

Effect of bentonite modified by silane on rubber blends properties

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Abstract. The presented paper deals with the preparation of bentonite modified by silane and its application into polymer matrix. Natural bentonite was modified with 3-(Trimethoxysilyl) propyl-methacrylate in two different solutions. These two solutions had the same composition (ethanol, water and 3-(Trimethoxysilyl) propyl-methacrylate) but in one solution, pH was modified. These bentonites modified by silane were characterized by Fourier transform infrared spectroscopy. The modified bentonites were mixed into rubber matrix as partial replacement of commonly used filler – carbon black of the N339 type. The polymer blends were investigated from the aspect of the rheological and curing characteristics (minimum torque M_L , maximum torque M_H , optimum time of cure t_{c90} , processing safety of blend t_s). Moreover, the quality of the silanization reactions was investigated. Measurements were done using PRPA 2000.

Keywords: bentonite, silanization, fillers, curing characteristics, silane

1 Introduction

Surface modification is a good way to improve the dispersive properties and increase the surface activity of filler. The most of particulate fillers are inorganic and their surfaces have poor compatibility with hydrocarbon polymers. Among other effects, this can result in processing problems, such as high viscosity, poor dispersion and poor mechanical properties [1, 2].

In order to obtain a positive effect of the surface treatment, it is necessary to select the suitable modifier for the treatment, with respect to the filler and the matrix. Organosilanes along among the most frequently used surface modifiers [1, 3, 4].

In the material research of the polymeric materials, the current trend includes research of polymers in combination with clay minerals. The economic as well as environmental aspects are the reasons for the mentioned investigation of clay minerals with polymers [5, 6]. Clay fillers, in contrast to carbon black, have lower compatibility with the rubber matrix, and for this reason, the silane-binding agents are used to improve the interaction of the clay filler with the rubber chains [1, 7, 8].

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Surface modification of clay fillers has attracted much attention because the obtained products exhibit properties suitable for many applications in material science and environmental engineering. Modification is generally considered to be an attractive and effective method because due to this method, the clay particles (e.g. kaolin and montmorillonite) are more compatible with rubber matrix [9].

2 Experimental

2.1 Preparation of modified bentonite

The natural bentonite was used as initial material to be modified bentonite and this initial material was extracted from the locality called Jelsovy Potok. The chemical composition of natural bentonite is given in Tab. 1 while content of montmorillonite was 80 %. Before the surface modification, natural bentonite was dried in dryer at the temperature of 80 ± 5 °C to get constant weight. Then, this silane type was chosen to modify the bentonite surface: 3-(Trimethoxysilyl) propyl-methacrylate (TSPMA).

Table 1. Composition of natural bentonite in Weight %

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O
Weight %	59	20	0.3	0.2	2.2	4	0.7	0.4

The modification was carried out for two different solutions. The first solution consisted of ethanol-water mixture (70:30) with subsequent addition of silane (3 wt parts of modifying agent per 100 wt parts of filler) [9, 10]. The second solution had the same composition but its pH was treated with acetic acid. A bentonite sample was then added to both solutions and the two mixtures were stirred at 60 °C and 450 rpm for 2 hours. The resulting suspensions were filtered under reduced pressure and the prepared samples were dried in dryer at the temperature of 80 ± 5 °C. For further experiments, two prepared modified bentonites with a particle size < 25 µm were used.

2.2 Preparation of rubber blends

The five tread blends were prepared by two-step mixing in laboratory mixer of Brabender type with chamber volume of 80 cm³ and mixing process involved 60 revolutions per minute. The proper order of the steps in relation to additives and cure system was performed as it was predetermined. The specification of tread blends is given in Table 2.

Table 2. Specification and ratio of fillers

blends	Filler	ratio of fillers
R	-	-
S	carbon black	1
SB	carbon black + unmodified bentonite	3:1
SBM	carbon black + modified bentonite by silane agent MPSTA	3:1
SBM +pH	carbon black + modified bentonite by silane agent MPSTA +pH	3:1

2.3 Characterization of the modified bentonite

The detailed characteristics of unmodified and modified bentonites were obtained by measurements based on spectral (FTIR) analysis. The infrared absorption spectra of investigated unmodified and modified bentonites were obtained with Tensor 27 FTIR spectrometer in the 4000-400 cm^{-1} spectral range with the resolution of 4 cm^{-1} . The KBr disk technique was used.

2.4 Characterization of rubber blends

The processing capacity of rubber blend can be predicted using their curing characteristics. The rheological properties and curing characteristics were investigated by help of PRPA 2000 at the temperature of 150 °C during 30 min. The quality of the silanization reactions was investigated by PRPA 2000 at temperature of 100 °C, frequency of 100 CPM and at strain in the range of (1-450) %.

3 Results and discussion

3.1 Modified bentonite

IR spectroscopy is a well-known method to identify the functional groups and to make quantitative analysis. The IR spectra can commonly provide useful information on the surface modification of the bentonite. The FTIR spectra of the unmodified and modified bentonites are shown in Figure 1 and 2. The main peaks from the observed FTIR spectra of the unmodified and modified bentonites are summarized in Table 3.

Table 3. Selected stretching vibrations (cm^{-1}) of the modified bentonite

Type of vibrations	SB	SBM	SBM +pH
ν (Al-OH)	3627	3629	3628
ν (H-O-H)	3454	3457	3452
ν_{as} (CH_3)	-	2958	2960
ν_{as} (CH_2)	-	2931	2924
ν_{s} (CH_3)	-	2895	2854
ν (C-O)	-	-	1126
ν (Si-O)	1056	1038	1035

In the case of the all samples, the band at 3627-3629 cm^{-1} corresponds to the stretching vibration of the hydroxyl groups are bonded with aluminium atoms of the clay mineral. The broad band at 3452-3457 cm^{-1} is assigned to hydroxyl stretching vibrations of the H-O-H groups, of the free and interlayer water molecules on montmorillonite clay, and the band at 1035-1056 cm^{-1} is associated with the stretching vibrations of the Si-O groups. The intensity of the absorption band decreased with surfactant modification, and it gives evidence about a lower hydrophilicity in the interlayer region. For SBM and SBM +pH samples, the bands at 2854-2960 cm^{-1} are assigned to the C-H stretching vibrations of aliphatic CH_2 and CH_3 groups, indicating the presence of the organic component (silane) [11, 12].

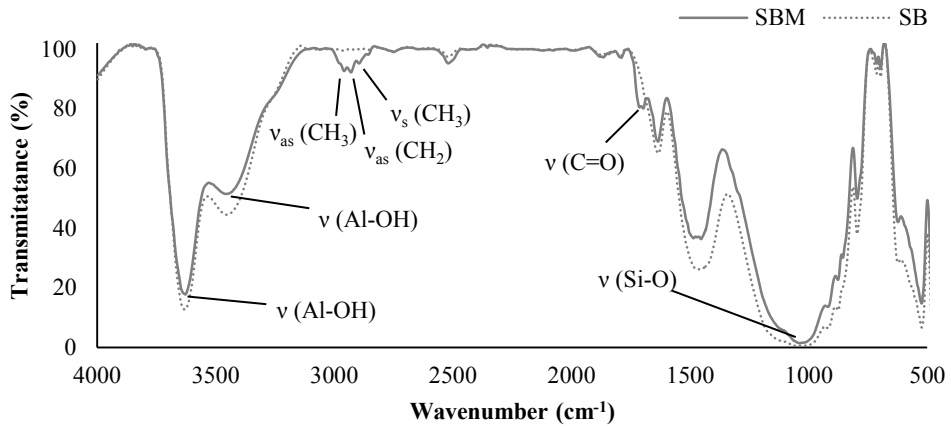


Fig. 1. IR spectra of sample SBM and SB

In case SBM +pH sample, the band at 1126 cm^{-1} is assigned to stretching vibrations of the C-O groups, indicating the presence of the organic component (silane) [11, 12].

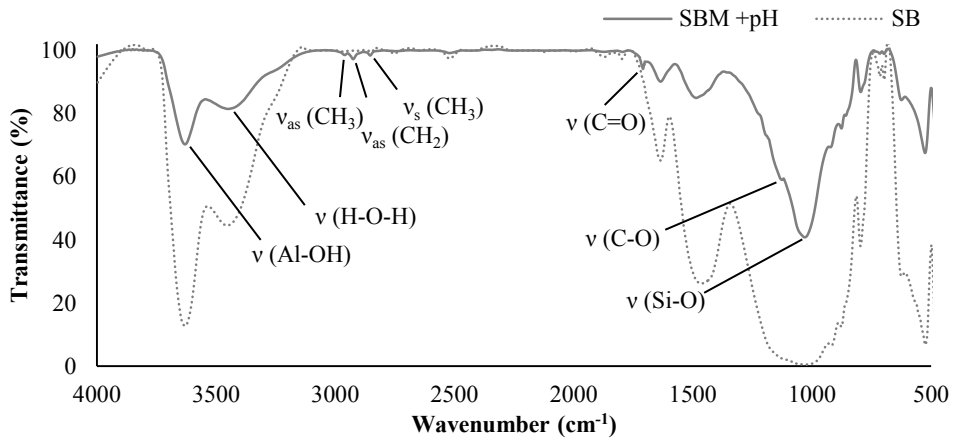


Fig. 2. IR spectra of sample SBM +pH and SB

3.2 Cure behaviour of the rubber blends

The effect of the modified filler on the course of sulphur curing process of tread blends was evaluated on the basis of curing characteristics. Based on the evaluated rheometric results of curing curves, the values of rheometric properties and curing characteristics are shown in Table 4. Graphical presentation of the curing curves is shown in Figure 3.

Table 4. Rheological and curing characteristics of rubber blends

blends	M_L (dN.m)	M_H (dN.m)	t_s (min)	$t_{c(90)}$ (min)
R	1.69	8.78	2.30	6.95
SB	1.47	6.88	3.55	12.43
SBM	1.36	6.94	3.64	11.78
SBM +pH	1.48	6.86	4.56	14.23

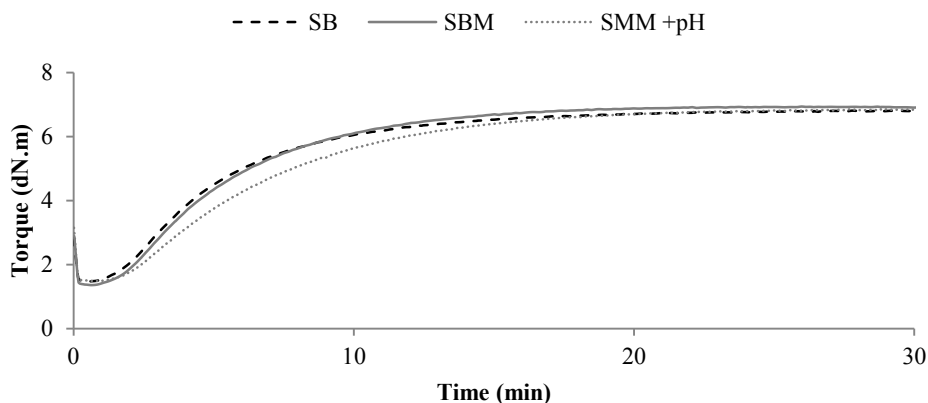


Fig. 3. Cure records of SB, SBM SBM +pH and R blends

The values of minimum torque and maximum torque for tread blend are lower in comparison with the reference blend values. The decrease of values indicates lower viscosity as well as lower stiffness of the tread blends at the beginning and end of the cure. From Table 4, it can be seen that the values of processing safety of tread blends are higher in comparison with the reference blend values. It can be assumed that the content of fillers in the rubber blends has a positive effect on processing safety, and it may affect the processing properties of the blends. In the case the optimum time, blends exhibited higher values in comparison with reference blend values [5].

3.3 The quality of the silanization reactions

The test was divided into two parts where the first part of the filler-filler interaction was determined at low strain (1%) and by this way, the size of the elastic moment (G') was recorded. In the second part, there was the higher strain (450%) and using this strain, the size of the torque moment (S') was determined (cohesion polymer network). The lower the filler-filler interaction, the better the dispersion of the filler used. This results in a higher efficiency of the silanization reaction. The torque value at high deformation angles indicates whether the effect of temperature in the silanization reaction could cause undesired curing of blend. The torque value should be as low as possible, otherwise there will be an increase in the degradation of the silane [13, 14]. The results are shown in Table 5 and depicted graphically in Figure 4.

Table 5. Values of G' and S' for determination of the silanization reaction quality

Blends	G' (1%)	S' (450%)
SBM	230.34	9.93
SBM +pH	247.76	11.15

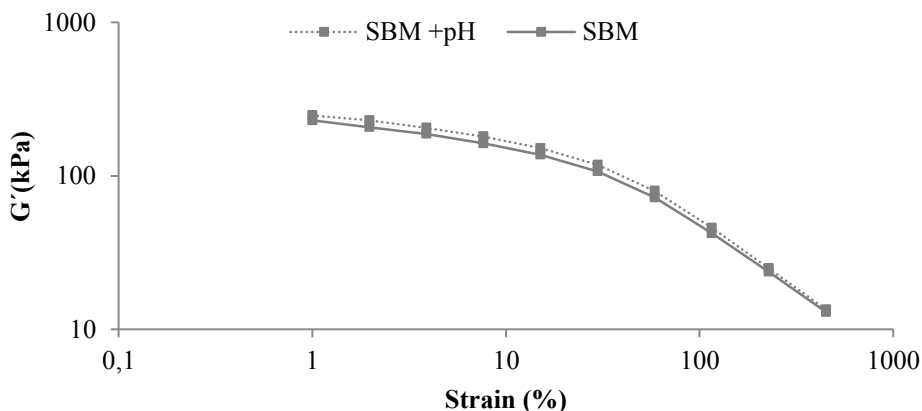


Fig. 4. The dependence of G' on strain for SBM and SBM +pH blends

From the measured results, the lowest value of the elastic modulus, and thus the lowest efficiency of the silanization reaction, showed a SBM blend and it indicates that the filler is well dispersed in the polymer matrix.

Conclusions

This study was based on modification of bentonite which was used as partial replacement of the high reinforcing filler – carbon black of N339 type. The polymer blends with the modified bentonites were used as a partial carbon black replacement and they were investigated from the aspect of rheological properties and curing characteristics. In addition, the quality of silanization reaction was investigated. The determination of the quality of silanization reaction shows that there is the lowest value of the elastic modulus - G' (1%) and thus there is the highest efficiency of the silanization reaction in relation to blend containing filler based on modified bentonite (SBM) and it leads to facts that the filler is well dispersed in the polymer matrix.

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