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Investigation of Silane Coupling Agents on the Filler-Filler and Filler-Rubber Interaction and Mechanical Properties of EVM/ATH Composites

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Abstract. Ethylene vinyl acetate copolymer (EVM)/aluminium trihydrate (ATH) composites were prepared. Vinyl-trimethoxysilane (VTMO), triethoxyvinylsilane (VTEO), ethyltrimethoxysilane (ETMO), amino-propyl-trimethoxysilane (AMMO) four kinds of silanes were used in this research. The effects of silane amount and different kinds of silane on the dispersion and adhesion of the ATH in EVM composites were characterized through RPA, electron microscopy, bound rubber. It was found that the addition of VTMO/AMMO/VTEO led to a dramatic increase in Payne effect and tensile property of the composites. Filler dispersion increased with silane adding, and the interaction of ATH and EVM was found in silane treated composites, in which silane had effective functional groups.

1. Introduction

Ethylene vinyl acetate copolymers (EVA) have a huge range of applications: electronic devices, electrical engineering, wire and cables, buildings, transportation (aircraft, cars), photovoltaic etc [1]. Copolymers with higher vinyl acetate content are elastomers, commonly abbreviated as EVM, and well known for their halogen free character and synergistic effects with many flame retardants [2].

The most common method to enhance flammability properties of EVA based materials is the incorporation of mineral fillers which upon heating release water, e.g. aluminum hydroxide (ATH) or magnesium hydroxide (MH) and other minerals-based hydroxides [3]. As these fillers have little reinforcement capabilities compared for example with silica and carbon blacks often low mechanical properties are found and processing can be difficult due to compound stickiness. Recently available pre-crosslinked EVM grades with higher polymer Mooney values were found to be resolve processing issues [4]. Higher polymer viscosities allow to better disperse mineral filler through higher shear in the mixing process.

In order to further enhance the mechanical strength of mineral filled compounds surface treatments for the fillers are essential. Xingui Zhang et al. used titanate coupling agents and maleated ethylene vinyl acetate copolymer (MEVA) as interfacial modifier in EVA/ATH composites and found that the combined addition of the two modifiers enhanced the tensile, flame retardant properties and thermal



stability of the composites [5]. Fatty acid was used as coating agent in EVA/clay/ATH composites and improvements in tensile and flame retardant property were also observed [6]. Epoxy silane used in EVA/VLDPE/MDH composites was found out to enhance the interfaces of the composites, and slowed down the decomposition of the matrix's main chains [7]. Wang Yong et al. used the macromolecule coupling agents as modifier and found out it improve the mechanical properties better than silane coupling agent in PE/ATH composites [8]. Silane coupling agent is mostly used for surface modification to promote interfacial adhesion and improve the properties of composites. While the reaction mechanisms of sulfur silanes in tire compound with silica have been studied extensively the role of silanes in peroxide cure and their interaction with the less surface active mineral fillers is not yet well understood.

In this paper, four kinds of silanes have been applied as coupling agents. The purpose is to investigate the difference of silane affecting the filler-rubber interaction and mechanical properties in EVA/ATH composites.

2. Experimental

2.1. Materials

EVM (Ethylene vinyl acetate copolymers) was supplied by Arlanxeo under the trade name Levapren 700 PXL (Mooney viscosity, ML (1+4)100 °C 60), Germany. Flame Retardant ATH (Aluminium hydroxide) was obtained from Nabaltec as grades Apyral 200SM (untreated), with an average particle size (D50) of 0.4 µm and a BET surface of 15 m²/g. Aflux 18 (primary fatty amine), used as anti-stick agent, was obtained from Rhein Chemie, paraffin wax LSB 20 was purchased from Pinsheng Chemicals Co. (Shanghai). Antioxidant Vulkanox TMQ (2,2,4-trimethyl-1,2-dihydroquinoline) was provided by Lanxess. Peroxide Luperox F40, (1,3(4)-bis(ter-butylperoxyisopropyl) benzene, 40%) was from Arkema, and the coagent Rhenofit TRIM/S, (70% trimethylolpropane trimethacrylate, 30% on silica) was obtained from Rhein Chemie. Silane-coupling agents VTMO (vinyltrimethoxysilane), Dynasylane VTEO (vinyltriethoxysilane) were supplied by Degussa, AMMO (3-trimethoxysilyl)-1-propylamine) and ETMO (ethyltrimethoxysilane) were obtained from Heowns. Ethylacetate(99%) was provided by JK Chemical.

2.2. Compounding and vulcanization

The formulation for EVM/ATH composites is shown in Table 1. For the preparation of EVM composites, EVM was first mixed with silane-treated ATH on a two-roll mill. ATH was pre-dried at 100 + -5 °C for 3 h prior to compounding. To obtain improved interaction between ATH and EVM matrix, ATH fillers were mixed with addition of different kinds of silane, the silane content varied from 0 to 1 phr. Then, Aflux 18, paraffin wax, TMQ was successively added within 2 min, peroxide Luperox F40 and coagent TRIM was added for an additional 2 min. Last, the mixture was compounded for additional 4 min. During mixing, the cooling water temperature was 4 °C. After mixing, the compounds were compression molded at 175 °C for the optimum curing time. It is important to note that no extra heating step except for the vulcanization itself was used in contrast to the so called "silanization" step in tire compounding.

2.3. Tests

Room temperature tensile properties, including tensile modulus, tensile strength, and elongation-to-break, were determined in accordance with the ISO-37. The tensile testing was carried out using Universal Tensile Testing Machine (Instron 3365) at a speed of 500 mm/min. Abrasion test was measured on an Bareiss abraser (AB 6230) to test durability and resistance to wear. The sample material is subjected to a specific distance of 40 m according to DIN53516 with a force of 10 N on the sample button. Dynamic rheological properties of the composites were measured on a rubber processing analyzer(Alpha,RPA2000) at a dynamic strain from 0.28% to 100%. The frequency and temperature were set as 1 Hz and 60 °C. Bound Rubber was determined by immersing 5 g uncured compound in 100 ml of ethyl-acetate for 24 h at 40 °C. Rubber-filler gel was separated by ultracentrifugation for a further

24 hours at 5200 rpm and 25 °C. The amount of bound rubber (BdR) is calculated using the following equation:

$$BdR(\%) = \left[mg - ms \times cf \right] \div \left[ms \times (1 - cf) \right] \times 100$$

where ms is the mass of the sample before extraction, mg corresponds to the mass of the rubber-filler gel after drying and cf is the mass concentration of the filler in the mixture. Thereby, the content of the rubber-filler gel is related to the rubber fraction without filler [9].

Formulations are shown below with filler contents of ca 59 wt%.

Table 1. Formulation in EVM/ATH compounds.

Compound	EVM	Al(OH) ₃	Aflux 18	Paraffine wax	TMQ	TRIM	Peroxide	Silane
(phr)	100	160	1	1	1	1	6.5	0 / 0.5 / 1

3. Results and discussion

3.1. Filler- filler interaction

Payne effect is accepted as the collapse of the filler network and the release of the trapped rubber in the filler network upon the application of shear [10]. It is expressed by the difference between G' at small strain and large strain.

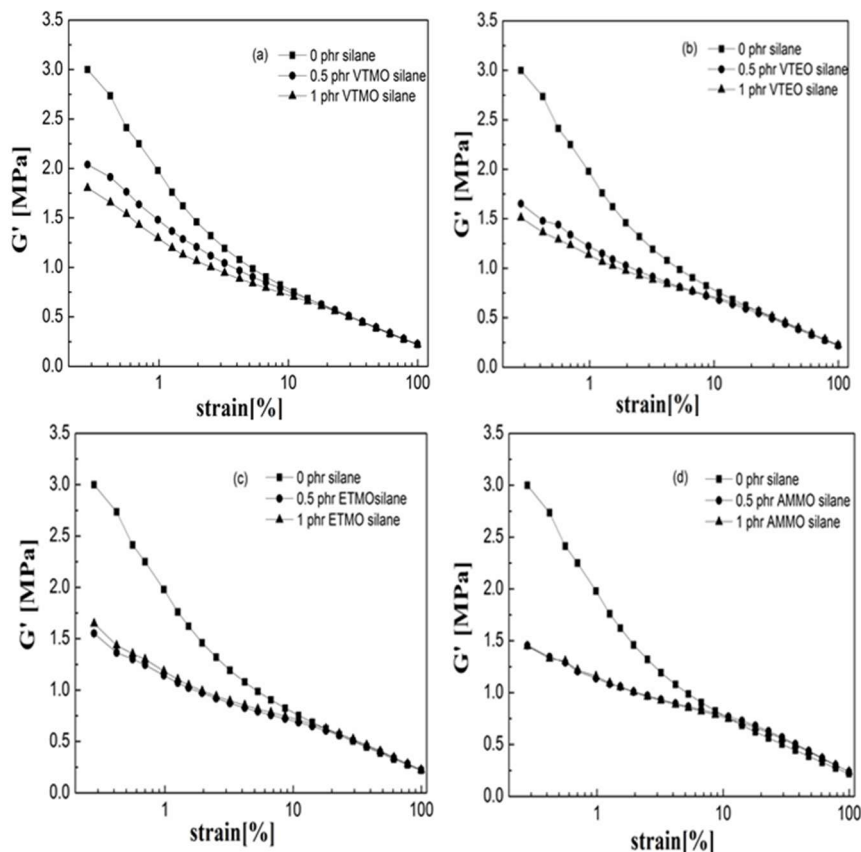


Figure 1. Relationship of silane amount with Payne effect in EVM/ATH composites (a) VTMO (b) VTEO (c) ETMO (d) AMMO

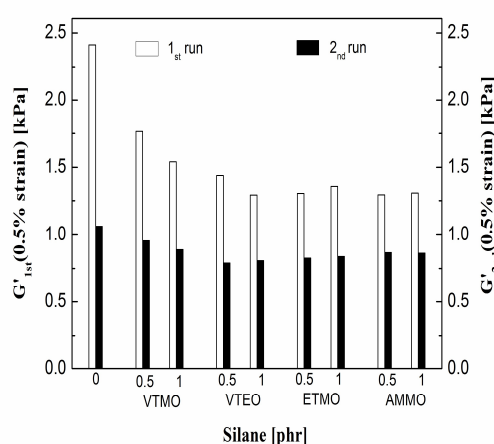
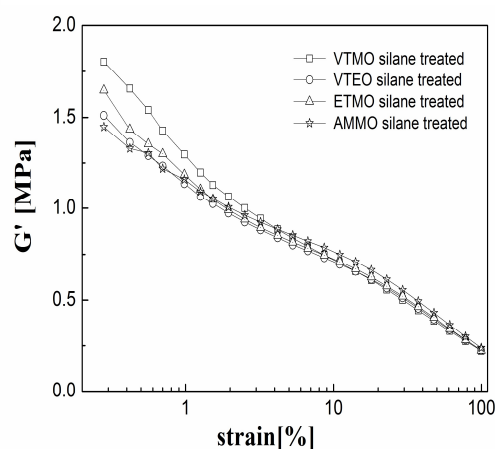
**Figure 2.** Effect of different silane on G' (0.5%)**Figure 3.** G' 1st for silane dosage of 1 phr

Fig. 1 showed that the G' (one strain sweep) for all the composites decreased upon increasing strain as expected. G' decreased significantly when all the silane was added which suggested that the incorporation of silane destroyed the ATH network and improved a more uniform dispersion of ATH in silane treated composites. G' at 0.5% strain (two strain sweeps) were studied to investigate the filler-filler networks as shown in Fig.2. It was found that the filler-filler networks were destroyed mostly in the first amplitude sweep. So, we only discussed the first sweep here. G' (0.5% strain) all decreased when silane was added. For all silanes dosages of 0.5 phr were sufficient except VTMO. VTMO needed 1 phr and was less effective to lower the G' (0.5% strain) values. From Fig.3 VTMO seemed to be less efficient to decrease the Payne effect, the efficient ranking is VTMO<ETMO<VTEO<AMMO.

3.2. Filler- rubber interaction

In filled non-cured rubber compounds bound rubber is defined as rubber which cannot be not dissolved by good solvent. Actually, it is absorbed on the filler surface, that is, the rubber is located on the filler-polymer interface. Normally, the filler-polymer interaction can be evaluated by bound rubber content. Bound rubber has been studied mainly with silica and carbon blacks but to our knowledge not with ATH.

Table 2. Bound rubber in VTMO/ETMO/AMMO/VTEO treated EVM composites

		VTMO	VTMO	ETMO	ETMO	AMMO	AMMO	VTEO	VTEO
Silane (phr)	0	0.5	1	0.5	1	0.5	1	0.5	1
BdR (%)	5.6	14.3	17.5	0	0	19.7	29.0	17.7	21.5

Here, BdR values between 0 and 29% were found. Mostly, bound rubber has been reported for diene rubbers and carbon black or silica. For silica (50 phr) in NR with and without silane values of 28 to 35% have been found [8,11]. Bound rubber is related to the available surface area, surface activity, surface wetting and comprising dispersity, polar and hydrogen bonding. Here, ATH alone give some bound rubber with EVM. Added silanes increased the bound rubber in the series AMMO>VTEO>VTMO. Surprisingly, ETMO compound did not give any bound rubber. If all the silanes are supposed to be preferentially located on the ATH surface including ETMO then this silane seems to shield the ATH from wetting by EVM.

3.3. Mechanical properties

The compounds without any silane gave a very characteristic stress-strain curve with a yielding at around 100% strain. That was the point of maximum reinforcement provided by the surface interaction between the EVM rubber network and the ATH surface. Beyond that point the filler lost its connection

to the rubber. The two vinylsilanes used here, VTMO and VTEO, are reactive in the peroxide cure system. They provided bonding to the rubber network and therefore high moduli demonstrated an efficient reinforcement. VTEO seems to be slightly more reinforcing than VTMO considering it was used in molar-wise lower amounts. methoxy and ethoxy-siloxane groups may have different reactivities. In stark contrast ETMO which did not have any reactivity to peroxide cure give stress-strain curves below that of compound without silane. Regardless any filler dispersion effect the ETMO shield the ATH from the EVM and did not provide any bonding to the network.

AMMO occupied an intermediate position as it provided reinforcement but no direct covalent bonding to the EVM network, presumably there was some hydrogen-bonding. The overall tensile strength values achieved here are quite high and may reflect the ability of the pre-crosslinked EVM grade to disperse and probably shear down the ATH filler particles to some extent due to the high polymer viscosity. Compound with ETMO silane gave rather low abrasion resistance, which was consistent with the tensile result in Fig.4. VTMO, VTEO and AMMO silanes clearly improved the abrasion resistance, but the preferable dosage is at least 1 phr.

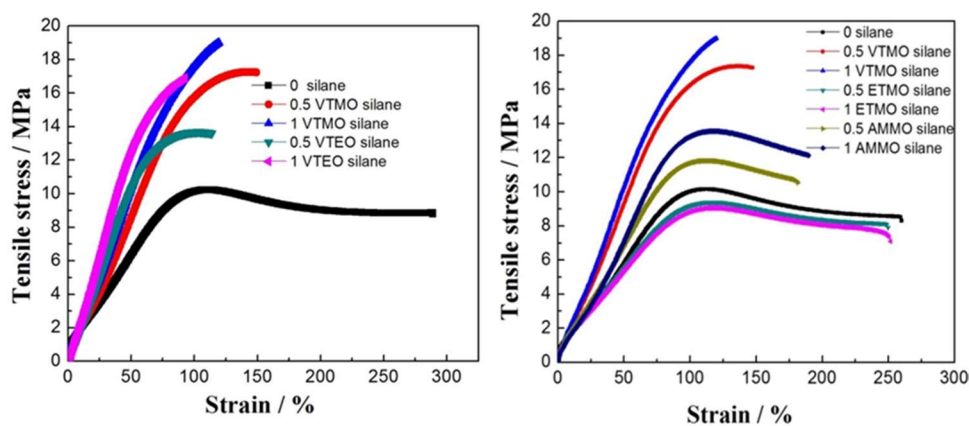


Figure 4. Stress-strain curves, compounds with different silane treatment

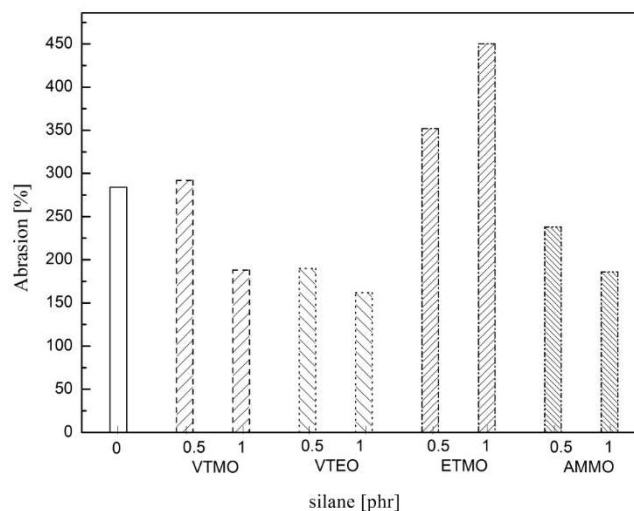


Figure 5. DIN abrasion properties in different kinds of silane treated EVM composites

4. Conclusion

ATH-ATH network was destroyed and its dispersion was improved in silane treated composites. AMMO and VTEO contribute a lot to the Payne effect. BdR was found and tensile strength and abrasion property were improved in AMMO, VTEO and VTMO treated composites.

Acknowledgments

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