Creation of Crosslinkable Interphases in Polymer Blends

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Veera Bhadraiah Sadhu is dedicating this work to his teacher Prof. A. Varada Rajulu, Sri Krishnadevaraya Univ. Anantapur, on the occasion of achieving 'the best teacher' award in 2003.

Summary: A new type of bi- and trifunctional coupling agents containing 2-oxazoline and/or 2-oxazinone as well as hydrosilane moieties has been prepared by hydrosilylation of the corresponding allyl ether containing precursors with poly(methylhydro)siloxanes. In heterogeneous model blends based on mono-carboxylic acid terminated polystyrene (PS) and mono-amine terminated polyamide 12 (PA), the oxazoline and oxazinone units can selectively react with the carboxylic groups or amino groups, respectively. Under this mixing conditions the hydrosilane partially crosslinks.
The morphology development of the three-component blends under melt mixing conditions is a rather complex process. We have shown that the coupling agents are immiscible with the polymers and form their own phase. Under proper processing conditions they locate at least partially at the PS/PA interface and can be used for further modification of the blend interphase, e.g. for crosslinking by hydrolysis. This crosslinking can be accelerated by the addition of a Pt-catalyst during the melt mixing.

Keywords: blends; crosslinking; interface; morphology; polysiloxanes

Introduction

Most polymer blends are thermodynamically immiscible and produce multiphase morphological structures.[1] To improve the compatibility between the blend components and therefore the blend properties, reactive compatibilization has become significant commercial interest.[2] The formation of block or graft copolymers by coupling reaction between functional polymers is the key point for the compatibilization of different immiscible polymers and also for the improvement of the adhesion between polymer-polymer interfaces.[3] These in situ formed copolymers are required to locate at the interface between two phases to act as efficient compatibilizer by lowering the interfacial tension and stabilizing the morphology against

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coalescence. Though, the in-situ formed copolymers may be easily pulled out of the interfacial region,[4-6] depending on the kinetics of the interfacial reaction.[7,8] This is due to the thermodynamic and hydrodynamic instability caused by the amount of accumulated block or graft copolymers at the interface.[7]

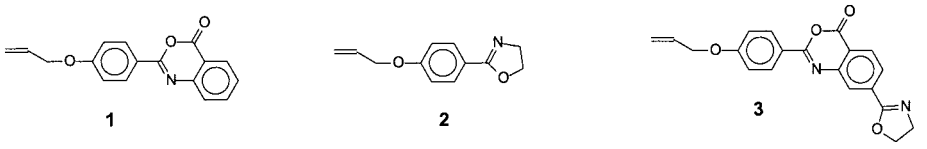
In this paper we focus on the creation of crosslinkable blend interphases by the use of novel types of poly(methylhydro)siloxane-containing coupling agents. Carboxylic acid terminated polystyrene (PS) and amine terminated polyamide 12 (PA) were chosen as model blend system. The new coupling agents contain oxazoline and/or oxazinone sites, which can react with the acid and amine functionalities, respectively, of the blend components. The preparation was done by hydrosilylation of the corresponding allyloxy-modified coupling agents[9,10] with poly (methylhydro)siloxanes. If the coupling agents react with both polymers of the blend, the remaining SiH bonds should locate at the interface and may be used for further modification reactions, e.g. for the creation of crosslinked and stable interphases. We studied the crosslinkability of the coupling agents, their reactivity to the blend components, their distribution in the blends, and their effect on the resulting blend morphology under different processing conditions.

Experimental

Materials

Carboxylic acid terminated polystyrene (PS, Mn = 28000 g/mol, PD = 1.68, functionality = 0.7) was prepared by the TEMPO-mediated free radical polymerisation using 4,4'-azo-bis-(4-cyanopentanoic acid) as an initiator.[11] To stabilize the product during processing the TEMPO living end group was removed by oxidation with m-chloroperbenzoic acid.[12] Mono-amine functionalised polyamide 12 (PA, M_n = 5000 g/mol, functionality of 250 mmol/Kg = 1) was received from Degussa AG. Poly(methylhydro)siloxane-co-dimethyl siloxane (1900-2000 g/mol, 25-30 mole% of MeHSiO), poly(methylhydro)siloxane (1500-1900 g/mol), and platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4 % platinum concentration) were received from Gelest ABCR.

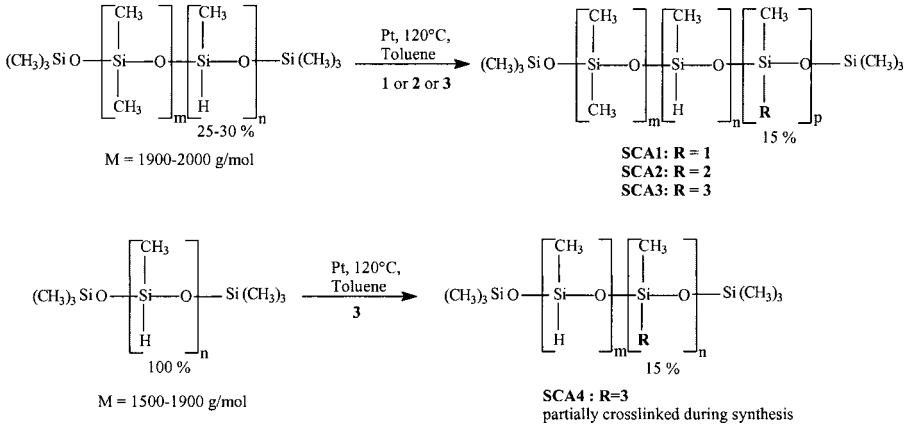
The allyloxy-containing coupling agents (Scheme 1) used in hydrosilylation reaction have been synthesized according to [9,10].



Scheme 1. Structure of the allyloxy-modified coupling agents used for hydrosilylation

Preparation of Polysiloxane-Containing Coupling Agents (SCA)

The hydrosilylated coupling agents are named SCA1 to SCA4. They were prepared according to Scheme 2.



Scheme 2. Hydrosilylation of various coupling agents (Scheme1: 1, 2 and 3) with different polysiloxanes

The synthesis of SCA3 proceeded as follows. To a dry three-neck round bottom flask fitted with a reflux condenser 9.6 g poly(methylhydro)siloxane-co-dimethyl siloxane and 3.2 g (15 mol % to Si-H) of the coupling agent 3 (Scheme 1) were added. The mixture was dissolved in 800 mL toluene and a catalytic amount of Platinum-divinyltetramethyldisiloxane complex (200 µL) was added. Dry air was purged through the reaction mixture for a couple of minutes. The reaction was allowed to proceed for 6 h at boiling. The toluene was removed by means of a vacuum rotary evaporator and the product was stored at lower temperatures.

The structure is confirmed by ^{1}H NMR in TFA-d_1: δ (ppm) 0.45 (CH_3Si), 0.5 ($OCH_2CH_2\underline{CH_2}Si$),

2.25 ($OCH_2C\underline{H}_2CH_2Si$), 4.21 ($OC\underline{H}_2CH_2CH_2Si$). 4.56 ($-CH_2N-$, oxazoline), 5.41 ($-OCH_2-$, oxazoline).

SCA1 and SCA2 were prepared analogously. The hydrosilylation of the coupling agent 3 (Scheme1) with poly(methylhydro)siloxane resulted in a partially crosslinked product. 45 % of the isolated product SCA4 were insoluble in toluene (24 h at room temperature).

Blend Preparation

The blends were prepared in a DACA Micro Compounder with a capacity of 4.5 cm^3 (200°C, 100 rpm, 10 min.). The blend composition was PS / PA / SCA = 80 / 15 / 5 (v%). The mixing was carried out by two processing methods. In the one-step mixing method all blend components were fed together to the Micro Compounder. In the two-step method PA and the SCA were mixed first and in a second step the corresponding amount of PA/SCA was mixed with the PS. The blends containing both SCA1 and SCA2 were prepared by premixing of PA with SCA1 and PS with SCA2. Every mixing step proceeded for 10 min. To catalyse the crosslinking sometimes Pt solution (20 µl) were added to the mixture.

Analysis

The ^1H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. Deuterated trifluoroacetic acid (TFA-d_1) was used as solvent. The morphology of the blends was investigated by scanning electron microscopy (SEM) using an SEM LEO 435 VP (Leo Elektronenmikroskopie) operating with an acceleration voltage of 5 to10 kV. The analysis was carried out on cryo cuts after chemical etching with trifluoroacetic acid for 4h at room temperature (TFA), which dissolves the PA phase and the non-crosslinked compatibilizer. All samples were sputtered with gold. Atomic force microscopy (AFM) was performed on smooth cryo-cuts by means of a NanoScope IV - Dimension 3100 (Veeco). 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[13] (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.

Results and Discussion

Synthesis of SCA and Model Coupling Reactions

The hydrosilylation reaction is the most widely used method for preparing organofunctional polysiloxanes starting from poly(methylhydro)siloxanes.[14] The reaction is usually catalysed by platinum complexes. In our approach, two model polysiloxanes were used for the reaction of allyloxy derivatives of various coupling agents in order to synthesize polysiloxane-containing coupling agents containing organofunctional groups in the side chain (Scheme 2). One has a low Si-H content (25-29 % of the monomer unit) and the second one consists of 100 % Si-H units. The reaction scheme and the detailed description of the syntheses of SCA3 as example are given in the experimental section.

To proof the selective reactivity of the coupling agent SCA3 has been melt mixed with the individual blend components in about stoichiometric composition of PA/SCA3 = 75/25 (v%) and PS/SCA3 = 95/5 (v%), respectively. Fig. 1 shows the ^{1}H NMR spectra (onsets) of SCA3 (a), PA (b), and their reaction product (c) and the proposed chemical structure of the reaction product. The strong reduction of the signal at 3.2 ppm (methylene protons neighboured to the amino endgroup) and the appearance of strong signals of oxazoline groups bounded next to the reacted oxazinone group (a' and b') indicates that an almost complete reaction the amino group occurred with the complementary oxazinone group. The decrease of Si-H (5.0 ppm) group concentration indirectly proves the crosslinkability of the polysiloxane coupling agents during melt mixing. This may be caused by the presence of moisture and the high temperatures (Scheme 3). The oxazoline groups remain stable under these conditions. We also tried to prove directly the coupling reaction of the oxazoline functional groups and carboxylic acid groups of PS in melt. Due to the higher molecular weight of PS and, therefore, the small amount on COOH-groups, and the overlapping of the peaks of the virgin components and the reaction product a direct proof was not possible. However, in earlier works the selectivity of the oxazoline-carboxylic acid reaction (and also of the oxazinone-amine reaction) was proven.[10,15]

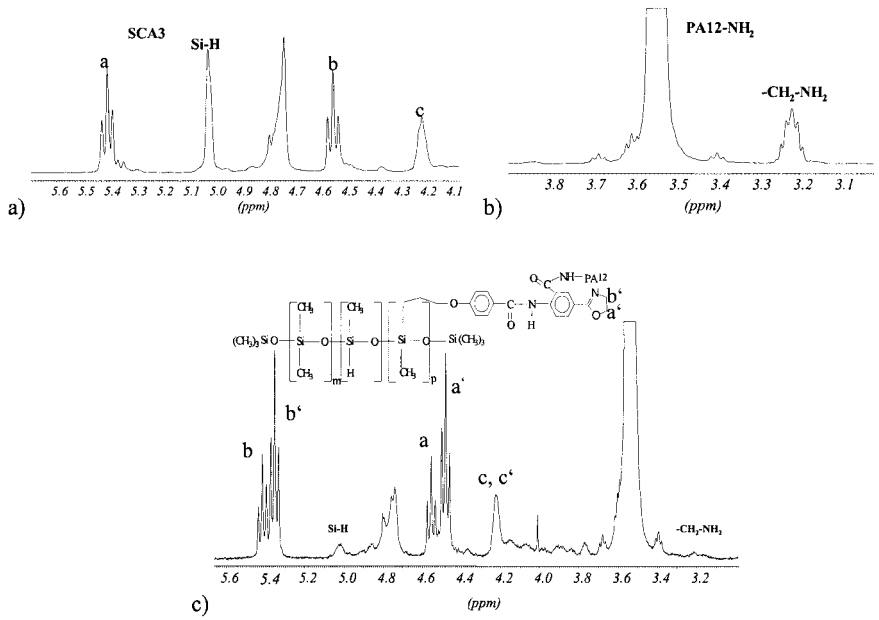


Fig 1. ^{1}H NMR spectra of a) the coupling agent SCA3, b) amino-terminated PA, and c) the coupling product between SCA3 and PA in melt. (measured in TFA-d_1).

Blend Morphology

AFM studies show that the SCA are immiscible with PA and PS and form an own phase. However, the size of the SCA3 is much smaller in PS (in the some 10 nm scale, not shown) than in PA where spheres in the size of 1 μm are visible (Fig. 2a). Such big SCA3 particles are not detectable in the PS/PA blend, neither after the one-step (Fig. 2b) nor the two step processing (not shown). The soft SCA3 (appearing dark in the phase contrast mode, right pictures) can be detected as small particles in the PS matrix (up to 200 nm size), within the PA particles in a some 10 nm scale (the detection is complicated by the overlapping with the partial crystalline structure of the PA), and also at the interface between PS and PA. In any case at least a partial location of the SCA (and therefore of the crosslinkable units) at the interface is possible.

SEM reveals that in the blends PA always forms the dispersed phase. Due to its rather low molecular weight (and therefore low viscosity) compared to the PS matrix and the favourable interactions between the amino and carboxylic groups of both blend components the particle size

is very small (200 – 500 nm, Fig. 3a). The addition of SCA1, SCA2, or SCA3 (Fig. 3b) results in a significant increase of the particle size with very broad size distribution (0.3 – 3 μm). We assume that the bulky functional groups of the SCA hinder interactions between the complementary carboxyl and amino groups of the blended polymers and that the rheological conditions in the blend components are changed due to the addition of the SCA and their reactions with the blend components. The low viscous SCA3 may even hamper the load transmission from the matrix to the dispersed phase in the shear field during melt mixing. Studies on the influence of the SCA on the rheological properties of the blends and their components are in progress.

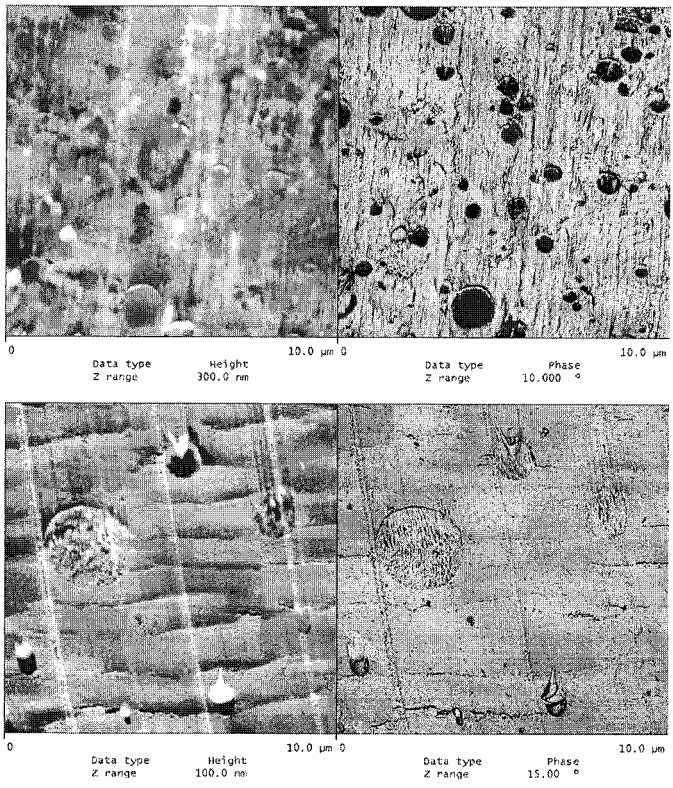


Fig. 2: AFM analysis of a) PA/SCA3 = 75/25 (v%) and b) PS/PA/SCA3 = 80/15/5 (v%)

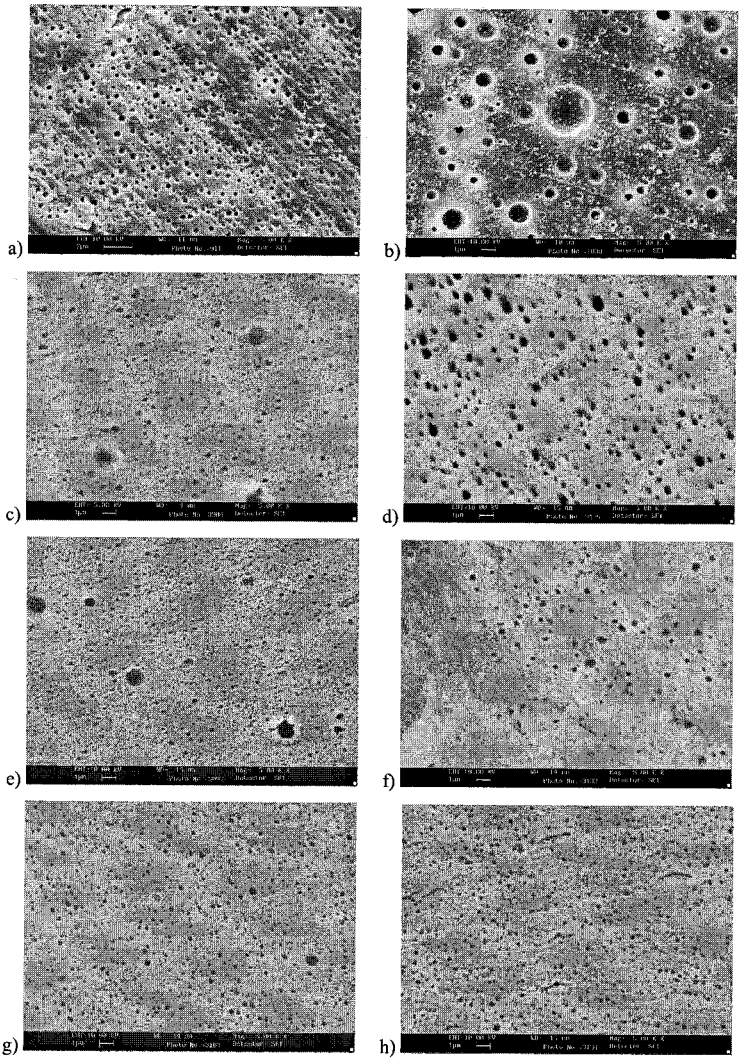
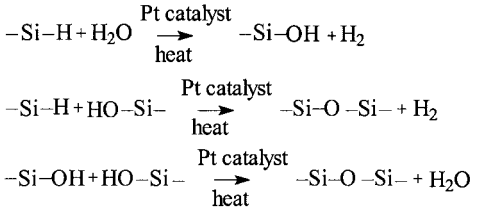


Fig. 3: SEM of PA/PS/SCA blends in dependence on the composition and processing conditions (frame size 24 × 17 μm; a) PA/PS = 84/16, etched cut; b) PA/PS/SCA3, one-step mixing; c) PA/PS/SCA3, two-step mixing; d) like b) with Pt; e) like c) with Pt; f) PA/PS/SCA1/SCA2 with Pt; g) PA/PS/SCA4, two-step mixing h) PA/PS/SCA4, two-step mixing with Pt).

When the SCA3 is premixed with the PA (which enables the reaction between components) and than PS is added the morphology is finer than in the one-step process (Fig. 3c), where the SCA3 locates favourably in the PS phase due to the better compatibility. The addition of Pt catalyst, which favours the crosslinking of the hydrosilane units according to Scheme 3, results in finer blend structures as well in the one-step process (Fig. 3d compared to Fig. 3b) as in the two-step process (Fig. 3e compared to Fig. 3c). The increased crosslinking density seems to favour a fine distribution of the PA phase. Even a mixture of PA/SCA1 with PS/SCA2 exhibits a rather fine morphology but only when Pt is added (Fig. 3f). The Pt-catalysed crosslinking enables the coupling between SCA1 and SCA2, which are chemically bound to the PA or PS, respectively. Thus the adhesion between both blend components is enhanced and a better dispersion during the melt mixing is possible. When the partially pre-crosslinked SCA4 was used a very fine distribution of the PA phase is observed (Fig. 3g), indicating similar good adhesion between both polymers. An increased crosslinking density due to the addition of Pt hardly influences the blend morphology (Fig. 3h). The pre-crosslinking and the additional crosslinking during processing seem to be sufficient for good interfacial adhesion.



Scheme 3: Crosslinking reactions of polyhydrosilanes during processing

Summary and Conclusions

The use of polymeric hydrosilane containing coupling agents (SCA), which can prepared by hydrosilylation of allyloxy containing functional precursors with polyhydrosiloxanes, represents an attractive way for the modification of the interface in heterogeneous polymer blends, e.g. by crosslinking. We investigated the influence of the novel type of coupling agents on the morphology of reactive PS/PA blends. The processing conditions and the degree of polysiloxane crosslinking, which can be increased by the addition of Pt catalyst, strongly influence the

dispersibility of the minor PA phase in the PS matrix. To achieve fine dispersions good adhesion between the phases is necessary. This can be reached by premixing the SCA with the complementary reactive polymers followed by blending the premixed components. Crosslinking of the SCA, which is in any cases at least partially located at the PS/PA interface, supports the load transfer from the matrix to the particles in the shear field during melt mixing, thus causing fine dispersions of the PA phase in the PS matrix.

The described mixing mechanism offers the opportunity to locate reactive sites at the interface of heterogeneous blends suitable for crosslinking and other chemical modification. To study the effects of such modifications will be a part of our future work.

Acknowledgements

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