Effect of alternative filler from glass industry on the selected properties of friction polymer matrix in automotive industry

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Abstract. This paper is focused on the preparation of polymer blends with addition of alternative filler from glass industry in various granularity (>40 µm, 40–32 µm, 32–25 µm, 25–0 µm). The polymer matrix (PMX3) consists of melamine resin, phenolic resin and nitrile rubber. This polymer matrix composition is commonly applied in friction composite systems in automotive industry. The surface activity of various filler fractions was studied. The rheological properties, such as minimum torque, maximum torque, optimum vulcanization time and scorch time of prepared friction polymer matrix were tested, using the PRPA 2000 rheometer. Mooney viscosity of new prepared polymer matrix was studied with help of Mooney Viscosimeter 91.03 Gottert testing machine.

1. Introduction
The requirements for the resulting products as well as the technological processes used in the automotive industry are being changed significantly. The ever-increasing demands of consumers bring requirements to reduce fuel consumption, emissions and weight along with the preservation and increase of quality, durability, safety and environmental protection. To meet these demanding requirements, the continuous development of innovative solutions to obtain new products with better quality parameters is essential condition. Due to increased interest in environmental protection and unstoppable technical progress, there is an increasing need to develop new materials. With the growing number of reports on the dangerous effects of asbestos in the 1960s, there was a significant change in the development of the friction materials. Polymer composite materials provide a wide range of possibilities for developing of new and more efficient friction materials which are useful in practice. Based on the innovative technologies and advanced materials, it is important to point out that developmental and experimental trends differ in terms of the investigated effects of various fillers and components and the solution of problems is resulting in the production or the search for the use of biological materials in order to reduce the negative impact on the environment. The introduction of new green solutions and practices helps to reduce the negative impact on the environment [1].

This work deals with the study of the properties of alternative filler based on industrial waste from glass production and investigation various glass waste fractions in polymer blends used in the production of friction composite systems.
2. Materials and methods

2.1. Preparation of samples
The investigated polymeric system (PS) with PMX3 code designation was made of a mixture of melamine resin, phenol-formaldehyde resin and nitrile-butadiene rubber, while this PS is commonly used as a polymer matrix of friction composite systems reinforced with various organic, inorganic and metal fibres, yarns or fillers. PMX3 granules were plasticized for 3 minutes at 80 °C ± 2 °C and 80 kN ± 1 kN in the Plastograph EC plus laboratory mixing machine (Manufacturer: Brabender) under constant operating speed of 50 rpm. Alternative filler with different fraction (>40 µm, 40–32 µm, 32–25 µm, 25–0 µm) was added into blend in amount of 3 phr. After addition of filler into blend, the given blend was mixed for 3 minutes because of better incorporation of the filler into the blend. Polymer blend was homogenized by using laboratory twin-cylinder (calander) – LaboWalz W 80 T machine (Manufacturer: VOGT) in order to obtain the slab in thickness of 2 mm. Before another processing procedure, the blend was left for 24 hours at laboratory temperature of 25 °C ± 2 °C.

2.2. Surface characterization of various fractions of filler by gas
Surface activity of filler was investigated by BET gas adsorption analyzer (Manufacturer: Quantachrome AntosorbetQ). Samples were degassed by heating in inert atmosphere of vacuum before every performed measurement. Glass holder with sample was dipped or immersed into cold liquid with its access to the used gas. The temperature of every sample was 150 °C and measurement was performed for 4 hours.

2.3. Investigation of rheological properties of polymer blends
Rheological properties of prepared blends with different fractions of filler were investigated by PRPA 2000 (Manufacturer: AlphaTechnologies). From obtained slabs, the samples were cut to the needed shape for rheological measurement – Cutter 2000 (Manufacturer: AlphaTechnologies) was used to prepare the required samples. After reaching of the testing temperature (180 °C), the test chamber was opened. Tested sample was embedded into rotor, chamber was closed and traction of rotor was turned on. A cellophane film was used for protection of testing chamber and rotor. Test was performed for uncured polymer blend at 180 °C with frequency of 1.66 Hz at 60 minutes and 5 % oscillation angle.

2.4. Study of Mooney viscosity
Mooney viscosity of prepared blends with different fractions of filler was studied by using Mooney Viscometer 91.03 Gottert testing machine. The samples were cut to the needed shape for viscosity measurement by using Cutter 2000 (Manufacturer: AlphaTechnologies). After reaching of the testing temperature (120 °C), the tested sample was placed above and below the rotor and then the platens were closed under pressure. The rotor was rotating at a constant speed of two revolutions per minute (2 RPM) and by means of a precise transducer system located below the die assembly, the torque exerted on the rotor head was measured and recorded within the system data files.

3. Results and discussion
In results and discussion, the results of surface activity of various filler fractions, vulcanization characteristics and Mooney viscosity of polymer blends are summarized.

3.1. Surface activity of various filler fractions
Measurements of surface activity of various filler fraction are shown in table 1. Static gas adsorption offers a powerful tool for characterizing of the filler surface. The mentioned BET method can help us to obtain the specific surface area and give us detailed information on the energetic surface heterogeneity and the porosity or the surface roughness. The adsorption isotherm at a given temperature characterizes the amount of adsorbed gas in thermodynamic equilibrium as a function of pressure [2].
Table 1. Adsorption of filler fractions.

| Fraction of filler | BET (m$^2$ g$^{-1}$) |
|--------------------|----------------------|
| >40 µm             | 0.4                  |
| 30–40 µm           | 0.8                  |
| 25–32 µm           | 0.7                  |
| 25–0 µm            | 2.2                  |

In table 1, it is possible to see adsorption of different fractions of filler. With decrease of filler particle size, adsorption increased. Increase of filler adsorption represents its higher surface activity. From the given results it is possible to see that the surface activity initiate and provide attachment of polymer chains to particle surface and it leads to formation of polymer-filler interface and connection polymer-filler system is enhanced by higher surface activity of filler [3]. This statement was confirmed by the results from the measurement of rheological properties where optimum cure time and thus optimum properties were obtained in the case of the polymer blend with the smallest filler particle size (25–0 µm).

3.2. Rheological properties

Measured values of rheological properties of prepared blends with different size of alternative filler are in table 2. The minimum and maximum torques represent the first described properties. Minimum torque is the lowest torque in the vulcanization curve and it is equal to viscosity of the blend heated to vulcanization temperature – this torque value characterizes the blend stiffness. Maximum torque is the highest torque in the vulcanization curve and it is equal to the value of the shear modulus of the vulcanized blend at the given temperature. This torque value characterizes the stiffness at the end of vulcanization process [4].

Table 2. Vulcanization characteristics of polymer blends (PMX3).

| Type of samples | $M_{\min}$ (dNm) | $M_{\max}$ (dNm) | $t_{c90}$ (min) | $t_{s02}$ (min) |
|-----------------|------------------|------------------|----------------|----------------|
| Standard        | 0.25             | 177.20           | 5.45           | 0.43           |
| >40 µm          | 0.67             | 193.34           | 4.87           | 0.41           |
| 30–40 µm        | 0.50             | 200.92           | 3.92           | 0.40           |
| 25–32 µm        | 0.68             | 200.75           | 4.43           | 0.42           |
| 25–0 µm         | 0.59             | 200.80           | 4.86           | 0.44           |

In figure 1, there are the values of minimum ($M_{\min}$) and maximum torque ($M_{\max}$) for polymer blends with different size of alternative filler in PMX3 blend as well as the standard blend for mutual comparison of results. The lowest values of $M_{\min}$ and $M_{\max}$ torque were observed for standard blend without filler. With decrease of filler particle size in blend, $M_{\max}$ torque increased. The filler particle size can be one of the reasons for this mentioned condition, while it can be closely connected with better incorporation of filler into polymer matrix as well as increased stiffness of polymer blends. Obtained results show that filler had stiffening effect in PMX3 polymer blend [4].

Optimum cure time ($t_{c90}$) is the time required for the torque to reach 90 % of the maximum achievable torque ($t_{c90}$) and relates to the time which is necessary for the cured rubber to achieve optimal properties [5]. Scorch time is the time required at a specified temperature (or heat history) for a rubber blend to form incipient crosslinks. When a scorch point is reached after a blend is exposed to a given heat history from the factory processing, the blend is not able to be processed [6].
In Figure 2, there are the values of optimum cure time \((t_{c90})\) and scorch time \((t_{s02})\) for PMX3 blend with different alternative filler particle size and standard blend for mutual comparison of results. With decrease of filler particle size in blend, there is decrease in values of optimum cure time \((t_{c90})\) in comparison with standard blend. The lowest time needed for vulcanization of blend was observed for blend with filler particle size of 40–32 µm. Results shows that filler particle size in blend did not have a significant effect on scorch time \((t_{s02})\). In terms of vulcanization costs, the most suitable blend would be the blend with 40–32 µm filler particle size. From the point of optimum cure time \((t_{c90})\), the most suitable blend is the blend with the smallest filler particle size (25–0 µm).

3.3. Mooney viscosity

Mooney viscosity is a measure of the viscosity of a rubber or blend determined in a Mooney shearing disk viscometer. It is indicated by the torque required to rotate the disk embedded in a rubber/blend specimen and enclosed in the die cavity under specified conditions. Viscosity of rubber or blend plays important role in its processing behaviour. Deviation in the blend viscosity will critically affect its processability, especially in terms of calendering, extruding or injection moulding. It is necessary to point out that viscosity parameter has to be predetermined and maintained within specified limits. As the processing behaviour of the blend changes with respect to its temperature, it is possible to predict how it is going to behave during processing. With the help of Mooney Viscometer, we can predict behaviour of blend with respect to temperature and time during processing [7, 8]. Measured values of
Mooney viscosity (ML 1+4) and scorch time ($t_s$) of prepared blends with different alternative filler particle size are in table 3.

| Type of samples | Mooney viscosity (ML 1+4) | Scorch time $t_s$ (min) |
|-----------------|--------------------------|-------------------------|
| Standard        | 71.44                    | 11.87                   |
| >40 µm          | -                        | -                       |
| 30–40 µm        | -                        | -                       |
| 25–32 µm        | -                        | -                       |
| 25–0 µm         | 75.05                    | 9.96                    |

In table 3, it is possible to see Mooney viscosity (ML 1+4) and scorch time ($t_s$) for polymer blends with different filler particle size. The Mooney viscosity and scorch time were obtained only for standard polymer blend (unfilled blend) and for polymer blend with the smallest filler particle size (25–0 µm). This mentioned condition can be caused by filler particle size and formation of large agglomerates in polymer blend and it is resulting in the increase of stiffness of polymer blend and thus Mooney viscometer was not able to detect individual parameters of polymer blend with higher filler particle size than 25–0 µm. Torque, which is possible to be measured by using Mooney viscosimeter, is only from 0.01 to 200 MU.

4. Conclusion

Results of rheological properties and Mooney viscosity showed that alternative filler had stiffening effect in PMX3 polymer blend. Effect of alternative filler particle size in blends was also visible in values of rheological properties and Mooney viscosity. The occurrence of stiffening effect of filler and formation of large agglomerates in polymer blends led to the condition that it was not possible to obtain results from viscosity and scorch time which was measured by using Mooney viscosimeter. Results from surface activity measurement showed that with higher surface activity of filler, it is possible to obtain better interaction in polymer - filler system as well as better determined material properties of studied polymer blend (PMX3).

As a target for the future, there is the effort to study and propose of the most available environmentally friendly plastificator for production of softer polymer blends with alternative filler containing the smallest studied filler particle size (25–0 µm) because of potential wide range application of innovated blends in industry.

5. References

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