Curing characteristics and rheological properties of bentonite-filled rubber blends

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Abstract. The study deals with the examination of the rheological behaviour of rubber blends which were filled with bentonite. The filler - polymer as well as the filler - filler interactions were studied and determined from the frequency sweep and strain sweep rheological measurements. The used natural bentonite was extracted from the locality called Jelsovy Potok. The natural bentonite had a fine fraction with a particle size of 15µm a 45 µm and it was added into rubber blends as a partial replacement of commonly used filler. The rubber blends were characterised on the basis of curing characteristics (minimum torque M_L, maximum torque M_H, optimum time of cure t_(90), processing safety of blend t_p). Moreover, the complex viscosity and Payne effect were also specified. The required measurements were done by using PRPA 2000.

1. Introduction
Recently, the properties of filled rubber blends have attracted a significant attention in many contexts. Many experiments have shown that the addition of even small loadings of fillers to the polymer matrix can result in order of magnitude property enhancements over that of the neat polymer [1].

The preparation and development of rubber blend prescriptions requires a number of factors that have to be taken into account. As the first of all, it is necessary to consider what kind of application the blend will be prepared for. The influence of the chemicals and additive, which affect the price, properties and processability of the rubber blend, is also very important factor. Moreover, the environmental aspect of production is necessary to be taken into account. Various mineral-based alternatives are used in this regard. These fillers are important in terms of lower environmental impact. However, in order to implement them into the practice, they have to be studied and tested precisely. Development is finished only if the product can be repeatedly and commonly produced in the required quality [2].

In recent years the use of layered silicates (clay minerals) as fillers in polymers has attracted great interest. The dispersion of individual high-aspect ratio clay platelets to form nanocomposites has been shown, even at very low filler concentrations, to lead to dramatic improvements in several properties: increased modulus and impact strength, better dimensional stability, higher heat distortion temperature, reduced flammability, and enhanced barrier properties. These improvements are primarily due to the stronger interfacial interaction between the matrix and clay platelets (approx. 1 nm thick), as compared with conventional filler-reinforced systems [3, 4].

Bentonite is one of the most popular clay rocks with exceptional adsorption properties. The main clay mineral present in bentonite is montmorillonite, which belongs to the smectite mineral group. The properties of bentonite result from the crystal structure of this group. The particles of montmorillonite
have negative charges on their faces due to the isomorphic substitutions in its structure. This negative charge is compensated by the presence of the cations in the interlayer space, which are not fixed and have the character of so called “exchangeable cations” (i.e. Na\(^+\), K\(^+\), Li\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) [5, 6]. This study is focused on the preparation of rubber blends containing the natural bentonite.

2. Experimental

2.1. Materials

Our selected samples of natural bentonite were taken from the area of Jelsovy Potok. The prepared samples differed in particle size, representing the fine fraction with a particle size of 15 μm and 45 μm. Using EDX analysis, the content of individual oxides in natural bentonite samples was determined and the given oxides are listed in Table 1.

| Sample | SiO\(_2\) (%): 68.22 | Al\(_2\)O\(_3\) (%): 20.04 | Fe\(_2\)O\(_3\) (%): 2.47 | CaO (%): 4.20 | K\(_2\)O (%): 1.02 | MgO (%): 2.76 | SO\(_3\) (%): 0.77 |
|--------|----------------------|--------------------------|------------------|-----------|----------------|-------------|-------------|
| B 15   |                      |                          |                  |           |                |             |             |
| B 45   |                      |                          |                  |           |                |             |             |

The prepared samples were used as a partial replacement for commonly used carbon black fillers.

2.2. Preparation of bentonite-filled rubber blends

The five rubber blends were prepared by two-step mixing in laboratory mixer (Plastograph®EC plus Brabender) with chamber volume of 80 cm\(^3\) and mixing process involved 50 revolutions per minute. The proper order of the steps in relation to additives was performed as it is predetermined. The accelerator and sulphur were added at the end of the mixing process to avoid the occurrence of premature crosslinking reaction. The prepared B 15 and B 45 samples were added with lower filling or loading (5 phr) and higher filling or loading (10 phr). The composition and designation of rubber blends is given in Table 2.

| Designation                          | Ingredients                         | Content (phr) |
|--------------------------------------|-------------------------------------|---------------|
|                                      | SMR10                               | 100           |
|                                      | Zinc Oxide                          | 3             |
|                                      | Stearic acid                        | 2             |
|                                      | Carbon black N550                   | 50-60         |
|                                      | Bentonite                           | 0-10          |
|                                      | Oil                                 | 1.5           |
|                                      | CBS                                 | 1.5           |
|                                      | Sulphur                             | 2.5           |

2.3. Determination of rheological properties

2.3.1. Curing characteristics. The curing characteristics of the bentonite-filled rubber blends were obtained, using an oscillating rheometer (PRPA 2000), which was employed to determine the minimum
torque \( (M_L) \), maximum torque \( (M_H) \), processing safety of blend \( (t_s) \) and optimum time of cure \( (t_{c(90)}) \).

Samples of the respective blends were tested at 160° C with oscillating arch of 1° and frequency of 1.67 Hz. The cure rate index (CRI) of the rubber blend was calculated, using the following equation:

\[
CRI = \frac{100}{t_{c(90)} - t_s}
\]

2.3.2. Complex viscosity. The low frequency region of the rheological plot reflects the effect of structure of natural bentonite on the viscoelastic properties of the nanocomposites. Therefore, to explore the influence of clay on the rheological behavior of the nanocomposites, the dependence of modulus and \( \eta^* \) on the frequency \( (\omega) \) was studied at low frequencies. The complex viscosity of the bentonite-filled rubber blends was determined by an oscillating rheometer (PRPA 2000).

2.3.3. Payne effect. The Payne effect is known to be a special feature of the tensile behavior of rubber composites containing fillers. It manifests itself as a dependence of the storage and loss modules on the amplitude of the applied stress. Above a certain amplitude of the critical deformation, the accumulation modulus decreases rapidly with increasing amplitude at relatively large deformations [7, 8]. The Payne effect was assessed on the basis of the storage shear modulus \( (G'') \) data, obtained with an oscillating rheometer (PRPA 2000). The strain test was performed in the range from 0.28% to 100% strain at 1 Hz and 100°C. The Payne effect \( (\Delta G'') \) was calculated by subtracting the values of storage shear modulus at 0.28% and 100% strain. The difference of \( G'' \) at 0.28% and 100% strain was taken as a measure of filler - filler interaction [9].

3. Results and discussions

3.1. Curing characteristics

The curing characteristics of rubber blends clearly reveal the influence of the investigated fillers on the properties of the final vulcanizates and the tendency of the filler particles to interact [9]. The results of the curing characteristics for the bentonite-filled rubber blends and standard rubber blend (S) are shown in Table 3.

| Blends | \( M_L \) (dN,m) | \( M_H \) (dN,m) | \( t_s \) (min) | \( t_{c(90)} \) (min) | CRI (min\(^{-1}\)) |
|-------|-----------------|-----------------|----------------|------------------|----------------|
| S     | 3.36            | 47.06           | 1.17           | 4.07             | 34.48          |
| B15-5 | 3.09            | 48.27           | 1.27           | 3.51             | 44.64          |
| B15-10| 2.58            | 43.18           | 1.56           | 3.79             | 44.84          |
| B45-5 | 3.03            | 43.49           | 1.43           | 3.64             | 45.25          |
| B45-10| 2.75            | 39.15           | 1.33           | 3.54             | 45.25          |

Figure 1 shows the curing characteristics for standard blend and bentonite-filled rubber blends. The values of minimum torque \( (M_L) \) for all bentonite-filled rubber blends were lower in comparison with the standard blend. The lower the \( M_L \) value, the weaker the filler - filler interaction, resulting in lower viscosity of the blend [10].

In the case of maximum torque, almost all of the rubber blends exhibited lower values in comparison with the standard blend. This can be attributed to the decrease in the cross-linking density of vulcanizates and to the viscosity of rubber compounds and it indicates the low rubber - filler interaction [11, 12]. Table 3 shows the variation of maximum torque value for B 15-5 sample, which has higher value in
comparison with the standard blend. Higher maximum torque indicates a good state of cure and the high stiffness suggests that the blend is equal to have good mechanical properties [13].

In practice, the time (t) is the most suitable for the safety of the blend because until the given time, the disulfide bridges are formed, when exposed to temperature and pressure in the blend and this process is connected with formation a three-dimensional network, causing the change in material from plastic state to elastic. Compared with the standard (S), the values increase slightly. From this fact, we can assume that fillers, which are based on natural bentonite, have a positive effect on the processing properties of blends [14].

Figure 1. Cure curves for rubber blends.

Time (tc90) shows us that the optimum time of cure should not exceed the measured time. This is mainly due to the cure itself and it is related to the so-called pre-cured blends. All rubber blends exhibit the decrease in the values of the optimum time of cure, compared with the standard blend. The values of processing safety for all rubber blends were higher, compared with the standard blend (S).

In the case of curing rate index (CRI) (Figure 2), all blends exhibited higher values, compared with standard blend. Higher CRI implies that the cure rate is fast and it is desirable for increasing the yield in the most of industrial applications [13].

Figure 2. The curing rate index (CRI) for rubber blends.
3.2. **Payne effect**

The quality of the polymer - filler and filler - filler interactions was evaluated by determining the dynamic properties of the filled blends, with emphasis on the strain-dependence of the storage shear modulus. Results from dependence of storage shear modulus on deformation for rubber blends are shown in Figure 3 and Figure 4.

**Figure 3.** Dependence of storage shear modulus on deformation for S, B 15-5, B 15-10 rubber blends before cure (a) and after cure (b).

The measured results show that the B15 blend with lower filling reached almost identical storage shear modulus before and after curing as the S blend. It can be seen from Figure 4 that in the area of low deformation, the value of the storage shear modulus of the blend B 15 with higher filling is significantly lower in compared with S blend.

**Figure 4.** Dependence of storage shear modulus on deformation for S, B 45-5, B 45-10 rubber blends before cure (a) and after cure (b).
The dependence of the storage shear modulus on the deformation of S and B 45 blends with higher and lower filling, before and after cure, shows that in the B 45 blend with the higher filling, there was a significant decrease in storage shear modulus values in the area of low deformation of the blend. In the B 45 blend with lower filling in the area of low deformation before cure, the values of storage shear modulus decreased slightly, compared with S but after cure, they decreased more significantly.

In this study, the Payne effect was calculated from the difference between storage shear modulus before and after cure and the results are shown in Table 4.

Table 4. Payne effect ($\Delta G'$) for the rubber blends before and after cure.

| Sample | before cure | after cure |
|--------|-------------|------------|
|        | $G'_0.28\%$ (kPa) | $G'_0.02\%$ (kPa) | $\Delta G'$ (kPa) | $G'_0.28\%$ (kPa) | $G'_0.02\%$ (kPa) | $\Delta G'$ (kPa) |
| S      | 629.96      | 118.48     | 511.48       | 3073.08       | 1234.42       | 1838.66       |
| B 15-5 | 576.87      | 110.65     | 466.22       | 3077.94       | 1204.45       | 1873.49       |
| B 15-10| 423.86      | 102.28     | 321.58       | 2375.59       | 1079.71       | 1295.88       |
| B 45-5 | 574.14      | 111.29     | 462.85       | 2608.94       | 1070.06       | 1538.88       |
| B 45-10| 481.24      | 103.03     | 378.21       | 2126.35       | 923.85        | 1202.50       |

Figure 5. Payne effect values for the rubber blends before and after cure.

In the Figure 5, we can see that from the aspect of the given interaction, Payne effect values for almost all of the examined samples were lower significantly, compared with S blend. For blends, where the $G'$ value decreased significantly, this phenomenon can be identified as the consequence of the interruption of the filler - filler interaction, and there could also be a "disassembly" of the three-dimensional rubber - filler network [9]. However, the B 15 blend with lower loading showed the higher Payne effect value in comparison with the standard sample, indicating the better filler - filler interaction.

3.3. Complex viscosity

The following figures show the dependence of the complex viscosity ($\eta^*$) on the oscillation frequency for the bentonite-filled rubber blends as well as the standard blend.
Figure 6. Dependence of viscosity (η*) on frequency for S, B 15-5, B 15-10 rubber blends.

Figure 6 shows that the complex viscosity of all blends decreases with increasing frequency, indicating non-Newtonian, pseudoplastic behavior of the materials [15]. The values η* of the B 15 mixture with a lower filling approach S with increasing frequency and this finding indicates a good interaction of the filler in the polymer matrix and this fact is also confirmed by the results referring to the minimum torque [4]. On the other hand, the B 15 blend with a higher filling shows a slight decrease in the viscosity values, which was probably caused by a higher filling amount.

Figure 7. Dependence of viscosity (η*) on frequency for S, B 45-5, B 45-10 rubber blends.

From Figure 7, we can conclude that the viscosity values for B 45 blends, with higher and lower filling, decreased significantly, compared with the standard blend. We hypothesize that this behavior may have been influenced by the larger particle size, indicating a worsening of the filler - filler interaction.

4. Conclusion
The work dealt with the preparation of model rubber blends, using fillers, based on natural bentonites. Its main aim was to assess the interaction of natural bentonite in a polymer matrix which was studied
and determined from the frequency sweep and strain sweep rheological measurements. From the overall comparison of all examined characteristics, we can conclude that the B 15 blend with lower filling has the most comparable values to the standard rubber blend. This finding indicates the given rubber blend as the potential blend for further research.

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