Elastomeric Compounds with Silica. Lower Hysteresis in the Presence of Functionalised Isoprene Oligomers

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Summary: Silica as reinforcing filler brings about a low hysteresis in elastomeric compounds. Aim of this work was to promote a better silica-elastomer interaction by using, as minor ingredients of a compound, isoprene oligomers having a functional group as the chain end. The effect of the functionality was investigated by analysing the complex viscosity of silica-oligomers binary mixtures as well as the morphological and rheological properties of masterbatches and compounds based on isoprene rubbers. A better silica dispersion and a lower Payne effect were clearly observed in the presence of functionalized oligomers.

Keywords: atomic force microscopy; complex viscosity; compounds; functional oligomers; Payne effect.; Polyisoprene; silica

Introduction

Technology evolution of a tire vehicle has nowadays to satisfy the requirements of sustainable development. In this perspective, a major role is played by the reduction of fuel consumption, that is clearly correlated with the forces that resist to the movement of the vehicle. The contribution of a tire to these forces is estimated to be between 20 and 40%[1],as a function of the tire type, and the impact of a tire on the environment is evaluated to be due for about 70% to fuel consumption.[2]

There is thus the need to reduce the so called rolling resistance (RR) proposed by a tire and materials have a fundamental importance for that: compounds that give a minor contribution to RR[3] are characterised by a low dissipation of energy during dynamic deformation. The portion of dissipated energy is related to the so called loss factor, i.e. the ratio between viscous and elastic modulus, known as dynamic hysteresis. Fillers are the ingredients that build up most part of the hysteresis of filled vulcanizates and the filler networking is recognized as the dominant factor.[4]

Among the reinforcing fillers, silica is known to bring a minor contribution to compound hysteresis, provided that good distribution and dispersion of silica are achieved.[5,6] Prerequisite for that is an intimate interaction of silica and elastomer, that is instead hindered by their different nature, hydrophilic and hydrophobic respectively. To overcome this problem, a coupling agent is used, also on the industrial scale: bis-3-(triethoxysylilpropyl)tetrasulfane: Si(OR) groups react during mixing with sylanols present on silica surface, while tetrasulfane group is split during vulcanization thus finally providing the silica-elastomer-linkage.[7,8]

A new approach has been developed over the last years, aimed at modifying the surface tension of the elastomers by introducing functional groups. Many examples are available in patent literature. Functional groups are introduced along the macromolecular chain,[9–11] basically by grafting, or as chain end groups,[12–14] taking advantage of the living character of

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the anionic polymerization. In most examples, functional groups are present on high molecular mass elastomers and improvements of silica dispersion as well as reduction of hysteresis are claimed.[9–13]

Aim of this work was to study the role of chain end functionalised isoprene oligomers for the reduction of energy loss in silica based compounds, by particularly investigating their effect on filler networking. The isoprenoid nature of the oligomers was selected because it is well known that compounds based on polyisoprene rubber are characterised by a low hysteresis. The objective of the research was thus to achieve an appreciable reduction in energy loss of silica based compounds without modifying the chemical nature of a main component, i.e. the elastomer, only by adding a minor amount of an oligomer with only a functionalised chain end. Functionalised oligomers were prepared with a polymerization degree (DPn) of about 50 through living anionic polymerization and polar groups of different type, reported for the modification of high molecular mass elastomers, were employed: 1,3-dimethyl-2-imidazolidinone (IMZ),[15] N,N-diglycidylaniline (DGA),[16] glicidylisopropylether (GIE).[17] The interaction with silica was studied in binary mixtures composed by the elastomer and silica as well as in masterbatches and compounds based on isoprene rubber. In the two latter cases, the functionalised oligomers were used in a minor amount. Silica dispersion in masterbatches was investigated through Atomic Force Microscopy[18] whereas the effect of the functionalised oligomers on filler networking in sulphur cured compounds was studied by examining the dependence of elastic modulus on strain amplitude[4].

Experimental Part

Materials

n-Heptane (Carlo Erba RPE) was refluxed for 8 hours over Na/K alloy and then distilled under N_2. Isoprene (Fluka 98%) was refluxed for 8 hours over CaH_2 and then distilled under N_2. N,N,N′N′-tetramethylethylenediamine (TMEDA) (Fluka, 99%) was dried over KOH. 1,3-Dimethyl-2-imidazolidinone (Aldrich, 98%), N,N-diglycidylaniline (Aldrich, purum), glicidylisopropylether (Aldrich, 97%) were used without further purification. Dichloromethane (Carlo Erba, RPE) was used without any purification. Silica 1165 MP was purchased from Rhodia. The following ingredients for compound preparation were used as received: 1,4-*cis* polyisoprene (Goodyear), ZnO (Zincol Ossidi), stearic acid (Sogis), N-cyclohexylbenzothiazol-2-sulfenamide (Flexsys), N-(1,3-dimethylbuthyl)-N-phenyl-*p*-phenylenediamine (6-PPD) (Crompton) and sulphur (Solfotecnica).

Polymerizations: General Remarks

All the chemicals were stored under nitrogen. All manipulations were carried out under dry nitrogen atmosphere using Schlenk techniques. Polymerizations were performed in a 700 ml Büchi glass autoclave equipped with a mechanical stirrer, a thermocouple, a jacket where cool water was allowed to circulate.

Synthesis of Isoprene Oligomers

The procedure for the preparation of oligomers of isoprene with DPn of about 50 is reported as follows. In the Büchi autoclave were introduced, in the following order, 150 ml of n-heptane, 129 g (1.89 mol) of isoprene and 50 μl ($3.16\ 10^{-4}$ mol) of TMEDA. The solution was thermostated at 0 °C and 29 ml (37.7 mmol) of sec-BuLi were added under stirring. The temperature of the polymerization solution was allowed to increase up to 50 °C and the solution was then maintained under stirring at this temperature for 6 hours. At this time, isoprene conversion was verified to be complete. 10 ml of the polymerization solution were treated with MeOH acidified with HCl, washed until neutral pH and the oligomeric sample, isolated by evaporating the solvent, was then characterised.

Synthesis of Functionalised Isoprene Oligomers

The polymerization solution obtained as reported before was cooled to room temperature and treated with a n-heptane solution of the modifier, using a (functional group) / (carbon-lithium bond) molar ratio of 1.2. The solution was maintained under stirring for 2 hours. After washing with acidified water and pure water, the solvent was evaporated and the isolated chain end functionalised oligomers were then characterised.

Characterisation of Isoprene Oligomers

SEC analyses were performed with a Waters instrument equipped with 5 Styragel columns (2HR3, 2HR4, 1HR5) and UV (Waters 440) as well as RI (Waters 410) detectors, by using CH_2Cl_2 as the diluent and o-dichlorobenzene (ODCB) as internal standard. Calibration was performed with polystyrene standards.

^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 400 MHz in the Fourier transform mode at room temperature. Samples were dissolved in $CDCl_3$ at room temperature (2% w/v concentration). ^1H NMR spectrum was acquired with a 90° pulse, 20 s of delay between pulses, 16 transients were stored in 32 K data points using a spectral window of 4400 Hz. ^{13}C NMR spectrum was acquired with a 90° pulse, 3 s of delay between pulses, 15000 transients were stored in 12 K data points using a spectral window of 20080 Hz.

Silica/Functionalised Oligomers Binary Mixtures

Preparation. In a 100 ml round bottomed flask, 4 g of isoprene oligomers were dissolved in 30 ml of dichloromethane, under stirring. 1 g of Silica 1165 was then added and the resulting suspension was kept under vigorous stirring for several hours. The solvent was removed first under nitrogen flow then by keeping the solid at 80 °C under reduced pressure.

Characterization

Measurements of viscosity were performed in a Rheometer Physica MCR 300 with plate/plate geometry, with plate diameter of 25 mm and maintaining a plate-plate distance of 0.05 mm. Analyses were carried out in frequency sweep in a range from 0.1 to 100 Hz, moving from high to low frequencies, at a temperature of 25 °C and under a constant strain of 10 %.

Masterbatches and Compounds

Preparation of masterbatches. Masterbatches were prepared in a Haake PolyLab internal mixer with a 180 ml mixing room. 90 g of IR were put in the mixer at 50 °C and, after one minute of rubber mastication, 45 g of the isoprene oligomer followed by 60 g of silica were added. Mixing was carried out for 5 minutes at 50 °C.

Preparation of compounds. 120 g of IR rubber were introduced in the above mentioned internal mixer, kept a t 80 °C. After one minute of rubber mastication, were added in one step 72 g of silica, 7.2 g of isoprene oligomer, 2.4 g of stearic acid and 2.4 g of 6-PPD. Mixing was carried out for 6 minutes and the masterbatch was discharged at 140 °C. Vulcanization ingredients: 3.0 g of ZnO, 1.4 g of sulphur and 2.4 g of CBS, were added in a second mixing step, performed in the same internal mixer, for 4 minutes and at a maximum temperature of 70 °C.

Characterization of Masterbatches and Compounds

Atomic Force Microscopy (AFM) AFM analyses were performed on 2 micron thick masterbatch sections, obtained with a cryogenic microtome, by using a Multimode IIIA Veeco equipped with a cantilever Pointprobe FM-100. The force constants of the cantilever is 5.5 N/m, the resonant frequency is 84.1 KHz. Pictures were obtained in Phase Detection mode with a resolution of 512 samples per line at a scan rate of 2 seconds/line.

Curing and rheological analyses were performed with a vulcameter RPA 2000-Alpha Technologies with biconical geometry. The sample was cured at 170 °C for 10 minutes and, before strain sweep test started, was cooled and conditioned to

50 °C for 10 minutes. The analyses were carried out from 0.28 to 40 % of strain at 50 °C and under a frequency of 10 Hz.

Results and Discussion

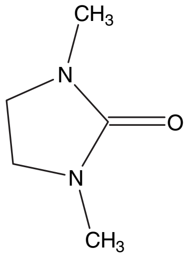
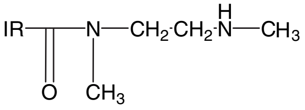
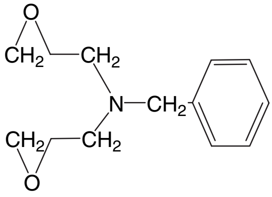
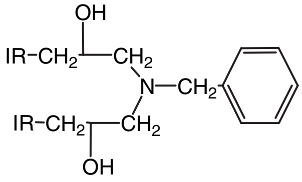
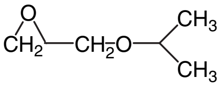
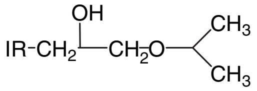
Isoprene Oligomers

Chain-end functionalised isoprene oligomers were prepared through alkyl-lithium initiated anionic polymerization as this type of polymerization is known to give rise to stable anionic chain ends. In particular, sec-butyl lithium was used as the initiator for the favourable ratio between propagation and initiation reaction and an activator such as TMEDA was used to enhance the insertion efficiency of the monomer into the carbon-lithium bond in a non polar solvent such as heptane,[19] on the assumption that the reduction of 1,4-cis content, i.e. the appropriate microstructure to have a low hysteresis, would be only to a minor extent. In fact, microstructure of the isoprene oligomers, as detected by ^{1}H and ^{13}C NMR was found to be as follows: 1,4-cis/1,4-trans/3,4 = 75/20/5.

In Table 1 are reported the chemical compounds employed for chain end modification (modifiers) as well as the functional groups that are expected to be formed after reaction with carbon-lithium bond. These modifiers, already reported in patent literature, [16–18] were selected as representative of different classes of chemical functionalities.

On the basis of the chemistry implied by a reaction with a carbon-lithium bond, 1,3-dimethyl-2-imydazolidinone should give rise to an internal amidic functionality and to a secondary amino group as the chain end. N,N-diglycidylaniline should bring to the formation of two hydroxy groups, provided that a molar ratio of at least 2:1 between the oligomeric isoprene and the modifier is employed. A hydroxy group close to a dimethylether should be obtained from glicydilisopropylether. Oligomeric sample without any functionality

Table 1.
Modifiers employed for the preparation of chain end functionalized isoprene oligomers

	Modifier	Chemical structure after the reaction
IMZ		
DGA		
GIE		

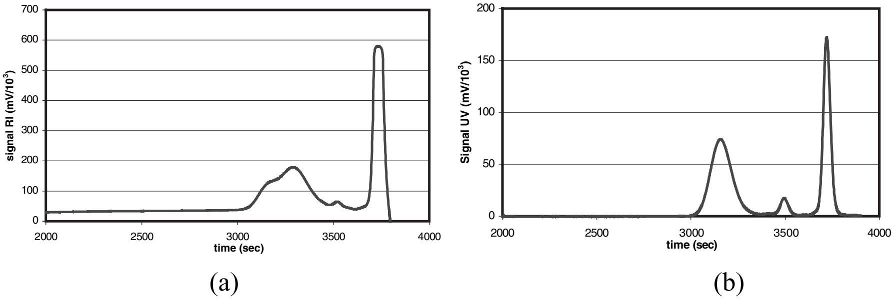


Figure 1.
SEC curve of IMZ modified isoprene oligomers (a):RI-SEC (b) UV-SEC.

as the chain end is finally obtained by quenching the polymerization with methanol.

Oligomers were characterised through ^{1}H- and ^{13}C NMR and Size Exclusion Chromatography (SEC). SEC was applied not only to measure the molecular mass of the oligomers (as polystyrene equivalent) but also to verify the presence in the oligomers of modifiers sensitive to UV radiation, such as IMZ and DGA. NMR allowed to determine DPn and the chemical structure of the functionalised chain ends and thus to assess quantitatively the efficiency of the coupling reaction between the modifier and the growing chain.

Through SEC analysis, the molecular mass of isoprene oligomers was found to be 3500 g/mol indicating a DPn of about 50. In SEC curves, the assignment of peaks was performed on oligomers prepared with an excess of the living chain. In Figures 1a–b SEC-RI and SEC-UV curves of a sample with IMZ as the modifier are shown. In the SEC-RI curve, two peaks can be observed in the 3000–3500 sec range: the one at lower retention time can be attributed to the modified oligomer Peaks at higher retention times are respectively due the unreacted modifier and to the internal standard (ODCB, see experimental part). This attribution is confirmed by the SEC-UV curve that shows, in the range of oligomer retention time, only the peak of IMZ-terminated oligomer sensitive to UV radiation.

DPn was determined from ^{1}H NMR analysis (see Figure 2), through the ratio between the peak areas of the signals

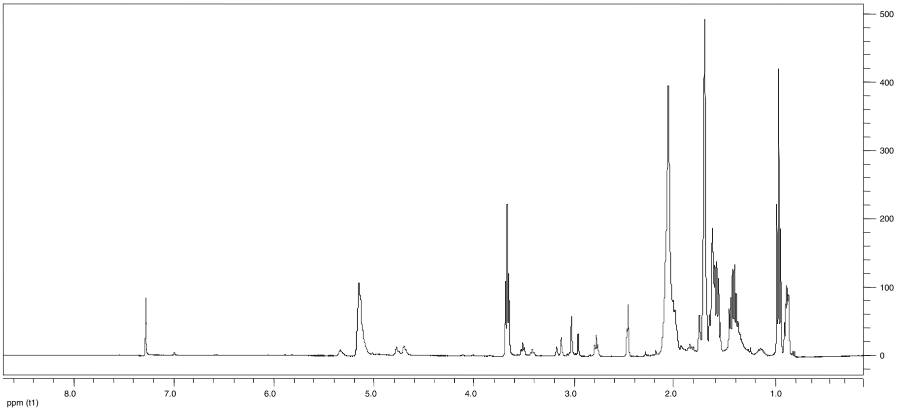


Figure 2.
^{1}H NMR of the isoprene oligomer.

attributed to the methyl groups due to the initiator (at 0.88 ppm) and to the protons of the chain double bonds (in ppm range = 4.5–5.5).

The ratio between peak areas of signals attributed to functional end group and to chain double bond allows to assess the efficiency of modification reaction. With all the modifiers the coupling efficiency was found to be as high as 90%. Detailed assessment of chemical structure of functionalised chain ends was carried out on isoprene oligomers with DPn = 9. The characterization of the oligomers terminated with IMZ is reported as an example. In the ^{1}H NMR reported in Figure 2, signals at 3.02 ppm and at 2.46 ppm, respectively due to the methyl close to the amidic group and to the methyl close to the amino group (Table 1), confirm the occurring of the ring opening reaction of imidazolidone by means of the living isoprenyl chain.

Silica-Oligomers Binary Mixtures

Binary mixtures composed of an isoprene oligomer and silica, in a 4:1 weight ratio, were obtained by using the typical technique usually applied for the adsorption of a polymer onto a solid phase. The interaction between the oligomer and silica was studied by analyzing the viscosity of the mixture with a rheomether, in frequency sweep from 0.1 to 100 Hz and at a temperature of 25 °C. Preliminary tests were carried out to assess the limit strain for having a linear viscoelasticity behaviour, upon measuring G' over a range of strain amplitudes. A limit strain of 10% was observed and was thus adopted for the characterization of the binary mixtures. Results obtained with IMZ and GIE as the modifiers, in comparison with an unmodified oligomer, are shown in Figure 3. Measurements were reproduced several times. In the case of the mixture based on the oligomer modified with GIE, two curves are reported to show the good reproducibility of the test.

A visual inspection revealed the poor homogeneity of the mixture based on the oligomer without any functional group. In fact, values of complex viscosity could be obtained only at a frequency higher than 24.2 s-1 whereas they were not measurable moving to lower frequencies, probably as a consequence of the formation of larger silica agglomerates. For the functionalised oligomers, viscosity was measured over the whole frequency range, to show a strong positive influence of the functional group. A decrease of viscosity is observed as the frequency is raised, suggesting a breaking down of the interactions between silica particles. By interpreting an increase in viscosity as an indication of a stronger interaction between silica and the oligomer, IMZ could thus give rise to a stronger interaction than DGA.

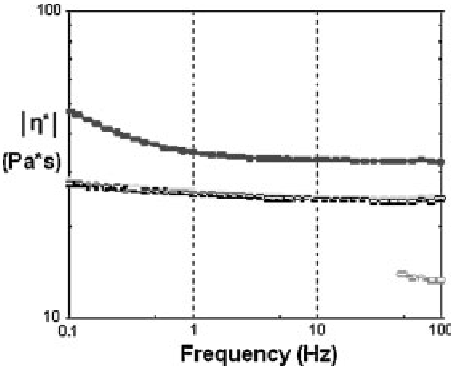
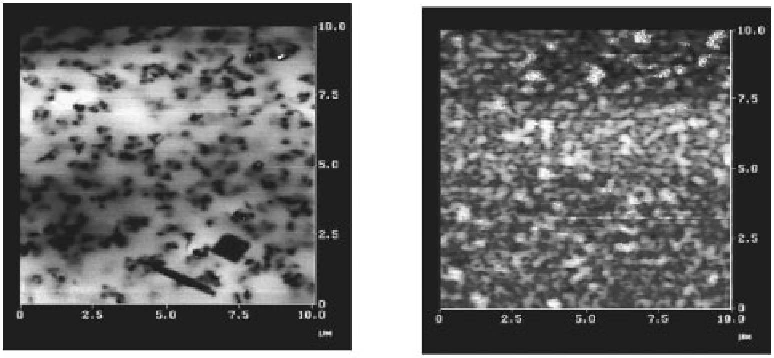


Figure 3.
Complex viscosity curves of modified isoprene oligomers/silica mixtures (1:4 w:w). Modifiers: Blu (upper) curve = IMZ; green and black (middle) curves = GIE, red (lower) curve = without modifier.

Masterbatches and Compounds

Functionalised isoprene oligomers were added in a minor amount both in masterbatches and in compounds based on isoprene rubber and on silica as the only filler.

Masterbatches had the following composition, expressed in phr, where the term "phr" means the parts by weight of a given component of the crosslinkable elastomeric composition per 100 parts by weight of the diene elastomeric polymer: isoprene rubber 100, silica 60, (functionalized) oligomer 6. Silica dispersion was investigated by using Atomic Force.



(a) (b)

Figure 4.
AFM pictures of masterbatches: (a) without any modifier (b) with IMZ modified oligomer. Scales are in μm.

In Figure 4 are shown AFM pictures taken from masterbatches with IMZ-modified and unmodified oligomers.

AFM images provide a relative measure of loss factor between microscopic phases. In AFM maps, light and dark areas are respectively attributed to higher and lower tan δ domains, that in turns are characteristics of the rubber soft matrix and of silica particles. In the sample with IMZ functionalized isoprene oligomer, silica particles appear smaller and their dispersion better. These findings indicate that a good silica dispersion is achieved only when a functional group is the chain end of the isoprene oligomers.

Compounds based on isoprene rubber and with 60 phr of silica were prepared and cured with a typical sulphur recipe (see Table 2).

Shear storage modulus G′ was measured as a function of the strain amplitude. At low strain amplitudes the modulus is constant, whereas it decreases as the amplitude of deformation is increased. This non linear behaviour of shear storage modulus is known as ‘‘Payne Effect’’ [18] and is attributed to the presence of a filler network in the polymer matrix: the increase of strain amplitude causes the disruption of the filler network and, as a consequence, the release of the rubber trapped in the network with a reduction of the effective filler volume. In the literature, it is widely accepted that the ‘‘Payne effect’’ is essentially,[4] if not only, due to these phenomena. The difference between G′ values at low and high strain amplitudes (ΔG′) is thus a measure of the presence of a filler network in the polymer matrix. The disruption of the filler network is a hysteretic process and the energy dissipation is proportional to ΔG′ value. Payne effect was investigated in masterbatches of Table 2 to verify the role of functionalised oligomers in reducing filler aggregation and thus compound hysteresis. Results are collected in Table 3.

Table 2.
Recipe of compounds in phr (per cent rubber)

Ingredients	Phr
IR	100
SiO_2	60
IR oligomers	6
Stearic Acid	2
ZnO	2.5
Sulphur	1.2
CBS	2
6-PPD	2

Table 3.
Payne effect of compounds with isoprene oligomers as ingredients. ΔG′ was measured between 0.28% and 40% strain amplitude ($\Delta G' = G'_{0.28\%} - G'_{40\%}$) at 50 °C and 10 Hz.

Oligomers	ΔG′(KPa)
unmodified IR	7772
IR-IMZ	6394
IR-DGA	6285
IR-GIE	6183

From the results of Table 3 it clearly appears that the presence in the compound of a functionalised oligomer reduces to an appreciable extent the Payne effect. Minor differences can be observed among the three functional groups.

Conclusions

Isoprene oligomers with a functional group as the chain end were used in minor amount in masterbatches and compounds based on isoprene rubber and silica as the only filler. They seem to cause an improvement of silica dispersion and a decrease of Payne effect.

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