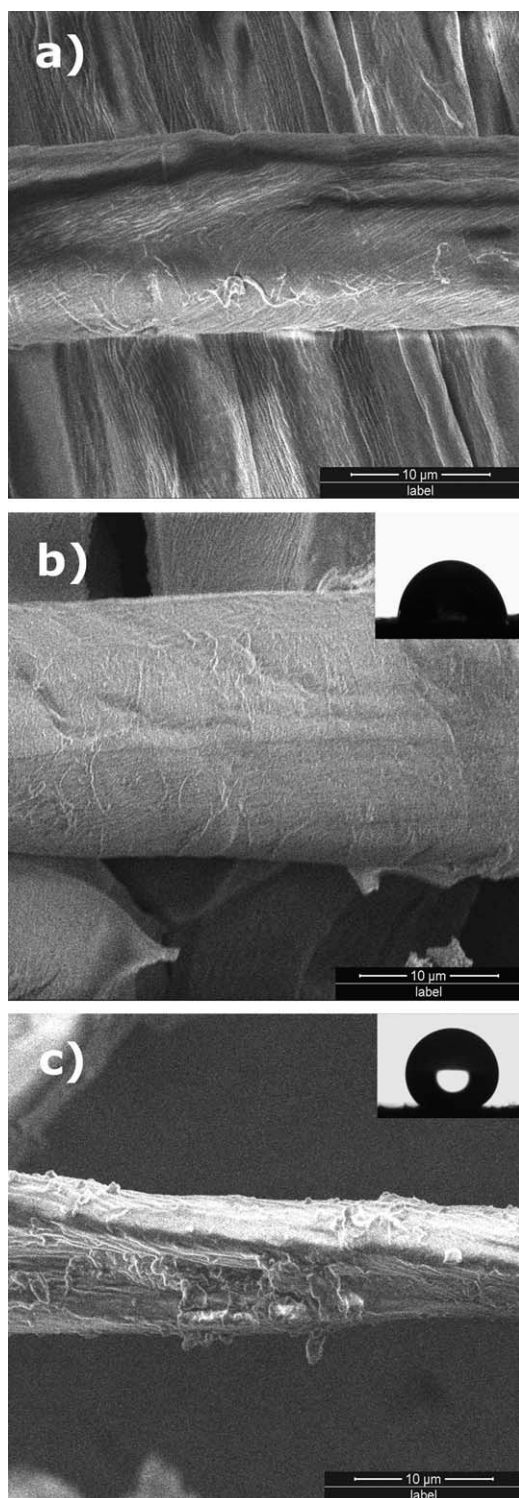


Figure 9 SEM images of the (a) as-received cotton, (b) cotton fiber coated with PSMA (30 mol % of the initial anhydrides were ammonolyzed with NH_3), and (c) the cotton fiber coated with PSMA30 (30 mol % of the initial anhydrides were imidized with PDMS-NH_2 and 30 mol % of the initial anhydrides were ammonolyzed with NH_3). Shown in the insets are the images of static water droplets on the respective samples. For the as-received cotton, the deposited water droplet disappeared instantly.

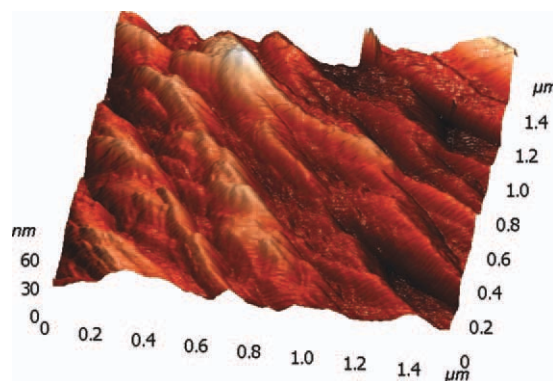


Figure 10 AFM three-dimensional image ($1.4 \times 1.4 \mu\text{m}^2$) of the PSMA30-coated cotton fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

described in the Experimental section to check the durability of the coating on the cotton. Table I shows the amount of the polymer impregnated (weight percentage) onto the cotton samples with or without crosslinker before and after washing.

As can be seen in Table I, the noncrosslinked PSMA coating on the cotton sample was completely removed during the washing step; this was expected because maleic anhydride-containing polymers can be hydrolyzed relatively easily at high pH, followed by dissolution of the polymer in water. After the noncrosslinked PSMA-coated cotton was washed, water droplets placed on the surface of the cotton sample spread instantly, as was observed for the uncoated cotton. After the washing step of the noncrosslinked PSMA30, part of the coating could still be found on the cotton (see Table I). However, more than 85 wt % of the PSMA30 coating on the cotton was removed after the washing step, and the contact angle value decreased from 135.7 ± 1.2 to $113.0 \pm 1.9^\circ$. This indicated that a high amount of impregnation of the polymer onto the cotton may not be necessary.

The effects of crosslinking were investigated by the reaction of the remaining 40% of anhydride groups in the PSMA and the PSMA30 with ADH, the crosslinker, which was added to the latex before

TABLE I
Amounts of Polymer Impregnated (wt %) in the Cotton Samples with or Without Crosslinker Before and After Washing

Sample	Amount of polymer impregnated in the cotton before the washing (wt %)	Amount of polymer impregnated in the cotton after the first washing (wt %)
PSMA	24 ± 3	0.3 ± 0.1
PSMA + ADH	33 ± 5	20 ± 3
PSMA30	29 ± 2	3 ± 1
PSMA30 + ADH	31 ± 2	26 ± 4

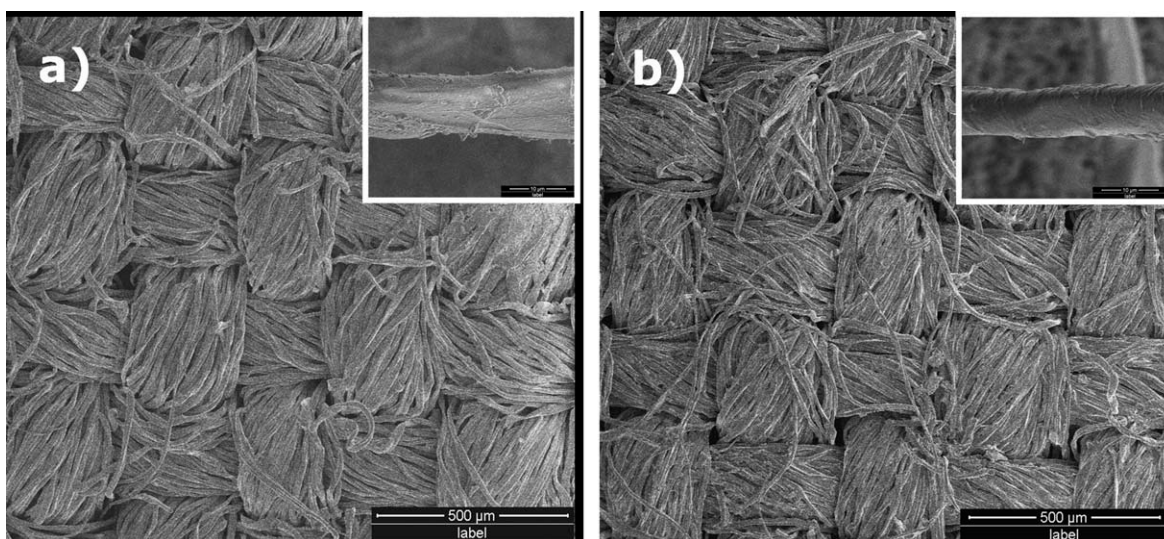


Figure 11 SEM images for the (a) cotton coated with PSMA30 crosslinked with ADH before washing and (b) cotton coated with PSMA30 crosslinked with ADH after washing. Shown in the insets are the images of the individual coated cotton fibers.

the cotton fabric was treated. The resulting samples were characterized before and after washing. As Table I shows, some of the crosslinked PSMA coating on the cotton sample was removed after the washing step. The reason for this was that there were still 30 mol % anhydride groups remaining in the (obviously not 100%) crosslinked PSMA, and these groups may have been hydrolyzed at high pH values. However, approximately 90 wt % of the crosslinked PSMA30 coating remained on the cotton sample after the washing step [see Table I and Fig. 11(a) and 10(b)]. The same contact angle values ($\sim 136^\circ$) that were acquired before the washing step were measured for the washed cotton coated with crosslinked PSMA30. To conclude, PSMA (see Table I) or PDMS (see ref. 22) individually was not enough to produce a durable and hydrophobic coating. This means that the crosslinked PSMA30, which was a combination of PSMA and PDMS, offered a good coating durability and a highly efficient water-repellent coating. The Supporting Information (Fig. S4) shows the SEM images of the cotton samples coated with crosslinked PSMA before and after washing.

The ATR-FTIR spectra of the surfaces of the untreated cotton, PSMA-treated cotton, and PSMA30-treated cotton are shown in Figure 12. We observed in the spectra of the PSMA- and PSMA30-treated samples the presence of new absorption bands between 1850 and 1700 cm^{-1} , which were attributed to the carbonyl stretching of the anhydride-containing PSMA or the partially imidized anhydride-containing PSMA30. The absorption bands of the primary and secondary -OH deformations of the cotton appeared in the region at about 1057 , 1162 , and 1373 cm^{-1} .⁴⁰ Note that the -OH

stretching vibrations between 3150 and 3600 cm^{-1} present for untreated cotton were still visible in the spectra of the treated cotton samples. This may have indicated that only a thin coating was deposited on the surface ($<1\text{ }\mu\text{m}$), as previously mentioned by Siriviriyannun et al.⁴¹ Moreover, the SEM pictures of the uncoated cotton [Fig. 8(a)] and coated cotton [Fig. 8(b)] showed that the coating was so thin that the individual cotton fibers were still visible. This indicated that only the surface of the individual fibers

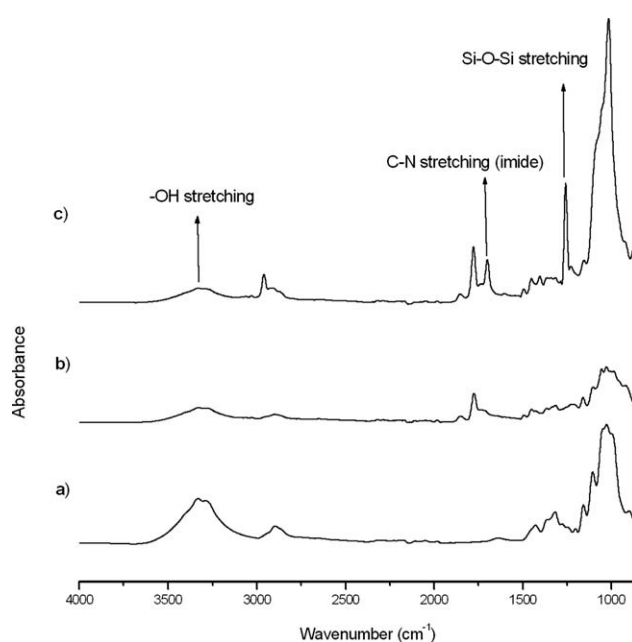


Figure 12 ATR-FTIR spectra of the (a) as-received cotton, (b) cotton coated with PSMA, and (c) cotton coated with PSMA30.

was coated with PSMA or PSMA30 [Fig. 9(b,c)], without the formation of a thick layer on the surface of the cotton fabric.

CONCLUSIONS

The imidization reaction between the model compound CDA and PDMS-NH₂ was successfully investigated in detail. According to the NMR and ATR-FTIR results, the imide compound was successfully obtained. After the imidization of PSMA with PDMS-NH₂, the ATR-FTIR results showed the presence of imide and PDMS in the modified PSMA. The percentage imidization of the PSMA partially imidized with PDMS-NH₂ was calculated with two different FTIR imide peaks, and the results (28.4 and 29.8 mol %) were in good agreement with the theoretical value of 30 mol %. A self-emulsifying latex with an average particle diameter of approximately 145 nm was successfully prepared by partial ammonolysis of partially imidized PSMA without the use of any added surfactant. The latex had a ζ potential of approximately -56 mV; this indicated sufficient electrostatic stabilization. Strong electrostatic interactions were responsible for this stabilization. The particle size distribution of the latex was not seriously affected by changes in the pH of the latex. The latex was stable in the pH range 4-10. The water contact angle value of a piece of cotton coated with the PDMS-modified PSMA30 latex showed that a hydrophobic surface was formed with a static water contact angle of $135.7 \pm 1.2^\circ$. The washing studies showed that the durability of the crosslinked PSMA and PSMA30 coatings was better than that of the noncrosslinked ones, and the same contact angle values were measured for the cotton coated with crosslinked PSMA30 after the washing step. The crosslinked PSMA30 provided a durable, hydrophobic coating. The preparation and evaluation of waterborne coatings based on differently modified PSMA latices is currently under investigation in our laboratories.

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