Influence of coupling agent on the Bound rubber and Dynamic Properties of aluminum sodium silicates filled HNBR composites

Weina Bi1, *, Yu Guangshui1, Jujie Sun1, Christoph Goegelein2, Martin Hoch3, Joerg Kirchhoff2 and Shugao Zhao1
1 Qingdao University of Science and Technology, Qingdao, 266045, China
2 ARLANXEO Deutschland GmbH Polymer Testing, Leverkusen, 51369, Germany
3 ARLANXEO High Performance Elastomers (Changzhou) Co. Ltd. Shanghai, 200021, China

*Corresponding author e-mail: bwn@qust.edu.cn

Abstract. Hydrogenated acrylonitrile-butadiene rubber (HNBR) was used as polymer matrix and micrometer aluminum sodium silicate mineral filler was used as dispersed phase to prepare silicate mineral / polymer composites. Different Triethoxy silane coupling agents were chosen to modify sodium silicate, the vulcanization properties, physical mechanical properties and dynamic mechanical properties of silicate / polymer composites were studied. The results showed that the addition of silane improved the dispersity of sodium aluminum silicate effectively in hydrogenated nitrile rubber. Although the mechanism of actions between VTEO, GLYEO, AMEO silanes and rubber was different, the interactions between filler and rubber were enhanced. These three kinds of triethoxy silane improved the physical and mechanical properties of sodium aluminosilicate / hydrogenated butyronitrile composites obviously.

1. Introduction

The initial purpose of adding mineral fillers to polymer materials is to reduce costs. Nowadays, the addition of these fillers to polymers is more important to improve the rigidity and dimensional stability of the materials, and to endow the materials with certain special physicochemical properties, such as compression resistance, impact resistance, corrosion resistance, insulation and others [1].

Silicate fillers used for polymer modification include talc, kaolin, mica, wollastonite.

The aluminum sodium silicate studied in this paper is also a silicate mineral material, which is mainly used to improve the dispersion and stability of pigments, and can replace titanium dioxide to reduce the cost. Sodium aluminum silicate can also be used to fill rubber, playing a reinforcing role, and improve the thixotropy of rubber.

Sodium aluminum silicate structure is shown in Fig. 1: nonpolar siloxane group (Si-O-Si) constitutes the hydrophobic part of the surface. Free hydroxyl groups and hydrogen bonding formed by the adjacent hydroxyl groups of silicon atoms form the hydrophilic part of its surface. There are three types of hydroxyl on the silicate surface, as shown in figure 1, I. Separate hydroxyl (silane alcohol groups); II. Paired hydroxyl, belongs to the neighboring silicon atoms; III. Combined hydroxyl, two to four
hydroxyl groups nearby; In addition, sodium aluminum silicate has: 

IV. Aluminum alcohol group (Al-OH); 
V. Sodium silicate group (Si-O-Na) [2-4].

Fig. 1 The structure of aluminum sodium silicate

Like other inorganic nonmetallic mineral fillers, sodium aluminum silicate has different interfacial properties and poor compatibility with organic polymers, so it is difficult to disperse uniformly in the matrix, which leads to the decrease of some properties of the material. However, because the presence of hydrophilic groups on the surface of sodium aluminum silicate contributes to the physical adsorption of organics, it is easy to react with a variety of substituents: surface active substances [5-7], hydrophobic inducers or adhesive irritant compound, such as silane coupling agents [8-10]. It can modify the surface of sodium aluminum silicate to react with groups on the surface of silicate. It can cover the filler, improve the dispersion of the filler, and bond between the filler and polymer during vulcanization, and finally improve the properties of the material.

In this paper, four kinds of triethoxysilane were used to modify the micrometer grade aluminum silicate filler to study the effect of different silane on the properties of sodium aluminum silicate / hydrogenated butadiene-acrylonitrile composites.

2. Experimental

2.1. Materials
HNBR was supplied by ARLANXEO with the trade name Therban 3907. Sodium aluminium silicate was obtained from Cabot. Anti-aging agent Vulkanox ZMB2/C5 was from Lanxess. Antioxidant Luvomax CDPA was from Lehmann & Voss. Peroxide Di (ter-butylperoxyisopropyl) benzene was from AkzoNobel. Silane-coupling agent AMEO/VTEO/GLYEO were supplied by Evonik. Silane OCTEO was obtained from Sigma-Aldrich.

2.2. Compounding and vulcanization
The formulation for Sodium aluminum silicate/HNBR composites is shown in Tab. 1.

Sodium aluminium silicates were first mixed with silane before mixing.

The mixing of sodium aluminium silicates and HNBR was carried out by an internal mixer(GK400N rubber and plastic test mixer), with discharging temperature at 130°C.

Peroxide, anti-aging agents and antioxidants subsequently was mixed with Sodium aluminium silicate/HNBR compounds on an open two-roll mill under 40°C. Finally, the mixes were vulcanized at 175°C to their respective cure time (t 90).

Tab. 1 Formulation in Sodium aluminum silicate/HNBR composites.

| Compound | HNBR (phr) | Sodium aluminum silicate | Vulkanox ZMB2/C5 | Luvomax CDPA | Peroxide | Silane |
|----------|------------|--------------------------|------------------|-------------|----------|--------|
| | 100 | 60 | 0.4 | 1.1 | 7 | 0 / 0.5 / 1 |
2.3. Tests
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 1Hz 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:

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

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 [11].

Dynamic mechanical analysis was carried out in shear mode, using DMA-2980 dynamic mechanical analyzer (TA Instrument, USA). The frequency of the tests was 10Hz; the temperature range is from −50 to 50°C at a rate of 3°C/min.

| Tab. 2 Structural formula and molecular weight of silane |
|---------------------------------------------------------|
| Silane | VTEO | AMEO | GLYEO | OCTEO |
| Structure | | | | |
| molecular weight (g/mol) | 190.31 | 221.37 | 278.42 | 276.49 |

3. Results and discussion

3.1. Bound rubber analysis

| Tab. 3 Bound rubber content in sodium aluminum silicate/ HNBR compounds |
|---------------------------------------------------------------|
| Silane / phr | 0 | 0.5 | 1 | 0.5 | 1 | 0.5 | 1 |
| VTEO | VTEO | AMEO | AMEO | GLYEO | GLYEO | OCTEO | OCTEO |
| Bound rubber content/ % | 58.6 | 57.3 | 56.3 | 58.8 | 59.4 | 57.7 | 59.5 | 58.6 | 55.7 |

It can be seen from Tab. 5 that the bound rubber content of the compound is about 58% with different silane added to the sodium aluminosilicate / butyronitrile hydride blends. It is considered that the addition of silane in this experiment has no obvious effect on the bound rubber content of aluminum silicate / nitrile hydride compounds.

3.2. Dynamic mechanical property

![Fig. 2 Relationship between storage modulus and strain of sodium aluminum silicate/ HNBR vulcanizates and compounds](image)
As shown in Fig.2, it can be seen that the storage modulus of all the filled compounds decreases obviously with the increase of strain amplitude except Therban 3907. This is caused by the destruction of filler network and slippage on the interfacial surface between the sodium aluminum silicate and HNBR molecules. Under low strain, the storage modulus of Therban 3907 is the lowest. When sodium aluminum silicate was added (without silane), the storage modulus of the compound increases rapidly due to the filler aggregation. When silane was added, it can be seen clearly that the storage modulus of the compounds decreases obviously, and the dispersion of sodium silicate filler increases, especially in OCTEO treated compounds.

As mentioned, the structure of sodium aluminum silicate contains three types of hydroxyl groups and aluminum alcohol groups. Because of these groups, siloxane on silane is hydrolyzed to silanol group. Silanol group can form hydrogen bond with hydroxyl group on sodium aluminum silicate surface. During the heating process, dehydration reaction was occurred between the coupling agent and the filler surface, and the silane coupling agent is covalently bonded with the filler, which greatly improves the dispersion of the filler.

According to the theory of surface energy, mineral filler belongs to high energy surface. In order to improve its compatibility with polymer matrix, the surface energy of matrix must be reduced by the hydrophobic group (R) of coupling agent. If the -R is saturated hydrocarbon bond, the surface energy can be lowest. That is why OCTEO treated compound has the lowest storage modulus.

The strain sweep of the vulcanizates was shown in Fig. 2b. The shear storage modulus G’ of sodium aluminum silicate filled with nitrile hydride vulcanizate is significantly higher than that of its compound (Fig .2a). With the increase of shear strain, nonlinear decrease trend of shear storage modulus of vulcanizates was observed. This was caused by the destruction of the network structure of sodium aluminum silicate particles, the destruction of the interaction between sodium aluminum silicate and HNBR rubber molecules and macromolecular chains.

At the same strain, the filler network is destroyed when silane was added. The filler aggregation decreases, and the shear storage modulus of vulcanizate decreases obviously. As the shear strain is less than 10%, the shear storage modulus G’ values of sodium aluminiumsilicate filled with nitrile hydride vulcanizate are as follows: 0 phr silane > VTEO > AMEO > GLYEO > OCTEO.

It is considered that the destruction of filler network is the main reason, and there is no slippage between filler and rubber macromolecules and the network destructions of macromolecular rubber chains when the shear strain is less than 10%. When the strain exceeded 10%, the order of shear storage modulus of vulcanizates changes as follows: VTEO > 0 phr silane > AMEO ≈ GLYEO > OCTEO.

Compared with the storage modulus of vulcanizate at strain 12%, it is found that the storage modulus of VTEO vulcanizate was the highest. When the strain exceeds 22%, the storage modulus of vulcanizates treated with GLYEO and AMEO almost exceed that of vulcanizates without silane.

This is because most of the filler network has been destroyed, and the interaction between rubber and fillers and the network of macromolecular rubber chains begin to take effect when the strain exceeds 10%.

VTEO silane is active in peroxide vulcanization system, vinyl double bond in VTEO can provide effective crosslinking point to connect with rubber network. During the process of vulcanization of HNBR, the cyano group on HNBR is partially hydrolyzed at high temperature, the epoxy group in GLYEO silane is active due to molecular tension which is Easy to be attacked by nucleophilic reagent and then cross-linked with rubber macromolecules. Amino groups in AMEO silane can form hydrogen bonds which contribute to the storage modulus of vulcanizates. OCTEO has no reactivity in peroxide vulcanization system. Although filler dispersion behaves best in OCTEO treated vulcanizate, OCTEO silane simply covers the filler.
3.3. Dynamic thermomechanical analysis

As seen from Fig. 3, the glass transition temperature of rubber molecular chain increased when silane was added, the peak value becomes larger, and the tanδ peak appears later. Compared with those without silane. The tanδ peak of the vulcanizates with OCTEO silane was the largest, followed by AMEO, VTEO and GLYEO. The tanδ depends on the internal frictions of the rubber molecular chains during the glass transition, which not only related to the molecular chain structure, but also with relevant the number of rubber molecules participating in the free movement of the deformation process in filled rubber system. The aggregation of fillers is reduced due to the addition of silane comparing with that in the system without silane. The inclusion rubber formed among aggregates were released, so the number of rubber that can be deformed freely is increased, and this part of rubber can participate in deformation which increasing the tanδ value.

4. Conclusion

The addition of silane can improve the dispersion of sodium aluminum silicates in HNBR rubber, OCTEO behaves obviously. The compounds and vulcanizates decrease nonlinearly with the increasing of strain. The interantion between fillers and rubber and the crosslinkings of rubber were enhanced in VTEO, GLYEO, AMEO treated composites. The glass transition temperature of HNBR rubber chains increased when silane was added.

Acknowledgments

This work was financially supported by ARLANXEO Deutschland GmbH, Polymer Testing fund.

References

[1] Zheng Shuilin, Lu Shouci. The application status and development prospects of surface active non-metallic mineral fillers in plastic products [J]. China Non-metallic Mineral Industry Guide, 1999, (1): 7-12.
[2] Werner R, Krysztakiewicz A, Jesionowski T. Effect of silane coupling agents on properties of sodium aluminium silicate P820 [J]. Pigment Resin Technol 2000, 29:281.
[3] Jesionowski T, Krysztakiewicz A, Werner R. Modified sodium aluminium silicates polyurethane fillers and paint pigment [J]. International Symposium EUROFILLERS’99 Villeurbanne, France, extended abstract.
[4] Jesionowski T, Krysztakiewicz A. Production of a highly dispersed sodium-aluminium silicate to be used as a white pigment or as a polymer filler [J]. Pigment Resin Technol 1996, 3:5.
[5] A. Krysztakiewicz, Czynniki wiązące w układzie napęlcacz–polimer [J]. Chemia Stosowana
1989 (33):561.

[6] F. Szanto, I. Dekany, A. Patzko, B. Varkonyi, Wetting, swelling and sediment volumes of organophilic clays [J]. Colloids Surf. 1986, (18): 359.

[7] A. Patzko, I. Dekany, Ion exchange and molecular adsorption of a cationic surfactant on clay minerals [J]. Colloids Surf. A: 1993 (71): 299.

[8] D. Wang, F.R. Jones, P. Denison, K.L. Mittal, Silane and other Coupling Agents, VSP, Utrecht, 1992.

[9] E.P. Plueddemann, Silane Coupling Agents, Plenum Press, New York, 1992.

[10] A. Pizzi, K.L. Mittal, Handbook of Adhesive Technology, MDI, New York, 1994.

[11] H. H. Le, K.Oßwald, S. Wießner, et.al. Location of dispersing agent in rubber nanocomposites during mixing process [J]. Polymer, 2013(54): 7009-7021.