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Crosslinkable coupling agents: Synthesis and use for modification of interfaces in polymer blends

Jürgen Pionteck*, Veera Bhadraiah Sadhu, Lothar Jakisch, Petra Pötschke,
Liane Häußler, Andreas Janke

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, D-01069 Dresden, Germany

Abstract

A novel coupling agent containing 2-oxazoline and 2-oxazinone as well as hydrosilane moieties has been prepared by hydrosilylation of the corresponding allyl ether containing precursor with a methylhydrosiloxane–dimethylsiloxane copolymer. This hydrosiloxane containing coupling agent, termed as SCA, was characterized by ^{1}H NMR and its crosslinkability was proven by DSC. SCA was used for the modification of the interfaces in heterogeneous polymer blends. In a model blend system based on mono-carboxylic acid terminated polystyrene (PS–COOH) and mono-amino terminated poly(methyl methacrylate) (PMMA–NH_2) the 2-oxazoline and 2-oxazinone units of SCA can selectively react with the carboxylic groups or amino groups, respectively. The remaining hydrosilane units partially crosslink under the used mixing conditions.

The morphology of the three-component blends prepared by melt mixing was evaluated. SCA is immiscible with the polymers and forms its own phase. The expected location of the SCA at the interface between the polymers was proven only in an annealed, strongly phase separated blend. Overall the effect of the compatibilizer on the morphology is very small. Neither the domain size nor the composition for phase inversion are significantly affected in this blend system by the presence of SCA.

Keywords: Blends; Interface; Coupling agents

1. Introduction

Blending of different polymers is a robust method for producing new structural materials from existing ones. However, most polymer mixtures are thermodynamically immiscible and display poor mechanical properties, owing to their coarse and unstable morphology and poor interfacial adhesion between the phases. To overcome this disadvantage often compatibilization is necessary. One way is the addition of block- or graft-copolymers [1–3] which have to be prepared separately. This method is rather costly and often not suitable for commercial blends. Furthermore, pre-made copolymers may form micelles instead of residing at the interface [4–6]. Additionally, when the added copolymers have a higher propensity to one of the blend components, they will locate in this phase instead at the interface if the thermodynamic equilibrium is reached [7].

Another commonly used method is the in situ compatibilization, where the copolymers are formed by coupling reaction between two appropriate blend components at their interface [8,9]. This method is more frequently used for industrial applications. The rate of copolymer formation and their amount play a vital role for the compatibilization of immiscible blends. To act as compatibilizer the in situ formed copolymers are required to locate at the interface between the two phases, thus lowering the interfacial tension, improving the phase adhesion, and stabilizing the morphology against coalescence. Recently, some investigations of reactive compatibilization have shown that the in situ formed copolymers may be easily pulled out of the interfacial region [10–13]. The pull-out mechanism mainly depends on the kinetics of the interfacial reaction, which controls the density of the copolymer formed at the interface and on the thermodynamic and hydrodynamic instability caused by accumulated block or graft copolymers at the interface [10,14].

Recently, Böhme et al. [15] described the syntheses of

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* Corresponding author. Tel.: +49 351 4658 393; fax: +49 351 4658 565.
E-mail address: pionteck@ipfdd.de (J. Pionteck).

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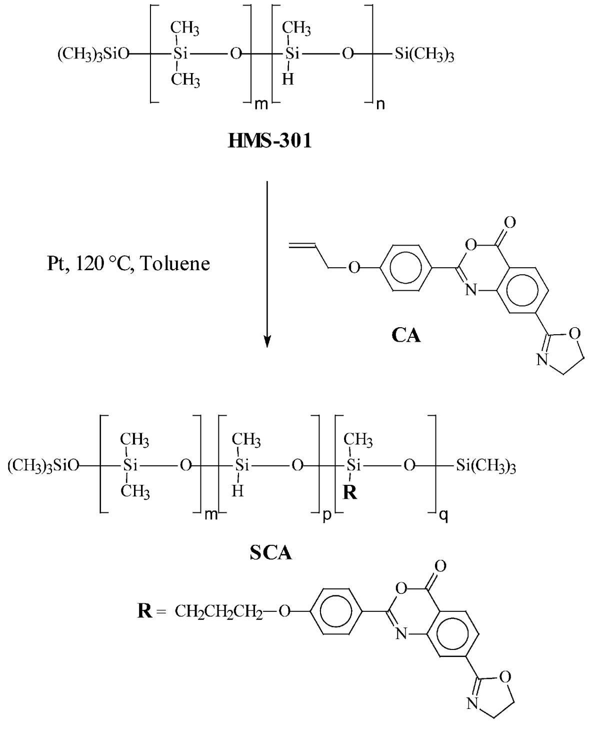
coupling agents containing three functional sites: 2-oxazoline and 2-oxazinone groups suitable for the reactive compatibilization of carboxylic and amino terminated polymers, and as third reactive side an allyl ether unit (CA, structure see Scheme 1). This kind of coupling agent can be used for structural designing of materials in molten state, for instance to prepare telechelic polymers and functionalized copolymers. In model reactions it was shown, that under reactive extrusion conditions the 2-oxazoline and the 2-oxazinone groups could selectively react with carboxylic and amino groups, respectively. The allyl ether group remained unaffected under these conditions.

In the present work we used this trifunctional coupling agent to prepare a novel type of polyfunctional coupling agent containing still 2-oxazoline and 2-oxazinone units but as third reactive site hydrosilane groups. The preparation was done by grafting CA onto a methylhydrosiloxane–dimethylsiloxane copolymer under hydrosilylation conditions. In this paper we describe the syntheses of the so-called silane-containing coupling agent (SCA) and its use for the modification of interfaces in polymer blends. As model blend system we have chosen amino-terminated poly(methyl methacrylate) (PMMA–NH_2) and carboxylic acid terminated polystyrene (PS–COOH). Both polymers are immiscible. If simultaneously the oxazoline unit reacts with PS–SCOOH and the oxazinone unit with PMMA–NH_2 the SCA should locate at the interface and form its own phase. The remaining hydrosilane units should be accessible for further modification, e.g. crosslinking. Our goal was to proof if such interfacial modification is possible and how it influences the blend morphology. The final goal will be the formation of co-continuous blend morphologies with a separated interphase. If such interphases can be controlled in its crosslinkability, the creation of materials with defined properties like diffusibility should be possible.



Scheme 1. Synthesis of SCA by hydrosilylation of the allyl ether containing coupling agent CA with HMS-301.

2. Experimental

2.1. Materials

Methylhydrosiloxane–dimethylsiloxane copolymer having the molecular weight of 1900–2000 g/mol and 25–30 mol% of MeHSiO (HMS-301), platinum–divinyltetramethyldisiloxane complex in xylene (2.1–2.4% platinum concentration, 'Karstedt's catalyst', both from Gelest ABCR), and toluene over molecular sieve (Fluka) were used as received. The trifunctional allyl ether containing coupling agent CA was prepared according to literature [15].

Carboxylic acid terminated polystyrene (PS–COOH, $M_n = 40{,}000$ g/mol, PD = 1.1, functionality $f \sim 0.6$) was prepared according to literature [16] by the TEMPO-mediated free radical polymerization using 4,4′-azo-bis-(4-cyanopentanoic acid) as initiator. To stabilize the product during processing the TEMPO end group was removed by oxidation with *m*-chloroperbenzoic acid [17]. Amine end group terminated poly(methyl methacrylate) (PMMA–NH_2, $M_n = 18{,}600$ g/mol, PD = 2.55, $f \sim 1$) was prepared by atom transfer radical polymerization (ATRP) using a protected amino containing initiator. The product was deprotected by treatment with trifluoroacetic acid [18,19].

2.2. Analytical methods

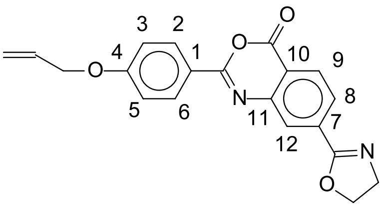
The ^1H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. Trifluoroacetic acid-d_1 (TFA-d_1) was used as solvent. The spectra were referenced on sodium 3-(trimethylsilyl) propionate-2,2,3,3-d_4 ($\delta(^1H) = 0$ ppm).

IR spectra were recorded with a BIO-RAD FTS 155 spectrometer using KBr pellets. Soluble compounds were measured as thin film (from THF) on a KBr disc. Differential scanning calorimetric (DSC) analysis was carried out with a DSC 7 (Perkin–Elmer), Pyris-software version 4.01, under nitrogen atmosphere at a scan rate of ±20 K/min in the temperature range of −50 to +240 °C.

2.3. Synthesis of 2-(4-allyloxy-phenyl)-7-(4,5-dihydro-oxazol-2-yl)-benzo[d][1,3]oxazin-4-one (CA)

According to the literature [15] CA was synthesized by conversion of 4-allyloxybenzoylchloride with 2-aminoterephthalic acid in the presence of triethylamine. The cyclization to the oxazinone ring was performed in thionyl chloride at 60 °C. The subsequent conversion of the formed acid chloride with 2-aminoethanol resulted in the corresponding 2-hydroxyethylamide, which was cyclized to the oxazoline with thionyl chloride in tetrahydrofuran at 0 °C. After treatment with aqueous sodium bicarbonate the final product was washed with water.

For comparison the ^1H NMR data in TFA-d_1 and typical IR absorbances of CA are given here:



^1H NMR (TFA-d_1): $\delta = 8.58$ (s, 1H, H^{12}), 8.57 (d, 1H, H^9), 8.39 (d, 2H, $H^{2,6}$), 8.35 (d, 1H, H^8), 7.25 (d, 2H, $H^{3,5}$), 6.02 (m, 1H, CH=), 5.42 (d, 1H, CH_2=), 5.41 (t, 2H, CH_2O), 5.36 (d, 1H, CH_2=), 4.77 (d, 2H, CH_2OAr), 4.55 ppm (t, 2H, CH_2N).

IR (KBr): 3077 (C=C), 1760 (C=O), 1649 cm^{-1} (C=O).

2.4. Preparation of the hydrosiloxane-containing coupling agent (SCA)

4.8 g HMS-301 (4.62 mmol) and 1.6 g CA (2.46 mmol) were added to a dry three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser with a $CaCl_2$ drying pipe. 400 mL toluene and a catalytic amount of platinum–divinyltetramethyldisiloxane complex (100 μL) were added. Dry air was purged through the reaction mixture for a couple of minutes. The reaction was allowed to proceed for 6 h at 120 °C. Toluene was removed by vacuum rotary evaporation and the product was stored at temperatures below 10 °C.

^1H NMR (TFA-d_1): $\delta = 8.58$ (H^{12}), 8.57 (H^9), 8.40 ($H^{2,6}$), 8.34 (H^8), 7.23 ($H^{3,5}$), 5.40 (CH_2O), 5.03, 4.79, 4,74 (SiH), 4.55 (CH_2N), 4.21 (CH_2OAr), 2.01 ($\mathit{CH_2}$ CH_2Si), 0.55–0.10 ppm (CH_2Si, CH_3Si).

IR (thin film): 2157 (Si–H), 1762 (C=O), 1650 cm^{-1} (C=O).

2.5. Model reactions

The heating of SCA in substance and model reactions of SCA with *n*-dodecylamine and lauric acid in stoichiometric ratios were performed in closed glass vials under melt conditions at 200 °C for 10 min.

2.6. Blend preparation and characterization

The blends were prepared by melt mixing for 10 min with 100 rpm in a DACA Micro-Compounder (DACA Instruments; two conical co-rotating screws with a bypass allowing the material to circulate for defined periods; capacity of 4.5 cm^3). The blends were prepared with various compositions at different temperatures of 180, 190, or 200 °C. To catalyze the crosslinking reaction sometimes Pt solution (20 μL) was added during mixing.

The extruded strands from the Micro-Compounder were cut by a microtome at room temperature and treated with O_2 plasma for 30 s to etch mainly the PMMA phase. Using toluene at room temperature both polymers and the non-crosslinked SCA are soluble and the crosslinked components can be separated by filtration.

The morphology of the blends was investigated on the plasma etched cut surfaces sputtered with gold by scanning electron microscopy (SEM) using an SEM LEO 435 VP (Leo Elektronenmikroskopie) operating with an acceleration voltage of 5–10 kV. Atomic force microscopy (AFM) was performed by means of a NanoScope IV-Dimension 3100 (Veeco) on smooth cut surfaces prepared at −60 °C. The measurements were done in the tapping mode. The topography and phase images have been detected simultaneously. The scan conditions we choose according to Magonov [20] (free amplitude >100 nm, set-point amplitude ratio 0.5) to get stiffness contrast in the phase image, that means bright features in the phase image are stiffer than dark areas. FTIR analysis was carried out by FTIR-spectrophotometer IFS 66v (Bruker) using Golden Gate ATR diamond crystals (SPECAC).

Rheological properties were analyzed by an ARES Rheometer (Rheometrics Sci) using a parallel plate–plate geometry with a plate diameter of 25 mm and a gap of 1–2 mm under nitrogen atmosphere at 200 °C. Frequency sweeps in the range from 0.1 to 100 rad/s and return from 100 to 0.1 rad/s were done, the second sweeps were used for interpretation. Pieces of extruded strands were placed between the heated plates and allowed to equilibrate for about 5 min. The strain used (3–20%) was within the linear viscoelastic range as checked by strain sweeps.

DSC of PS/PMMA blends was done with a DSC Q 1000 of TA Instruments with an auto sampler under equivalent conditions to the measurements with the DSC 7, but at temperatures from −60 to 220 °C. All samples were measured in a heating–cooling–heating cycle. The heat flow of the second heating was used for the analysis.

3. Results and discussion

3.1. Synthesis of SCA

Our goal was to synthesize a modified methylhydrosiloxane–dimethylsiloxane copolymer having 2-oxazoline and 2-oxazinone groups in the side chain and still containing Si–H groups in the main chain (Scheme 1). Therefore, the ratio of CA/HMS-301 was chosen to obtain 27% conversion of the Si–H groups which would result in a product with mean values of about 1.9 CA units and 5.1 Si–H units per polysiloxane chain. For the calculation the averaged data given by the producer have been used.

The used platinum–divinyltetramethyldisiloxane complex (Karstedt's catalyst) is described in the literature as an effective catalyst for hydrosilylation of allyl phenyl ethers. Marciniec et al. [21] used different platinum and ruthenium complexes as catalyst for functionalization of poly(methylhydro)siloxanes with allyl derivatives including allyl phenyl ethers. Conqueret et al. [22] have investigated the kinetics of the Pt-catalyzed hydrosilylation of some allyl aryl ethers by Si–H end groups of a monofunctional telechelic poly (dimethylsiloxane). On the other hand it is known from our earlier works that aliphatic substituted 2-oxazoline groups reduce completely under hydrosilylation conditions using Karstedt's catalyst [23]. When trying the hydrosilylation of 2-(4-butenyl)-1,3-oxazoline with tetramethyldisiloxane at 80 °C the reduction of the C^2 of the oxazoline ring could be proven by ^1H NMR. Even the less reactive Speier's catalyst based on H_2PtCl_6 caused the reduction of the oxazoline ring parallel to the formation of the hydrosilylated product with the closed oxazoline ring structure. Therefore, a possible reduction of the 2-oxazoline group and also of the 2-oxazinone ring has to be considered.

Additionally, the Si–H unit is sensitive to moisture. However, during synthesis a clear solution of the SCA in toluene was obtained. After removing of the solvent the product was partially crosslinked when stored at room temperature for longer periods. This might be due to the reactivity of the remaining Si–H groups caused by the presence of small traces of active platinum catalyst. However, at temperatures below 10 °C, the SCA was quite stable. After 6 months no crosslinking was observed.

Deviations from the averaged data given by the producer and the described possible side reactions during the hydrosilylation may result in a product with a composition deviating from the expected one. Therefore, the final product was evaluated by ^1H NMR. The results indicate that the coupling agent was completely undergone hydrosilylation reaction and attached as side chain on the polysiloxane chain. Fig. 1 shows the ^1H NMR spectra of pure HMS-301, CA, and SCA measured in TFA-d_1. A fine splitting of the signals of the oxazoline group at 5.40 ppm (CH_2O) and 4.55 ppm (CH_2N), and different signals for the Si–H protons in the region from 4.73 to 5.03 ppm are observed. This can be explained by chain scission of the Si–O–Si backbone caused by TFA-d_1 resulting in shorter units and Si–H groups with different substitutions. It is known, that trifluoroacetic acid (as a strong acid) attacks silicon and cleaves the network structures and also opens the cyclic structures of siloxanes [24,25].

In the SCA spectrum the representative signals of the allyl ether group completely disappeared and new signals respective to the silylpropyl groups are noticed. The new signal at 4.21 ppm corresponds to the CH_2OAr protons. The signals corresponding to the Si–H group are still present, indicating remaining Si–H groups. The proton ratio Si–H/Si–CH_3 for SCA amounts to 1/28 and agrees approximate with the theoretical value (1/29). An additional signal at 7.32 ppm indicates a small extent of side reactions of the Si–H groups with the oxazoline and/or oxazinone groups as discussed above. The ratio of the aromatic protons (7.23–8.58 ppm) to the aliphatic protons of the oxazoline ring (OCH_2, 5.40 ppm) is 6.4/2, which is in good agreement with the theoretical one of 7/2. Obviously, the aromatic substituted oxazolines are rather stable under the hydrosilylation conditions.

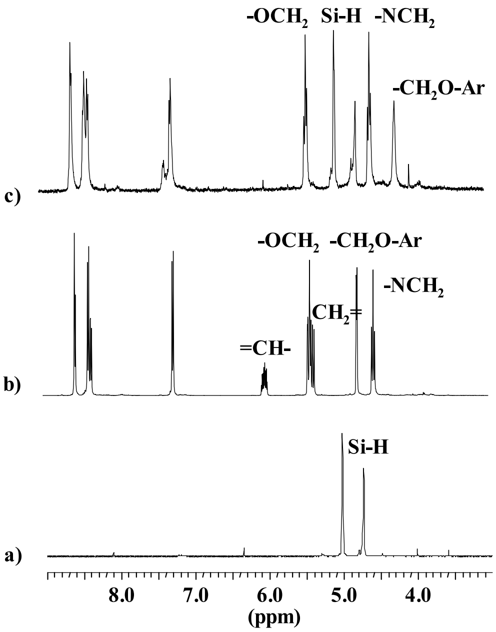
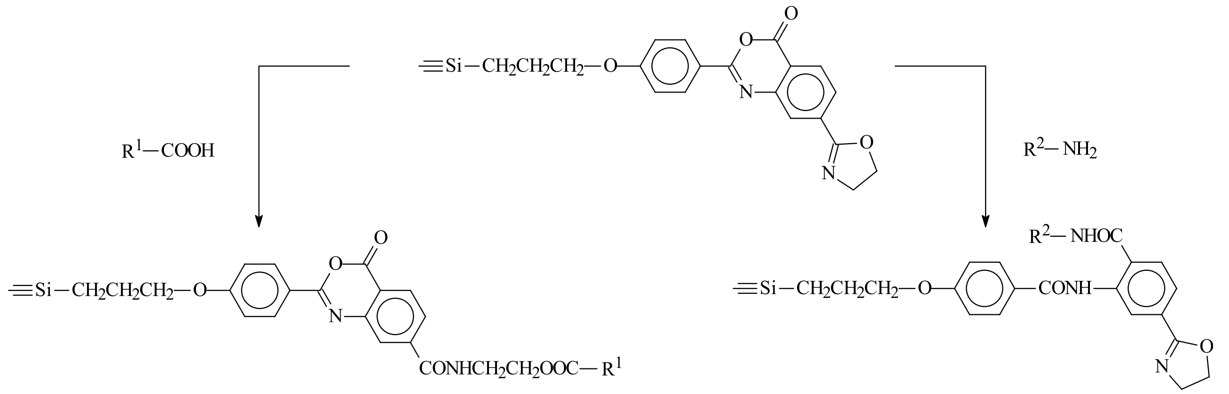


Fig. 1. ^1H NMR spectra of (a) HMS-301, (b) CA, and (c) SCA measured in TFA-d_1.

The FTIR spectrum (not shown, compare experimental part) of SCA corresponds with the ^1H NMR data. The characteristic absorbances for the 2-oxazoline, 2-oxazinone, and Si–H groups are clearly visible. Overall, we obtained a product with the expected structure which should be able to react selectively with amino and carboxylic units according to Scheme 2.

3.2. DSC measurements of SCA

The DSC curves of the HMS-301 + Pt-catalyst and SCA are shown in Fig. 2. Pure HMS-301 did not show an exothermic peak in DSC measurements (not shown) whereas with platinum catalyst an exothermic peak in the first heating run is visible starting at ca. 50 °C. In case of SCA a broad exothermal heat flow with two narrow peaks indicating crosslinking reactions can be observed beginning at much higher temperatures. The crosslinking indicates that traces of the catalyst must be still active in the separated product. The temperature shift is probably caused by steric hindrance due to the bulky side groups. The oxazoline and/or oxazinone units may also start to react with the Si–H units



Scheme 2. Selective coupling reactions of SCA.

during the DSC run, which can not be separated from the exothermal peak caused by the crosslinking. SCA shows an endothermic melting peak below 100 °C, possibly caused by the rigid side groups. CA itself shows a melting peak at 170 °C. As well the melting as the crosslinking are not observable during the second heat. Obviously, the crosslinking is almost finished during the first heating to 240 °C and following cooling run and a reordering of the rigid side groups is hindered.

3.3. Model coupling reactions of SCA

After annealing SCA for 10 min to 200 °C the intensities of the Si–H and oxazoline signals in the ^{1}H NMR spectrum are reduced compared to the spectra of the virgin SCA. Additionally, new signals of aromatic protons are visible. That is an indication for side reactions of Si–H groups with 2-oxazoline and/or 2-oxazinone groups during heating. The product is only partial soluble in toluene. These observations are in agreement with the results of the DSC analysis.

Model reactions were carried out in order to get more information about the SCA in terms of selective coupling reactions (Scheme 2) in combination with the crosslinkability of the remaining Si–H groups. When annealing SCA in presence of lauric acid or *n*-dodecylamine as low molecular weight model compounds at 200 °C for 10 min crosslinked products were obtained those are insoluble in toluene. However, all products are completely soluble in trifluoroacetic acid because of degradation of the materials by chain scission of the Si–O–Si backbone.

Fig. 3 shows exemplarily the ^{1}H NMR spectrum of the conversion product from the reaction of SCA with *n*-dodecylamine. Besides the signals for the Si–H groups at 5.03, 4.79, and 4.74 ppm the characteristic triplet signals for the remaining oxazoline group at 5.35 and 4.47 ppm are visible. The signal at 4.22 ppm corresponds to the CH_2OAr group and the signals at 3.50 ppm represent the Ar–CO–NH–CH_2 alkyl group from the reaction product of the 2-oxazinone group with the amine by ring opening. The typical signal for unreacted amino groups at 3.20 ppm (CH_2NH_2) is still visible in a small extent. ^{1}H NMR investigations of the melt reaction between SCA and amino-terminated polyamide12 have also proven the amine/oxazinone conversion, while simultaneously crosslinking take place (loss in SiH signal intensity) [26,27]. When the reaction between PMMA–NH_2 and SCA was investigated by ^{1}H NMR, a decrease in the intensity of the signal of the –CO–NH–CH_2–CH_2–NH_2 terminal group at 3.46 ppm and the signals of the remaining oxazoline groups could be observed. Unfortunately, the expected new signal for the resulting Ar–CO–NH–CH_2– group in the range of 3.5–3.7 ppm is overlapped by the broad signal at 3.75 ppm which represents the methyl protons of the PMMA side groups.

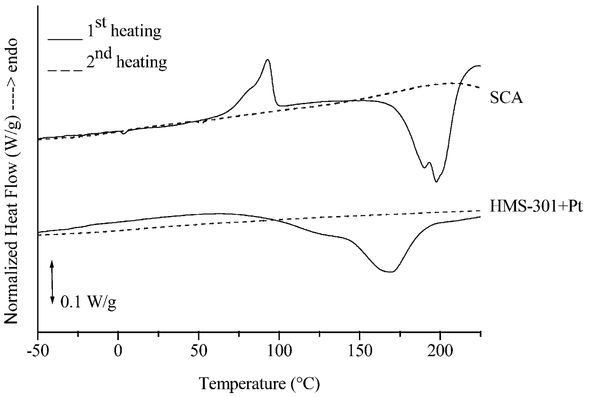


Fig. 2. DSC curves of HMS-301 + Pt and SCA.

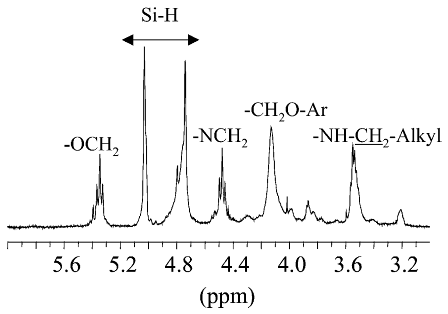


Fig. 3. ^{1}H NMR spectrum of the SCA-dodecylamine coupling reaction product (degradation product in TFA-d_1).

In case of lauric acid or when annealing SCA with a mixture of both model components much more side reactions take place. Nevertheless, the typical signals corresponding to the formed ester amide structure at 3.89 ppm (CH_2NHCO) and 4.46 ppm (CH_2OCO) were present in the ^1H NMR spectra. Model reactions with PS–COOH could not be analyzed by ^1H NMR due to the lack of a suitable common solvent for PS and the crosslinked SCA. The possible side reactions of the activated Si–H groups (besides self crosslinking via hydrolysis and condensation reactions) with the amino or carboxylic groups and with the 2-oxazoline and/or 2-oxazinone groups seem to be very complex and could not be investigated in detail.

3.4. PS/PMMA blends morphology

The blends of PS–COOH/PMMA–NH_2, with and without SCA, with different composition were prepared by melt mixing. In order to get good contrast between the dispersed PMMA phase (as we will see PMMA forms the dispersed phase up to 50 vol%) and the PS matrix, it is hard to find suitable etching conditions for selective dissolution of the PMMA phase. Both polymers, PS and PMMA, have similar solubility behavior. When the cut surfaces of the extruded strands were etched in acetic acid for 4 days at 60 °C to dissolve PMMA phase [28] the originally flat cut became convex and the material very brittle [27]. The SEM analysis of the etched cut surfaces revealed sometimes the expected particle-matrix morphology but in other cases strange, non-evaluable structures. Different solvent mixtures could not solve the problem. Only trifluoroacetic acid did etch the PMMA phase satisfactorily, however, it destroys and dissolves also the siloxane network formed during mixing. Finally we observed that treating the cut surface in oxygen plasma etches the PMMA phase resulting in sufficient contrast for SEM analysis.

In binary mixtures of SCA with PS–COOH or PMMA–NH_2 the coupling agent is finely distributed when the concentration is smaller than 5 vol%. Soft structures in the range of 50 nm in PS–COOH were detected by AFM. In case of PMMA–NH_2 it was almost not possible to detect any heterogeneities by AFM, indicating good compatibility or even partial miscibility. However, when the concentration is raised to 25 vol% large SCA domains in the size up to 20 μm (in PS) or 5 μm (in PMMA) are visible. We assume that during the processing crosslinking occurs in the SCA phase. Since at high concentrations the coalescence probability increases, large crosslinked domains are formed which can not be redispersed under the used shearing conditions.

PS–COOH/PMMA–NH_2 blends prepared with and without SCA in stoichiometric ratio (with respect to the functionality) of PS/PMMA/SCA = 80/20/1.5 vol% at various times of mixing of 5, 10, or 30 min showed similar morphologies. Dispersed PMMA particles with diameters of 50–200 nm were formed [27]. Additionally, larger particles (0.5–1 μm) were also observed in all cases. When extending the mixing time from 10 to 30 min no improvements in the phase morphology could be reached. Therefore, a mixing time of 10 min was taken as standard. Furthermore, different mixing sequences like premixing the SCA with one polymer before adding the other did not influence the morphology. Therefore, all other blends were prepared by melt mixing all components in one step.

To obtain more coarse morphologies or even phase inversion, blends were prepared with increasing PMMA content. This should allow a more easy detection of the effect of coupling agents on the morphology of the blends. The SCA content was raised to 3 vol% compared to 1.5 vol% in the stoichiometric blend. When the PMMA content is increased the blends had to be prepared at slightly higher temperatures (T was raised from 180 to 200 °C) in order to reduce the viscosity to stay in the operation limit of the Micro-Compounder. Fig. 4 shows the morphology of extruded blend samples treated with O_2 plasma. The plasma attacks all phases but PMMA degrades faster than PS. PMMA appears darker in images with a rough inner structure. It was not possible to detect the SCA phase by this method unambiguously but sometimes non-etched domains in the size of a few μm resisted which may be crosslinked SCA domains. The presence of SCA (with or without additional Pt catalyst) did not influence the size of the dispersed PMMA particles (Fig. 4(a)–(c)). Surprisingly, the dispersed particle size became even smaller when the content of PMMA is increased from 20 to 50 vol% (Fig. 4(d) and (e)) in the blends. Even though a reaction between PS–COOH and PMMA–NH_2 resulting in a block-copolymer formation can not be expected under our mixing conditions favorable interactions between the amino and the carboxylic group (like salt formation, hydrogen bridges) may cause the rather fine morphology in these blends. In accordance with [8], we were not able to detect any reaction between PS–COOH and PMMA–NH_2 by direct spectroscopic methods or indirect methods like SEC or rheological measurements, also not in the presence of Pt catalyst.

Overall, the influence of SCA on the blend morphology is rather small. Only near to the phase transition concentration some effects can be detected. Blends with a volume ratio PMMA/PS = 50/50 exhibit a particle-matrix structure with PS–COOH as matrix and dispersed PMMA–NH_2 particles. When SCA is present, which is visible in the AFM phase contrast images shown in Fig. 5 as dark spots (100 to few 100 nm in size, but also as bigger domains in the μm-scale), first signs of agglomeration appear: the average particle size increases and agglomerated, continuous phase-like structures are visible, especially in presence of the platinum catalyst (Fig. 5(c)).

At a content of 60 vol% of PMMA the blend morphology is changed to a co-continuous structure. Without SCA beside to the co-continuous features still particular distributed PMMA is visible. When comparing the images of Fig. 6(a) with Fig. 6(b) the strong influence of the

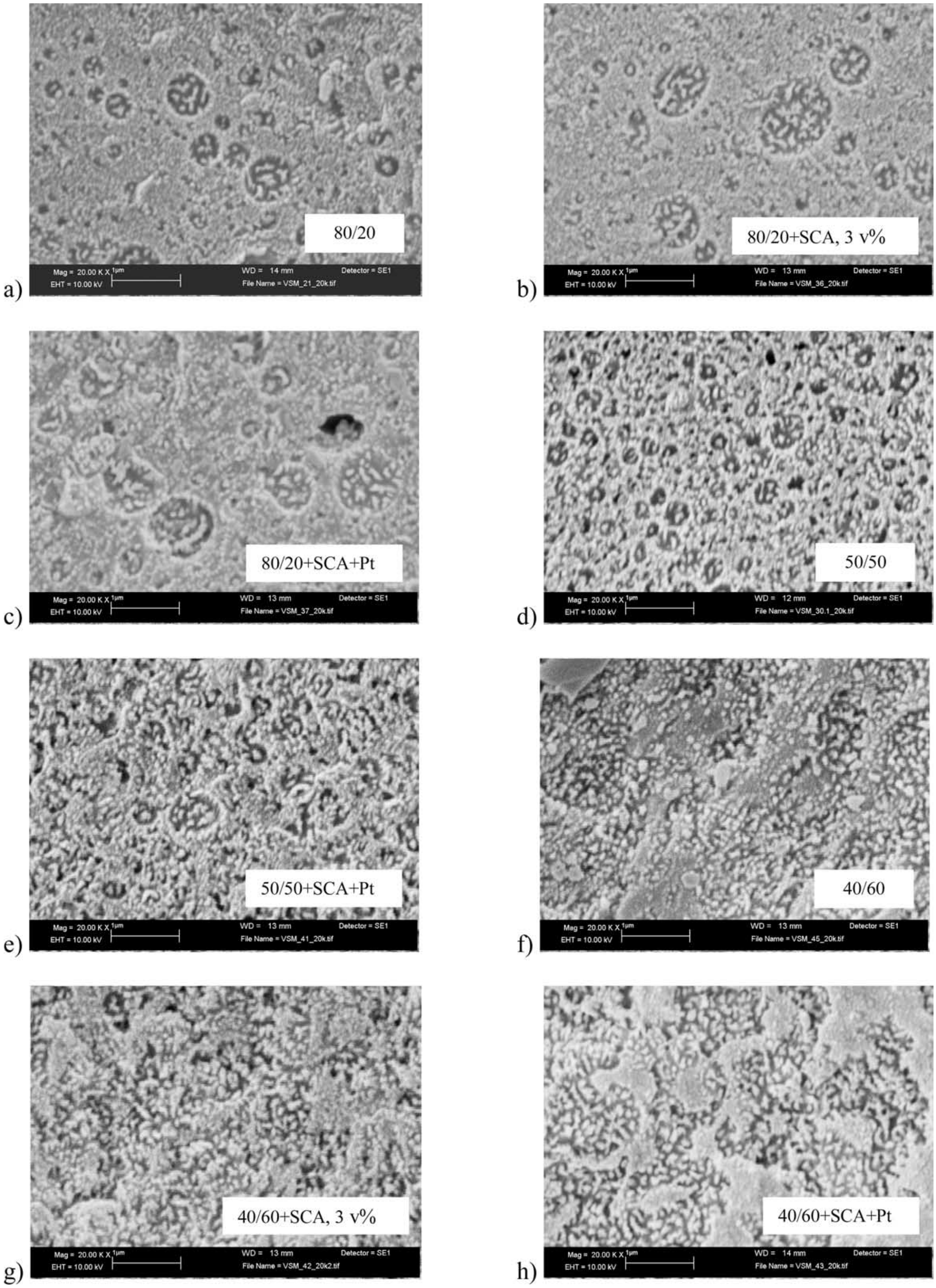


Fig. 4. SEM of O_2-plasma etched cuts of (a) PS–COOH/PMMA–NH_2, 80/20, 180 °C; (b) like a with SCA; (c) like b with Pt; (d) PS–COOH/PMMA–NH_2, 50/50, 190 °C; (e) like d with SCA and Pt; (f) PS–COOH/PMMA–NH_2, 40/60, 200 °C; (g) like f with SCA; (h) like g with Pt. (Pt = 20 μL, SCA = 3 vol%, frame size $5.7 \times 4.5\ \mu m^2$).

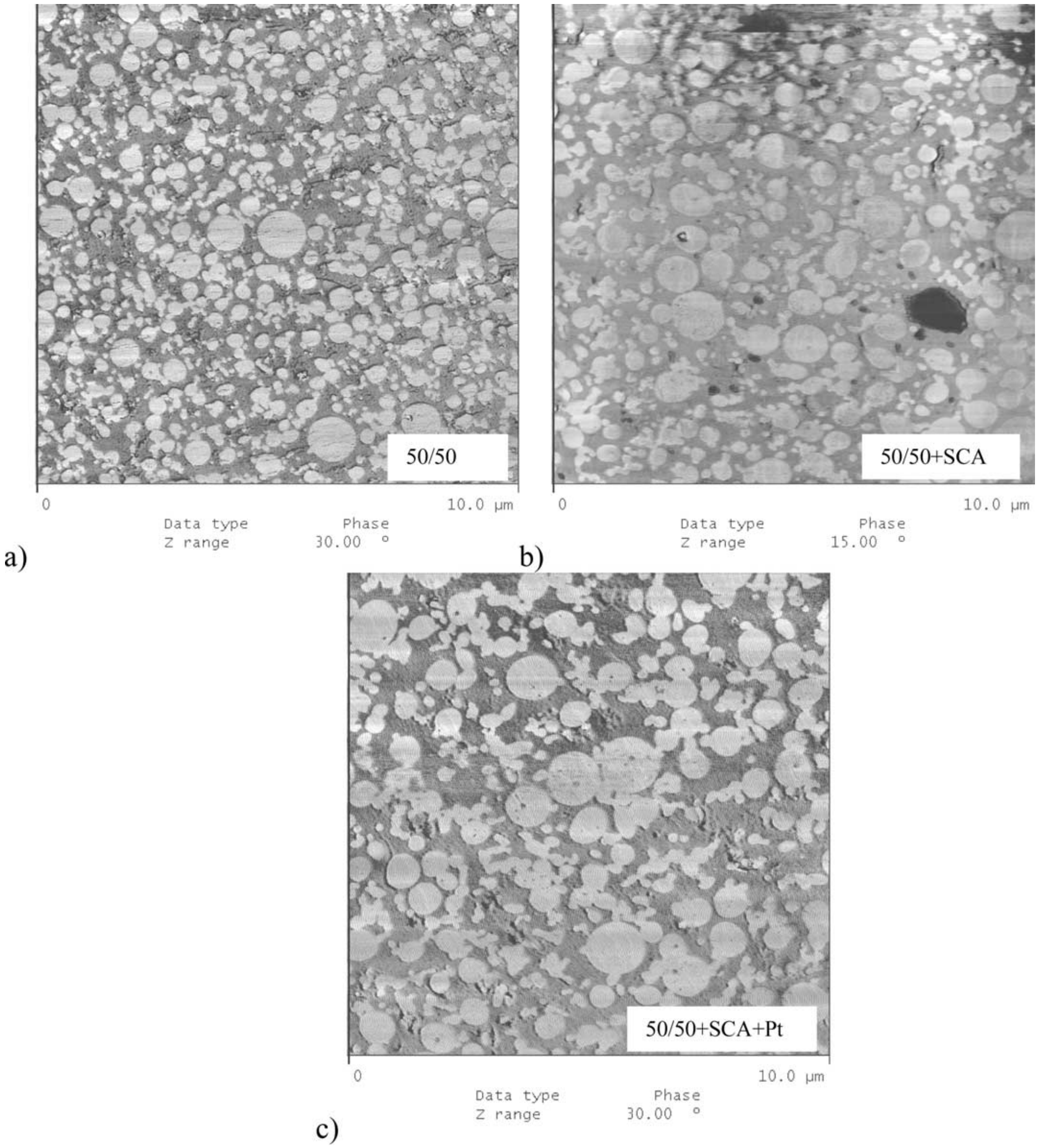


Fig. 5. AFM images in phase contrast mode of (a) PS–COOH/PMMA–NH_2 = 50/50 (vol%); (b) like a with SCA; (c) like a with SCA + Pt (frame size 10 × 10 μm^2).

processing becomes clear. At 190 °C the formed domains are smaller and the particle structure is dominating. At 200 °C bigger particles are formed and a high amount of the PMMA phase shows continuity. In the presence of SCA without or with additional Pt catalyst the spherical structures disappear completely and nice co-continuous morphologies are observed (Fig. 6(c) and (d)).

One goal was to locate the SCA in the interface between the two polymers blended. However, we were not able to detect SCA layers along the phase boundaries. A large amount of the 3 vol% SCA undergoes a strong phase separation forming big crosslinked domains (Fig. 6(c)). Parallel to that we observed small soft SCA particles distributed in both phases and partially at the interface. This became especially clear in samples annealed in quiescent melt at 200 °C for 30 min (Fig. 7(b)). Under these conditions the co-continuous morphologies shown in Fig. 6 are lost and phase inversion appears with PMMA forming the matrix and dispersed PS domains with a very broad size distribution ranging from 100 nm to 10 μm, independent of the presence of SCA or Pt catalyst. Parallel to that SCA particle become detectable in the size of 20–200 nm located to a large amount at the PS/PMMA interface.

Under shear the co-continuous structure is stable, as shown in Fig. 7(a) for the SCA and platinum containing blend prepared by melt mixing at 200 °C for 30 min.

The crosslinking of the SCA during processing was proven by the changed solubility. The blend solution of PS–COOH/PMMA–NH_2/SCA/Pt (40/60/3 vol%) in toluene is slightly turbid but a quantitative separation of the insoluble part was not possible. In order to quantify and analyse the crosslinked structures blends were prepared with higher

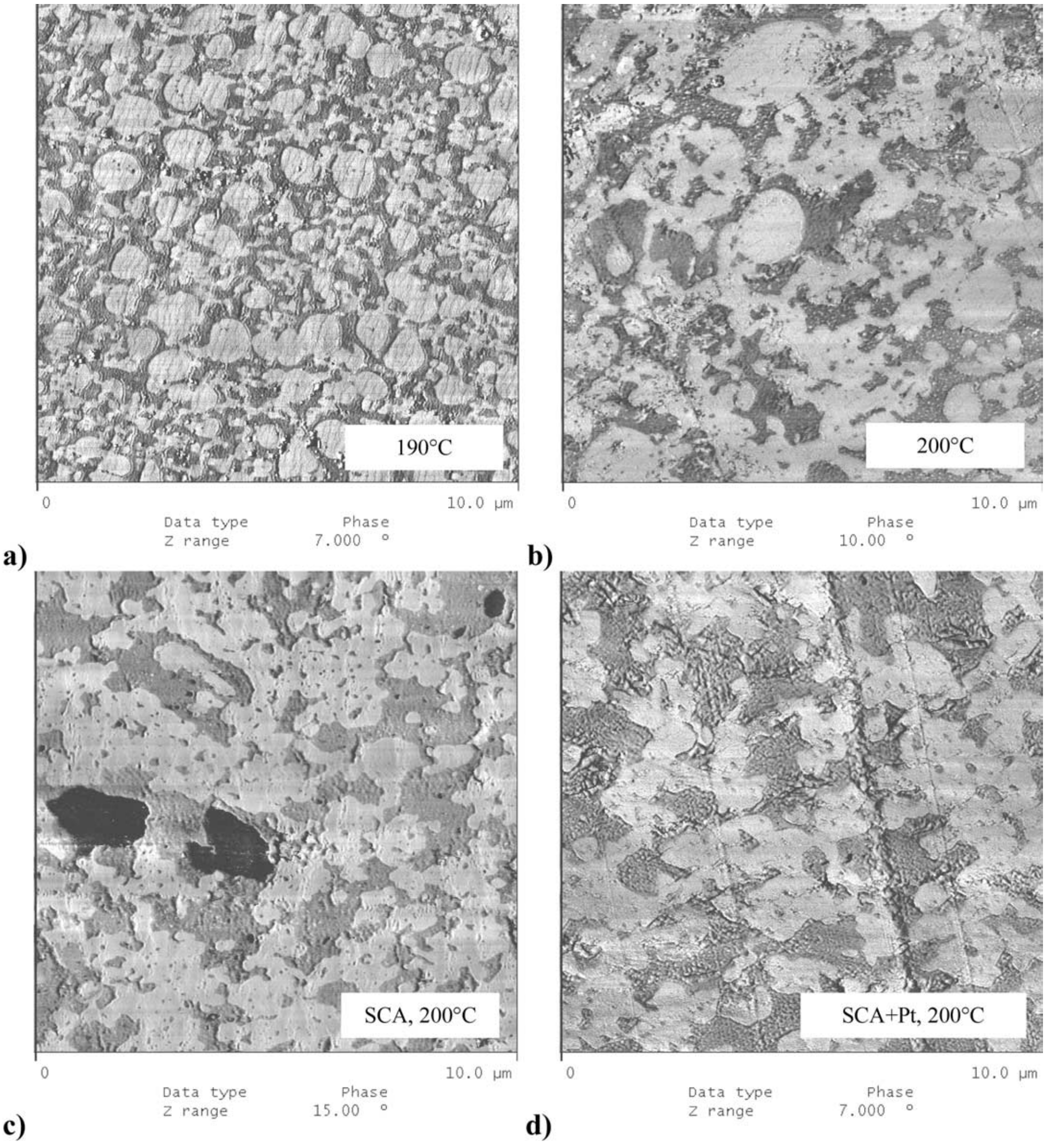


Fig. 6. AFM images in phase contrast mode of (a) PS–COOH/PMMA–NH_2 = 40/60 (vol%) prepared at 190 °C; (b) like a prepared at 200 °C; (c) like b with SCA; (d) like b with SCA + Pt (frame size $10 \times 10\ \mu m^2$).

content (10 vol%) of SCA with a PS–COOH/PMMA–NH_2 composition of 80/20 as well as 40/60 vol%, where the blends exhibits particle-matrix and co-continuous morphologies, respectively. Despite the higher content of coupling agent no remarkable changes are observed in the blend morphologies, except more large SCA domains are visible in both blends (80/20/10 and 40/60/10 vol%) which may be caused by the higher viscous material formed due to crosslinking and/or grafting during processing, as it was discussed earlier for PS–COOH/PA–NH_2/SCA blends [26]. The solution in toluene (0.5 g/8 mL) of the blend 80/20/10 vol% shows turbidity, the material in the composition 40/60/10 vol% forms a gel. After filtration with a PTFE membrane (pore size 0.2 μm) the gel content could be determined to be about 5%, and in the presence of platinum the gel content was ca. 10%, which is about the amount of the SCA present in the blend. FTIR analysis of the insoluble part qualitatively showed the presence of all blend components including PS, PMMA, and SCA (Fig. 8). The bands at 1005 and 792 cm^{-1} correspond to Si–O–Si bonds, 1605 cm^{-1} is characteristic for the aromatic stretching band of PS and SCA, and 1732 cm^{-1} characterizes the carbonyl ester group of PMMA. The intensity of the polymer signals is rather small. The strong phase separation of the SCA driven by its crosslinking reduces the surfaces area/volume ratio but only at the interface grafting can occur. The dilemma is that at low SCA contents, where no big SCA domains are formed, we are not able to separate the (crosslinked and grafted) SCA phase from the blend. The Si–H groups (ca. 2160 cm^{-1}) could not be detected, indicating its participation in crosslinking reaction through hydrolysis and condensation.

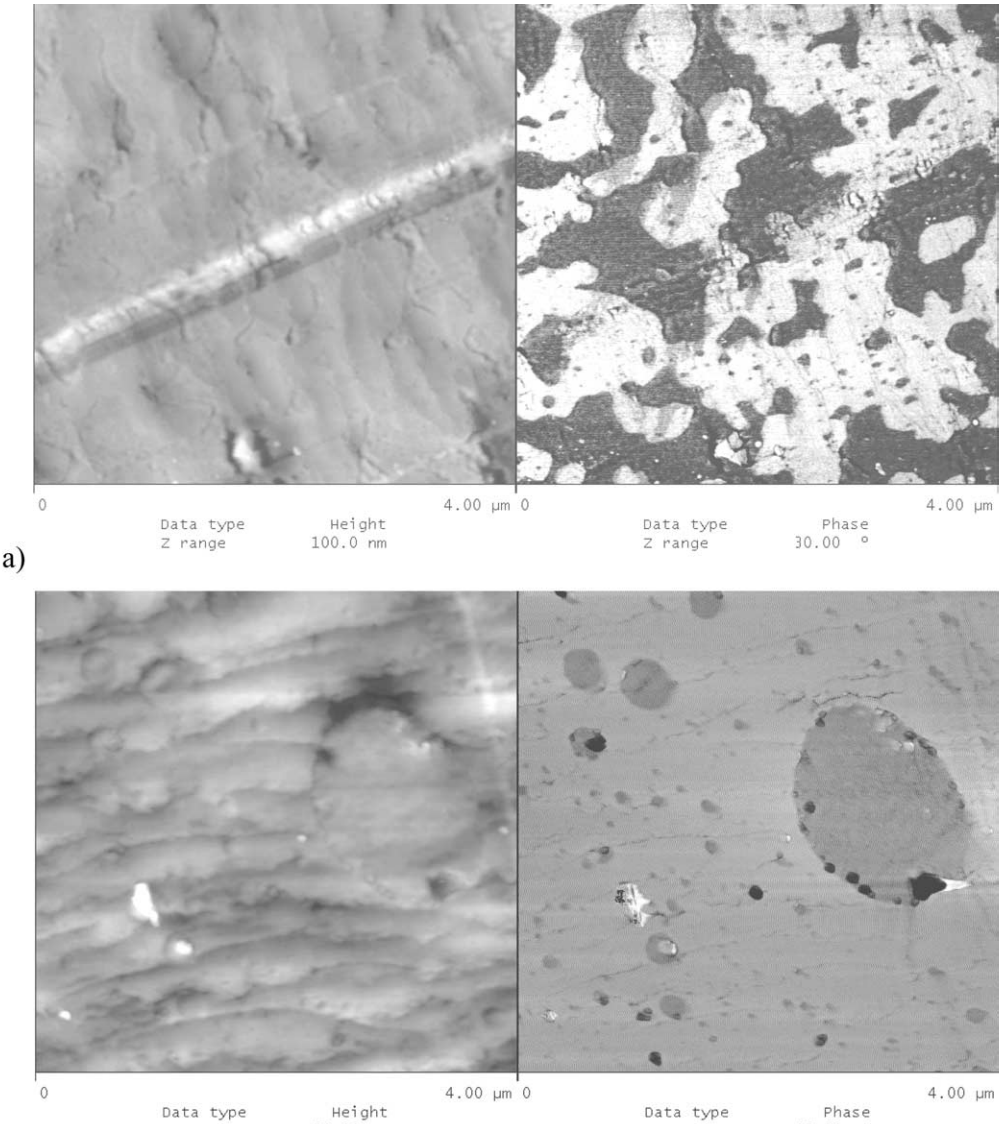


Fig. 7. AFM analysis of (a) PS–COOH/PMMA–NH_2/SCA/Pt, 40/60/3, melt mixed at 200 °C for 30 min; (b) PS–COOH/PMMA–NH_2/SCA, 40/60/3 melt mixed at 200 °C for 10 min and annealed at 200 °C for 30 min without shear (left: height profile, right: stiffness contrast; frame size 4×4 μm^2).

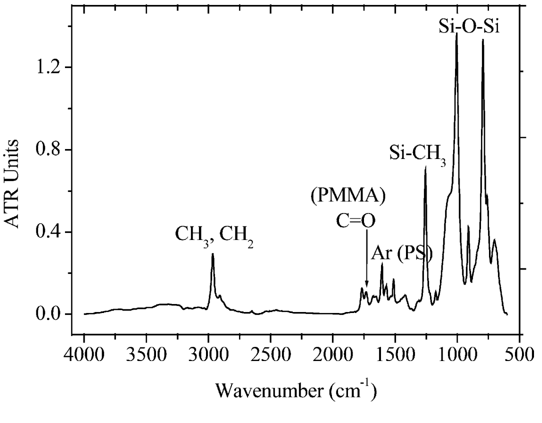


Fig. 8. FTIR spectrum of insoluble part in toluene of PS–COOH/PMMA–NH_2/SCA (40/60/10 vol%) blend.

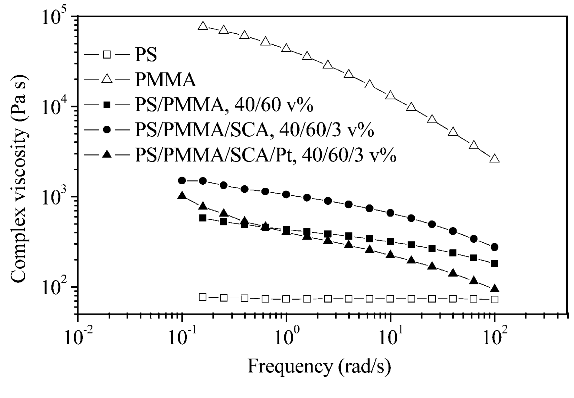


Fig. 9. Complex viscosity vs. frequency for PS–COOH/PMMA–NH_2 blends with and without SCA at 200 °C.

3.5. Rheological measurements of blends

The melt viscosity of PS–COOH and PMMA–NH_2 were measured at 200 °C (Fig. 9). Under these conditions, PMMA has much higher viscosity than PS, which is the reason that PS forms the matrix even at equivolume composition. PS shows viscosity values, which are nearly independent of frequency, whereas PMMA shows an intensive decrease vs. frequency. The addition of coupling agent SCA to PS–COOH or PMMA–NH_2 leads to an only very small increase in melt viscosity of the polymers ([27], not shown).The blend of PS–COOH/PMMA–NH_2 (40/60 vol%) has a viscosity in between the parent components (Fig. 9). With SCA (3 vol%) the viscosity is higher than that of the pure blend indicating enhanced interactions between the phases. In the presence of platinum catalyst the melt viscosity of the SCA containing blend is lowered at high measuring frequencies, but a stronger dependency of viscosity on frequency is observed. The viscosity increases when lowering the frequency which is indicative for co-continuous structure [29,30] and implies a higher perfectness of the co-continuity in presence of Pt catalyst. The lowered viscosity at high frequencies is probably caused by the lower interfacial area due to the higher perfectness and coarseness of the co-continuous structure (Fig. 4(g) and (h)).

3.6. DSC measurements of blends

PS–COOH used in the PS–COOH/PMMA–NH_2 blends has a glass transition temperature T_g of 102 °C and the T_g of PMMA–NH_2 is 116 °C. The T_g of PS is slightly lowered in the presence of SCA. In contrast, the T_g of PMMA slightly increases from 116 to 120 °C with 7 vol% (~6.3 wt%) of SCA (not shown). This indicates immiscibility of PMMA with SCA, though they have favorable interactions under the used conditions.

In the blends, the T_g's of both polymers could be separated, a sign of strong phase separation. In the pure PS–COOH/PMMA–NH_2 (40/60 vol%) blend, the T_g values of both components are increased slightly (Fig. 10, 104 and 125 °C for PS and PMMA, respectively). This indicates strong interactions between both components. At the same composition of the blend with 3 vol% of SCA the T_g's of the components remain same. However, with SCA + Pt catalyst, the T_g of PS is reduced to 96 °C and the T_g of PMMA reduces to its original value of about 120 °C, indicating stronger interactions of SCA towards PS and PMMA in the presence of catalyst. Such reduction in the T_g may be caused also by some degradation. However, when processing the pure components or the PS–COOH/PMMA–NH_2 blend under analogues conditions with or without Pt catalyst, no reduction in the molecular weight (GPC) or viscosity was detectable. PMMA–NH_2 itself showed at 220 °C a small increase in the molecular weight (without or with Pt), possibly caused by side reactions of the terminal amino group [19]. Therefore, we have chosen the blending temperatures as low as possible.

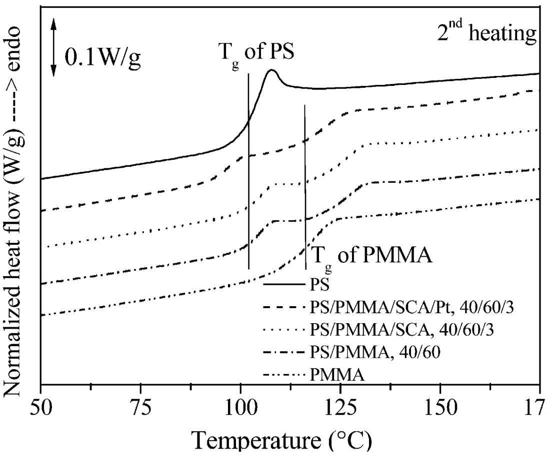


Fig. 10. Thermal analysis of PS–COOH/PMMA–NH_2 blends in the presence of SCA.

4. Summary and conclusions

A crosslinkable polysiloxane coupling agent (SCA) was successfully prepared by the functionalization of a methylhydrosiloxane–dimethylsiloxane copolymer with an allyl ether modified oxazoline and oxazinone containing coupling agent. The crosslinkability of the SCA and its selective reactivity to amino and carboxylic moieties could be proven by means of model reactions.

In PS–COOH/PMMA–NH_2 model blends the SCA was used for the modification of the blend morphology and the polymer–polymer interface. During blend preparation the SCA crosslinks partially, if Pt catalyst is present the crosslinking seems to be almost complete. Beside crosslinking grafting to both polymer components occur. At 50/50 vol% composition of the PS–COOH/PMMA–NH_2 blend the addition of SCA and Pt caused the beginning of the formation of co-continuous structures. In PS–COOH/PMMA–NH_2 = 40/60 (vol%) completely co-continuous structures are formed when SCA is present while in absence of the SCA a combined morphology is observed consisting of particle and continuous structures. However, the effect of the SCA on the morphology is rather small.

Different methods were tried to detect the location of the SCA in the blends. By means of SEM on etched cut surfaces only larger domains could be detected, while only AFM revealed the possibility to observe all three-blend components simultaneously. However, it was not possible to detect SCA interlayers between the PS and PMMA phases. Beside to big SCA domains small particles in the range of 50–200 nm could be observed in both polymer phases and at the polymer/polymer interface, especially at samples annealed in the molten state without shearing. Otherwise, the change from the co-continuous structure to a particle-matrix one during this annealing shows that the stabilizing effect of the SCA in these blends is rather poor.

However, the new SCA structures may be used in other, more reactive blend systems. When one succeeds with the approach to locate the SCA in the interface of co-continuous structures, such morphologies combined with the cross-linkability of the interface may be interesting for controlling the blend properties like its diffusion behavior. Furthermore, such SCA structures may be suitable for grafting of polymers and other organics on solid surfaces.

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References

[1] Anastasiadis SH, Gancarz I, Koberstein JT. Macromolecules 1989;22(3):1449–53.

[2] Sundararaj U, Macosko CW. Macromolecules 1995;28(8):2647–57.

[3] Hu W, Koberstein JT, Lingelser JP, Gallot Y. Macromolecules 1995;28(15):5209–14.

[4] Macosko CW, Guegan P, Khandpur AK, Nakayama A, Marechal P, Inoue T. Macromolecules 1996;29(17):5590–8.

[5] Kim JR, Jamieson AM, Hudson SD, Manas-Zloczower I, Ishida H. Macromolecules 1998;31(16):5383–90.

[6] Adedeji A, Lyu S, Macosko CW. Macromolecules 2001;34(25):8663–8.

[7] Koning C, Duin MV, Pagnoulle C, Jerome R. Prog Polym Sci 1998;23:707–57.

[8] Orr CA, Cernohous JJ, Guegan P, Hirao A, Jeon HK, Macosko CW. Polymer 2001;42(19):8171–8.

[9] Kim JK, Kim S, Park CE. Polymer 1997;38(9):2155–64.

[10] Charoensirisomboon P, Inoue T, Weber M. Polymer 2000;41(12):4483–90.

[11] Yin Z, Koulic C, Pagnoulle C, Jerome R. Macromolecules 2001;34(15):5132–9.

[12] Majumdar B, Keskkula H, Paul DR, Harvey G. Polymer 1994;35(20):4263–79.

[13] Charoensirisomboon P, Inoue T, Weber M. Polymer 2000;41(18):6907–12.

[14] Dedecker K, Groeninckx G. Polymer 1998;39(21):4993–5000.

[15] Jakisch L, Komber H, Böhme F. J Polym Sci Part A: Polym Chem 2003;41:655–67.

[16] Baumert M, Mülhaupt R. Macromol Rapid Commun 1997;18:787–94.

[17] Malz H, Komber H, Voigt D, Pionteck J. Macromol Chem Phys 1998;199:583–8.

[18] Sadhu VB, Pionteck J, Voigt D, Komber H, Voit B. Macromol Symp 2004;210:147–55.

[19] Sadhu VB, Pionteck J, Voigt D, Komber H, Fischer D, Voit B. Macromol Chem Phys 2004;205:2356–65.

[20] Magonov SN, Elings V, Whangbo MH. Surf Sci 1997;375:L385–L91.

[21] Marciniec B, Gulinski J, Kopylova L, Maciejewski H, Grundwald-Wyspianska M, Lewandowski M. Appl Organomet Chem 1997;11:843–9.

[22] Coqueret X, Wegner G. Organometalics 1991;10:3139–45.

[23] Malz H. Synthesis of end-functionalized polystyrenes and polypropylenes, PhD Thesis, Technical University of Dresden, Germany; 1999.

[24] Chujo Y, McGrath JE. J Macromal Sci Pure Appl Chem 1995;A32(1):29–40.

[25] Wilczek L, Chojnowski J. Macromol Chem 1983;184:77.

[26] Sadhu VB, Pionteck J, Pötschke P, Jakisch L, Janke A. Macromol Symp 2004;210:165–74.

[27] Sadhu VB. Creation of crosslinkable interphases in polymer blends by means of novel coupling agents, PhD Thesis, Technical University of Dresden, Germany; 2004.

[28] Jeon HK, Kim JK. Macromolecules 2000;33:8200–10.

[29] Pötschke P, Paul DR. Macromol Symp 2003;198:69–82.

[30] Pötschke P, Paul DR. J Macromol Sci Part C: Polym Rev 2003;C43:87–141.