

Applications of an Azide Sulfonyl Silane as Elastomer Crosslinking and Coupling Agent

L. GONZÁLEZ, A. RODRÍGUEZ, J. L. DE BENITO, A. MARCOS-FERNÁNDEZ

Instituto de Ciencia y Tecnología de Polímeros (C.S.I.C.), Juan de la Cierva, 3-28006 Madrid, Spain

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ABSTRACT: A new coupling agent, a silane sulfonyl azide has been synthesized. This agent was capable of reacting with either saturated or unsaturated rubbers. In unsaturated rubbers reinforcement with mineral filler was improved when compared with a commercial silane coupling agent.

For a saturated rubber, the response when this agent was added to the formulation was superior to the response reached using only a conventional peroxide to crosslink the polymer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1353–1359, 1997

Key words: azide sulfonyl silane; elastomer crosslinking; elastomer coupling agent

INTRODUCTION

For many years silane coupling agents have been used to improve the reinforcing response of mineral fillers when incorporated into polymeric matrices. These substances can make available two functional groups, an organofunctional and a sili-cofunctional group, the latter preferably being an alkoxy group, which reacts with the surface of the filler. In contrast, the organofunctional group, bonded via a short alkyl chain to the silicon atom, can be of a highly diversified nature, such as $-\text{SH}$, $-\text{NH}_2$, $-\text{CH}=\text{CH}_2$, etc., which reacts with the polymer during the curing process.^{1–5} In this work we study a new coupling agent type that presents greater reaction possibilities and hence is more versatile in relation to the nature of the polymer: silane sulfonyl azides. These are capable of reacting with any polymer that possesses carbon–hydrogen bonds. In any rubber type, in the presence of a mineral filler, the azide group reacts with the polymeric matrix whereas the trialkoxy-

silane moiety is able to react with the silanol groups at the filler surface. In the absence of filler, once the silane is grafted to the polymer backbone through the azide group reaction, the alkoxy-silane groups hydrolyze in the presence of water and self-condensation with silanol groups of neighboring chains takes place to form $\text{Si}-\text{O}-\text{Si}$ crosslinks. This condensation reaction can be favored with dibutyltindilaurate.

This article reports on the behavior of sulfonyl azide silanes (synthesized in our laboratory) in styrene-butadiene copolymer rubber (SBR) compounds in the absence and presence of amorphous silica and in a fully saturated rubber, ethylene-propylene copolymer (EPM).

EXPERIMENTAL

Materials

The first elastomer used was SBR, manufactured by Bayer under the trade name Krylene 1502. The styrene content was 23.5 wt %. The monomers were randomly arranged in the chain and were an emulsion polymerized rubber type. The second elastomer

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used was a Dutral Co 054 EPM from Enichem Elastomeri (ethylene/propylene ratio 58/42%).

Silane A 1100, 3-amine propyl triethoxysilane was supplied by Union Carbide. *p*-Carboxy benzenesulfonyl chloride was supplied by Aldrich. Sodium azide was from Panreac and the thionyl chloride was from Fluka.

Analytical Methods

An IR Perkin–Elmer spectrometer (model 457) was used to record the IR spectra. ¹H-NMR spectra were recorded with a 90-MHz Bruker spectrometer.

Compounding and Test Methods

Compounds were prepared by mixing the silane and the polymer in a Brabender type internal mixer to achieve elevated temperatures, with subsequent addition of curative ingredients on a 305-mm two-roll laboratory mill (friction ratio 1 : 1.4) using conventional procedures.

Measurements of the curing degree were conducted in a Monsanto Moving Die Rheometer (model MDR 2000 E) and the compounds were cured at their respective optimum times (*t*₉₇, time to 0.97 (MH-ML)).

Physical properties were determined on test specimens cured at 160°C at their optimum curing times as follows: tensile properties according to ISO 37-1977, tear strength according to ISO 816-1983, and the other physical properties to national standards.

Determination of Crosslink Density

The volume fraction of polymer in the swollen sample, *V*_r, was determined in the vulcanizates by means of equilibrium swelling in toluene at 30°C. The equilibrium swelling ratio can be used to calculate an absolute value for crosslink density, using the Flory–Rehner equation. In this work the value *V*_r was used to represent the crosslink density of the cured compounds.

Preparation of *p*-(Carbonyl azide) Benzenesulfonyl Azide

A solution of 10.47 g (0.047 mol) of *p*-carboxy benzenesulfonyl chloride in 50 mL thionyl chloride with 1 mL *N,N'*-dimethyl formamide was heated under constant stirring to 100°C and held at that temperature for 1 h. Subsequently the excess thionyl chloride

was distilled, and a *p*-(chlorosulfonyl) benzoyl chloride precipitate was obtained (yield 85%).

Five grams (0.114 mol) of sodium azide dissolved in 50 mL distilled water were added dropwise under stirring to a solution of 8.54 g (0.036 mol) of *p*-(chlorosulfonyl)benzoyl chloride in 100 mL acetone at a temperature below 5°C. This temperature was maintained for 1 h. The solution obtained was poured on ice giving rise to a precipitate, which was filtered and washed several times with distilled water. The product was dissolved in 25 mL acetone and reprecipitated by pouring it into a mix of water and ice; it was then filtered and vacuum dried at room temperature. The end product was a fine, salmon-colored powder. The yield of the reaction was practically quantitative.

ANAL. Calcd for C₇H₄N₆SO₃: C, 33.33%; H, 1.56%; N, 33.33%; S, 12.69%. Found: C, 33.12%; H, 1.65%; N, 33.29%; S, 12.82%. IR (KBr pellet): 3095 cm⁻¹, C—H aromatic ring stretching; 2180 cm⁻¹, asymmetric stretching of N₃ in —CON₃; 2140 cm⁻¹, asymmetric stretching SO₂—N₃; 1660 cm⁻¹ stretching C=O; 1190–1165 cm⁻¹, asymmetric SO₂—N stretching and symmetric —N₃ stretching. ¹H-NMR for (CD₃)₂CO/Cl₄C: δ = 8.14 (*d*) (—CH=C(SO₂N₃)—CH—); δ = 8.31 (*d*) (—CH=C(CON₃)—CH—).

Preparation of *N*-(3-(Triethoxy silyl)propyl)-*N'*-(*p*-benzenesulfonyl azide) urea (Si-BSA)

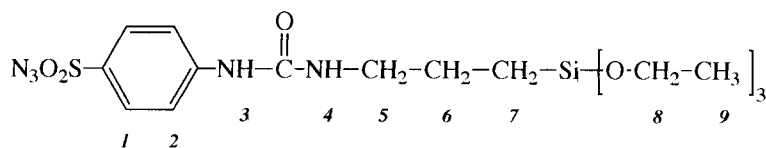
The next step was implementing the Curtius transposition. A solution of 2.52 g (0.010 mol) of *p*-(carbonyl azide) benzenesulfonyl azide in 250 mL dry benzene was heated and refluxed for 5 h. A sample was taken and IR analyzed, which demonstrated total conversion into *p*-isocyanate benzenesulfonyl azide. To prevent hydrolysis of the isocyanate group in the reactor, 2.21 g (0.01 mol) silane A-1100 were added at 50°C, which produced a flashy reaction.

The benzene was eliminated by vacuum distillation. The reaction product was an oily, greenish-yellow liquid.

ANAL. Calcd for C₁₆H₂₇N₅SO₆Si: C, 43.14%; H, 6.06%; N, 15.73%; S, 7.19%. Found: C, 42.87%; H, 6.52%; N, 15.31%; S, 7.09%. IR (KBr pellet): 2980 cm⁻¹, O—CH₂— stretching; 2120 cm⁻¹, asymmetric N₃ stretching; 1685 cm⁻¹, free C=O stretching; 1660 cm⁻¹ associated C=O stretching; 1540 cm⁻¹, symmetric N—C=O stretching; 1105–1085 cm⁻¹, Si—O stretching of the Si—O—CH₂—CH₃ groups (doublet). ¹H-NMR for Cl₃CD/DMSO-*d*₆: δ (H₁) = 7.89 (*d*); δ (H₂) = 7.72 (*d*); δ (H₃) = 9.23 (*s*); δ (H₄) = 6.52 (*t?*); δ (H₅)

= 3.13 (*q*?); δ (H_6) = 1.58 (*q*); δ (H_7) = 0.62 (*t*); δ (H_8) = 3.79 (*q*); δ (H_9) = 1.21 (*t*).

All the analytical results confirm the following structure of the compound:



RESULTS AND DISCUSSION

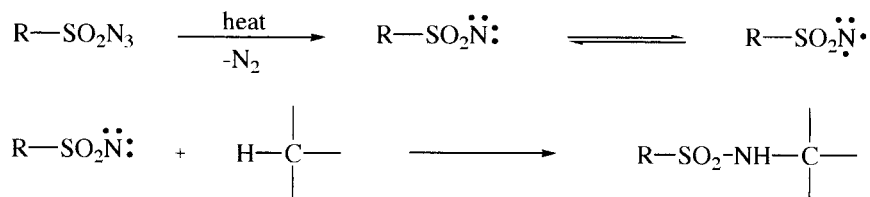
Possible Mechanisms of Chemical Reactions by Si-BSA

The new coupling agent possesses two reaction sites of different reactivity that were assessed from a theoretical point of view. Then the agent was incorporated into filled and unfilled polymeric matrices.

Sulfonyl Azide Chemistry

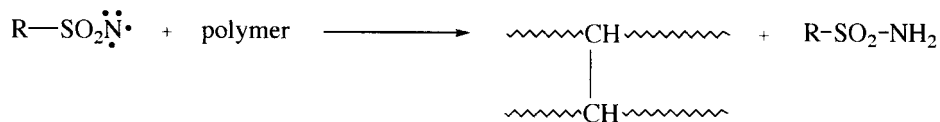
In the literature copious references can be found explaining the reaction mechanism of the differ-

ent azide types, particularly that of sulfonyl azide. The product decomposes thermally or under UV radiation,⁶⁻¹² thereby losing a nitrogen molecule and forming a nitrene group capable of extracting a hydrogen atom or inserting into a saturated carbon-hydrogen bond. This nitrene species, which shows an electron deficiency and a high reactivity, is initially present in singlet form, yet is in equilibrium with the triplet state. Each of these electronic states reacts differently with the polymer. The reaction mechanism for an aryl sulfonyl azide with a polymer could be schematically represented as follows:



The sulfonyl nitrene generated during thermal azide decomposition is initially found in singlet form. This can insert into the C-H bond of a polymer, attaching the azide-containing molecule to the polymer backbone. The nitrene may, however, progress to the triplet state, with an un-

matched electron pair. The reaction in triplet form is likely to abstract an hydrogen from the polymer and create a radical in the polymer backbone. Such radical could then react with other polymer chains and crosslink the polymer, as shown schematically:



Organosilane Chemistry

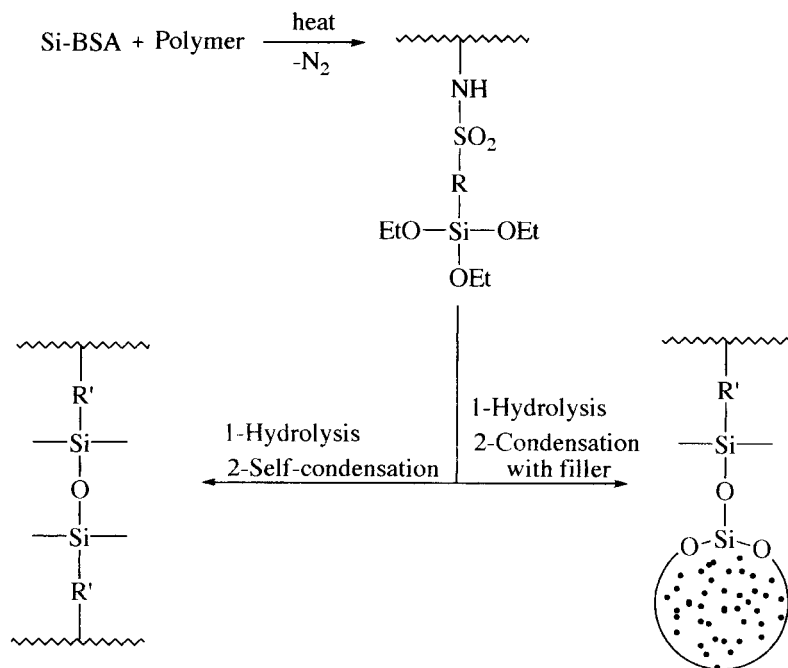
The use of organosilane as a means of increasing the reinforcing properties of polymers or mineral fillers in polymeric compounds is well known.¹⁻⁵ Silane adhesion promoters are monomeric silanes of the general structure $\text{R}'-\text{Si}(\text{OR})_3$, in which two reactivity sites may

be noted. In our case, the first site, represented by R' , is a functional sulfonyl azide, whereas the second centers around the silicon atom and consists of three hydrolyzable alkoxy groups ($\text{Si}-\text{OR}$). The alkoxy groups hydrolyze to form silanols ($\text{Si}-\text{OH}$), which can react with active silica, silicates, or other oxide surfaces, or condense with other silanols.

Silane condensation and filler reaction are shown in Schemes 1 and 2. Because the product Si-BSA incorporates an azide functional group suitable for reaction with the polymeric matrix, in practice this reagent allows two crosslinking routes, one as shown in Scheme 1 and another

shown in Scheme 2, if the filler dispersed in the polymer contains silanol groups.

The two reactions of Si-BSA with a polymer described above in the presence or absence of a silica-type filler could be represented as follows:



The hydrolysis reaction of the alkoxy group is favored by the presence of water. Hence, if the composite is postcured in hot water, its crosslink density due to either self-condensation or reaction with filler is significantly increased. Diffusion of water hydrolyzes the alkoxy groups, which then condense. This latter reaction can be catalyzed with dibutyltin dilaurate; however, this was not done in this research. When the polymer contains a mineral filler, such as silica, the water adsorbed onto its surface suffices to produce alkoxy silane hydrolysis.

Behavior of Si-BSA as Coupling Agent

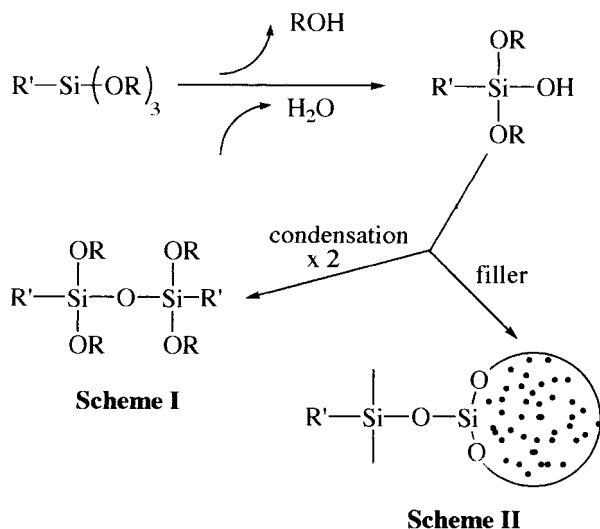
The behavior of Si-BSA as a coupling agent was studied in an unsaturated SBR rubber in the absence and presence of a filler as well as in a saturated rubber, in this case a filler-free EPM, which together tested the range of the reaction ability of the coupling agent.

SBR Compounds

Table I shows the formulations of the unfilled SBR compounds, with and without Si-BSA, as well as the rheological curing parameters at 160°C, which are similar for both compounds.

A first batch of rubber and Si-BSA was compounded using a twin mill. Then the blend was subjected to heat treatment in a Brabender for 5 min at 160°C and 60 rpm. Under these conditions azide group decomposition and reaction with the polymer took place. The minimum torque value (M_L , Table I) did not show a significant difference between the control compound and the Si-BSA compound, so that azide reaction via the triplet state leading to polymer crosslinking did not take place or only in small proportion, with the reaction via the singlet state being predominant. Addition of the remaining additives, accelerants, zinc oxide, stearic acid, etc., was done in an open mill at room temperature. The compounds were then vulcanized at 160°C to t_{97} .

For the purpose of determining the condensa-


Schemes 1, 2

tion reaction of the silanol groups (following Scheme 1) as indicated above, the vulcanizates were subjected to postcuring treatment by immersion in water at 90°C, with physical properties determined after different treatment times. Table II compiles the original and the hot water treated sample results at 2, 4, and 24 h. Increments in tensile strength, modulus, and hardness, reduction of elongation to break, and an increase in crosslink density, as expressed by the value of V_r , were observed in the compound containing Si-BSA. These results confirmed the proposed condensation reaction. A water treatment time of 2–4 h was sufficient to achieve these effects.

In the same rubber the effects of Si-BSA in the presence of a silica filler were studied. In this case,

Table I Formulations and Rheometer Properties of Unfilled SBR Compounds

| | Control | Si-BSA |
|-------------------------|---------|--------|
| Compounds | | |
| SBR 1502 | 100 | 100 |
| Si-BSA | — | 2 |
| Zinc oxide | 5 | 5 |
| Stearic acid | 2 | 2 |
| TMTD | 0.5 | 0.5 |
| Sulfur | 2 | 2 |
| Rheometer cure at 160°C | | |
| M_H (dN m) | 30.8 | 31.7 |
| M_L (dN m) | 4.3 | 5.0 |
| t_{97} (min) | 5.2 | 4.8 |
| t_{S5} (min) | 2.9 | 2.6 |

the compound with Si-BSA was not subjected to the heat treatment in the Brabender prior to vulcanization because the water adsorbed onto the silica surface produced the alkoxy silane hydrolysis and condensation reaction already in the compounding in the two roll mill. This would lead to crosslinking if the grafting to the polymer through the azide group was already done. Table III shows the formulations of the compounds as well as the physical properties of their vulcanizates. In this case the crosslinking mechanism operates according to Scheme 2, where postcuring with hot water was not necessary. A third composite was included in the experiment containing the commercial coupling agent, silane A-1100, at the same molar ratio as that of the Si-BSA containing compound. The rheological properties of the cur-

Table II Physical Properties of Unfilled SBR Vulcanizates at Different Hot Water Treatment Times

| Properties | Compound | Time (h) | | | |
|-----------------------------|----------|----------|--------|--------|--------|
| | | 0 | 2 | 4 | 24 |
| Tensile (MPa) | Control | 3.96 | 3.30 | 3.49 | 2.76 |
| | Si-BSA | 4.38 | 4.11 | 4.27 | 4.20 |
| Modulus 100% (MPa) | Control | 2.30 | 1.85 | 1.97 | 1.68 |
| | Si-BSA | 2.27 | 3.37 | 3.55 | 2.84 |
| Elongation (%) | Control | 210 | 230 | 215 | 165 |
| | Si-BSA | 228 | 170 | 160 | 158 |
| Hardness shore A | Control | 54 | 55 | 55 | 55 |
| | Si-BSA | 57 | 59 | 60 | 60 |
| Equilibrium swelling, V_r | Control | 0.2325 | 0.2330 | 0.2351 | 0.2332 |
| | Si-BSA | 0.2478 | 0.2582 | 0.2602 | 0.2631 |

Table III Formulations and Physical Properties of Silica Filled SBR Compounds

| | Control | A-1100 | Si-BSA |
|--------------------------------|---------|--------|--------|
| Compounds | | | |
| SBR 1502 | 100 | 100 | 100 |
| Ultrasil VN/3 | 30 | 30 | 30 |
| Silane A-1100 | — | 1 | — |
| SiBSA | — | — | 2 |
| Triethanolamine | 2 | — | — |
| Zinc oxide | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 |
| TMTD | 0.5 | 0.5 | 0.5 |
| Sulfur | 2 | 2 | 2 |
| Rheometer cure at 160°C | | | |
| M_H (dN·m) | 42 | 38 | 39.8 |
| M_L (dN·m) | 11 | 9.2 | 11.3 |
| t_{97} (min) | 7.3 | 7.0 | 7.5 |
| t_{S5} (min) | 2.3 | 3.0 | 2.6 |
| Vulcanizates properties | | | |
| Tensile (MPa) | 13.57 | 15.28 | 16.12 |
| 100% modulus (MPa) | 1.89 | 2.60 | 3.52 |
| 300% modulus (MPa) | 4.26 | 9.60 | 13.46 |
| Elongation (%) | 533 | 438 | 342 |
| Hardness, shore A | 57 | 60 | 62 |
| Tear, die Delft (N) | 24 | 29.3 | 35.8 |

ing process were similar for the three compounds under study. Yet, relevant differences came to light in the physical properties of the vulcanizates. The increase was moderate regarding tensile strength and considerable in the moduli, hardness, and tear strength of the samples containing the coupling agent, as compared to the values of the control compound. It should also be stressed that the physical properties of the vulcanizates containing Si-BSA were much better than those presented by the compound containing the commercial silane. This suggested that the efficiency of the coupling reaction between the filler and the polymer was higher with the coupling agent developed in our laboratory.

EPM Compounds

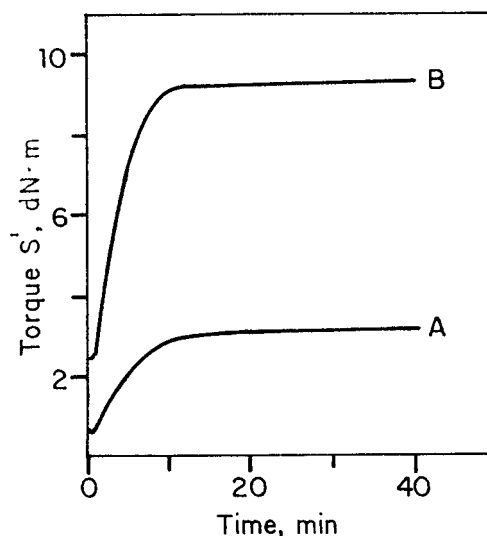
The effects of Si-BSA on a saturated ethylene-propylene rubber were studied. Table IV shows

Table IV Formulation of EPM Compounds

| Compound | A | B |
|------------------|-----|-----|
| EPM Co 045 | 100 | 100 |
| Dicumyl peroxide | 2 | 2 |
| Si-BSA | — | 2 |

the formulations of the compounds. Compound B was prepared in the same way as unfilled SBR compounds, whereas compound A was prepared without the heat treatment on the Brabender. The curing agent used was dicumyl peroxide. Figure 1 indicates the curing rheograms of the composites. The sample containing Si-BSA produced a much higher maximum torque, an effect that may be attributed to the self-condensation reaction of the polymer attached ethoxysilane groups previously hydrolyzed by means of water diffusion in the polymeric matrix. Also a distinct difference was found in the minimum torque. This difference was attributed to the fact that sample vulcanization was done several days after compound preparation and self-condensation, although slow, can take place at room temperature. Figure 2 shows the stress-strain graphs for both compounds. The composite containing Si-BSA subjected to postcuring treatment by immersion in hot water (90°C) for 24 h presented significantly better results than the control compound.

The behavior observed in the ethylene-propylene copolymer allowed the assumption that this coupling agent can be used when crosslinking certain polyolefins, such as polyethylene and polypropylene, materials that may occasionally require crosslinking to enhance their behavior at higher operational temperatures. The reaction of the azide function with the polymer did not give rise to any secondary polymer scission reactions,

**Figure 1** Rheometer curves of EPM. Compound A and B according to Table IV.

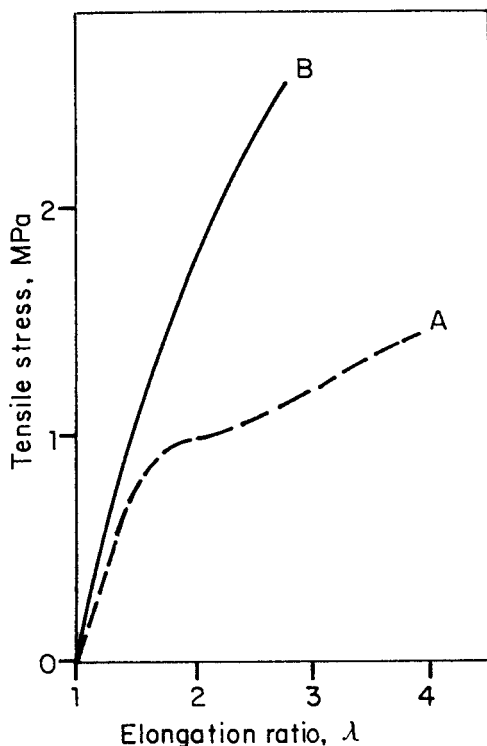


Figure 2 Tensile stress-strain curves for EPM compounds: (---) compound A and (—) compound B.

a phenomenon that frequently occurs when polyolefins are crosslinked with organic peroxides.

CONCLUSIONS

Si-BSA based coupling agents were used to improve the physical performance of mineral-filled or reinforced polymers. This agent is a bifunc-

tional molecule containing a trialkoxy silane moiety capable of reacting with the surface of an inorganic filler and an organofunctional group, such as the azide group, which reacts with the polymeric matrix. In addition, Si—OR hydrolyzes in the presence of moisture, giving rise to —SiOH groups, which subsequently condense into Si—O—Si and form an intermolecular crosslink. This process is accelerated by immersion in hot water.

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