Application of alternative additives in the polymer composite systems used in automotive industry

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Abstract. The paper deals with the application of alternative waste-based fillers from industry into two various types of polymer composite systems used in the automotive industry. The first type of alternative filler (GW) was obtained by treating the waste from the glass production. It was applied to the multi-component polymer matrix consisting of phenolic and melamine resin and nitrile rubber commonly used in the friction composite system for clutch facing production. Another type of alternative filler (EG) has been obtained from energetics where it is produced as a by-product of flue gas desulfurization. This type of filler was mixed into elastomeric composite system for tire production as a substitution of commonly used carbon black filler. The specific surface area of various fractions of alternative fillers used was determined and the influences of this fillers parameter on the rheology and vulcanization characteristics, as well as physical and mechanical properties of two types of newly prepared polymer systems have been investigated.

1. Introduction
The boom of the automotive industry is very closely linked to the continuous development of new types of materials and composites with specific properties. Best interest of producers is to continually improve the quality of the final products, with simultaneous reduction of production costs and the elimination of waste generated in technological production process [1]. The fulfillment of the claims above can be achieved by the application of new types of effective alternative additives based on selected suitable types of industrial waste. Selected kinds of wastes as a secondary raw materials, can become the alternative fillers in industrial production of polymer composite products, for example car tires, clutch facing, conveyor and transmission belts [2, 3]. Not all wastes or by-products can be used as alternative fillers. Especially application of inorganic materials into organic elastomers provides the possibility to significantly improve up the physical and mechanical properties of elastomers specifically hardness, tensile straight, modulus, but also rolling resistance and rebound resilience [4]. Composite materials show generally better properties than pure and homogeneous materials. The positive changes have been observed at very low concentration of inorganic mieral component in polymers [4, 5]. In addition to improving the properties of the resulting elastomer in the case of the
application of alternative waste-based additives, the low price of the final product and the greening of production are also the great benefits. This work deals with the properties of two different kinds of alternative fillers based on industrial wastes and their application in the polymer composite systems used in automotive. The first alternative filler (EG) arises as a byproduct in the flue gas desulphurization process in energetics. This filler was applied into the polymeric elastomeric compound for tires production. The other type of alternative additive (GW) comes from the weighing process of raw materials in glass production, where creates the waste in a sludge form. The chemical composition of this alternative filler is similar to the chemical composition of kaolin, which is commonly used in industrial production of polymer composites. Alternative additive (GW) was therefore applied in the polymer matrix of friction composite systems of clutch facing. Incorporation of filler into the polymeric matrix and its effect on the polymeric blend or on the vulcanizates properties depends on several factors such as: type of filler, particle size, specific surface area size, particle shape and filling factor. The influence of the specific surface area size of studied alternative fillers on rheological properties and physical and mechanical parameters of polymer composite systems was investigated in this paper.

2. Experimental – materials and methods

2.1. Study of specific surface area size of alternative fillers
For the study, four samples of various fractions of fillers (EG, GW) with particle size (>40 µm, 40–32 µm, 32–25 µm, <25 µm) were prepared by sieve analysis using the Sieve Shaker AS 200 control [6]. Specific surface area size (surface activity) of various fractions of studied alternative fillers was investigated using BET Gas Adsorption Analyzer (Manufacturer: Quantachrome Antosorbi iQ). Samples were degassed by heating in vacuum before every performed measurement. The temperature used was 150 °C and measurement was performed for 4 hours.

2.2. Preparation of polymeric systems with alternative fillers
Both types of alternative fillers studied (EG, GW) in four fractions prepared with particle size (>40 µm, 40–32 µm, 32–25 µm, <25 µm) were applied into polymer matrix of two types of composite systems used in automotive.

Preparation of elastomeric polymer systems with filler EG
The series of elastomeric systems with the addition of alternative filler EG have been prepared using the real rubber compound which is commonly used for tire production with a natural rubber grade SMR 10 as the elastomeric matrix. The filler EG was applied in equal amount (50 phr) to all prepared systems as a partial replacement for commonly used filler – carbon black. Four elastomeric systems with various particle size of the filler EG were prepared in two steps at the temperature of 90 °C using the Plastograph Brabender laboratory mixer. The filler EG was added to the polymer matrix together with carbon black. The mixing time for the fillers was determined for 180 seconds to ensure sufficient incorporation of fillers in the polymer matrix [7]. In order to increase the homogeneity of the blends after each mixing step, an additional homogenization was carried out by the laboratory twin-roll machine (Calander) (Calander) – LaboWalz W 80 T (Manufacturer: VOGT) for each blend. After the second step of mixing, the blend was left at laboratory temperature of 25 °C ± 2 °C for 24 hours [8].

Preparation of thermosetting polymer systems with filler GW
The thermosetting polymer system containing the mixture of melamine resin, phenol-formaldehyde resin and nitrile-butadiene rubber, which is commonly used as a polymer matrix for friction composite systems of clutch facing has been used. The original polymer system 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. After addition of alternative filler GW with four various particle size into polymer matrix in equal amount (3 phr), the polymer systems were mixed for
3 minutes because of better incorporation of the filler into the blend. Prepared polymer blends were homogenized using the laboratory twin-roll machine (Calander) – LaboWalz W 80 T (Manufacturer: VOGT) in order to obtain the sheet in thickness of 2 mm. Before another processing procedure, the blend was left for 24 hours at laboratory temperature of 25 °C ± 2 °C [8].

2.3. Determination of rheological properties and cure characteristics
Rheology and cure characteristics of polymeric systems prepared with addition of alternative fillers (EG, GW) have been determined using the Rubber Process Analyzer RPA 2000 in specialized laboratories (CEDITEK) at the Faculty of Industrial Technologies in Púchov. The samples were cut from obtained sheets to prepare the required shape of samples with the using of instrument Cutter 2000 (Alpha Technologies). Test was at the testing (cure) temperature (160 °C for elastomeric systems containing EG filler and 180 °C for polymer thermoset systems containing GW filler) with frequency of 1.66 Hz at 60 minutes and 5 % oscillation angle. Vulcanization characteristics, as a function of time and temperature, describe chemical processes. In the case of polymer systems with the content of alternative fillers, studied vulcanization process includes the crosslinking process and its course up to the maximum crosslinking effect as well as the reactions after the crosslinking process (e.g. reverse, plateau, marching module). Based on the reason for the possible industrial application of the prepared polymeric systems with EG and GW fillers, with an emphasis on economic and time aspects, a vulcanization temperatures of 160 °C and 180 °C were used. Rheology involves the study of deformation and mass flow [9]. The aim is to establish relationships between stress and deformation of materials, where neither Newton's Law nor Hooke's Law is enough to explain their mechanical behaviour [10]. The selected and investigated characteristics include: minimum torque ($M_t$), maximum torque ($M_H$), scorch time ($t_{90}$) and optimal cure time ($t_{c90}$).

2.4. Determination of physical and mechanical properties
The tensile properties (tensile strength and elongation at break) of prepared elastomeric vulcanizates containing the alternative filler EG were determined also using the Universal Tensile Testing Machine Autograph AG-X plus 5 kN (Shimadzu) according to ASTM [11]. The hardness of elastomeric vulcanizates containing the alternative filler EG was determined using a Shore A hardness tester. Samples were measured according to ASTM [12]. The measured values of physical and mechanical properties of the vulcanizates studied are summarized in Table 3 and graphically processed in figure 5 to obtain a better overview of the effect of specific surface area size of alternative filler fractions on the studied characteristics.

3. Results and discussion
In this part, there are summarized the results from sieve analysis with the study of specific surface area size of both types of alternative fillers (EG and GW), rheological properties, cure characteristics, hardness and tensile properties of prepared polymeric systems with the addition of fillers EG and GW. Subsequently, the influence of the specific surface area of the applied fillers on the measured parameters of polymeric systems prepared was evaluated.

3.1. Specific surface area size of alternative fillers
The surface activity of fillers can be expressed by the size of the specific surface area. Measured results for various fractions of studied fillers (EG, GW) with particle size (>40 μm, 40–32 μm, 32–25 μm, <25 μm) are summarized in table 1.

Static gas adsorption offers a powerful tool for characterizing of the filler surface. The mentioned BET method can help to obtain the size of specific surface area and gives the detailed information about the energetic surface heterogeneity and the porosity or the surface roughness. This different particle surface properties of two alternative fillers studied are also the reason why the filler EG from energetics exhibited much higher size of specific surface area compared to the GW filler from the glass industry. The adsorption isotherm at a given temperature characterizes the amount of adsorbed
gas in thermodynamic equilibrium as a function of pressure. Values of specific surface area size given in table 1 correspond to adsorption activity and also surface activity of different fractions of fillers. With decrease of fillers particle size, the size of specific surface area and thus the adsorption activity increased. Increase of alternative fillers adsorption activity 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 fillers.

| Labeling Filler type | Filler particle size (µm) | BET (m² g⁻¹) |
|---------------------|---------------------------|--------------|
|                     |                           | EG           | GW           |
| 1                   | >40                       | 6.9          | 0.4          |
| 2                   | 30–40                     | 9.8          | 0.7          |
| 3                   | 25–32                     | 10.9         | 0.8          |
| 4                   | <25                       | 11.2         | 2.2          |

3.2. Rheological properties and curing characteristics
The measured values of rheological properties and curing characteristics for two various polymeric systems prepared (elastomeric ES and thermosetting TS) with the addition of corresponding type of alternative filler (EG or GW) in the various fractions (1 = >40 µm, 2 = 240–32 µm, 3 = 32–25 µm, 4 = <25 µm) are summarized in table 2, and they are processed graphically in figures 1–4. The each one specific surface area size corresponding to individual fractions of the alternative fillers, will serve as a criterion for comparing the properties of polymeric systems prepared. The studied rheological properties of polymer systems were minimum (M_1) and maximum torque (M_H) and studied corresponding curing characteristics were the Scorch time (t_s02) and Optimal cure time (t_c90).

| System labeling | Minimum torque M_L (dNm) | Maximum torque M_H (dNm) | Scorch time t_s02 (min) | Optimal cure time t_c90 (min) |
|-----------------|--------------------------|--------------------------|-------------------------|-----------------------------|
| 1ES/EG          | 1.48                     | 17.13                    | 1.58                    | 3.62                        |
| 2ES/EG          | 1.70                     | 17.50                    | 2.05                    | 3.76                        |
| 3ES/EG          | 1.72                     | 17.71                    | 2.09                    | 4.11                        |
| 4ES/EG          | 1.81                     | 17.84                    | 2.27                    | 4.66                        |
| 1TS/GW          | 0.67                     | 193.34                   | 0.41                    | 4.86                        |
| 2TS/GW          | 0.50                     | 200.92                   | 0.40                    | 3.92                        |
| 3TS/GW          | 0.68                     | 200.75                   | 0.42                    | 4.43                        |
| 4TS/GW          | 0.59                     | 200.80                   | 0.44                    | 4.87                        |

*Notes: 1, 2, 3, 4 = particle size/ BET surface activity; ES = elastomeric system; TS = thermosetting system.

The value of minimum torque represents the stiffness of the unvulcanized tested sample taken at the lowest point of the curve. Maximum torque (highest, or plateau) represents the stiffness or shear modulus of the fully vulcanized tested sample at the vulcanization temperature [10].

From measured values of minimum and maximum torque, it is possible to see the effect of the specific surface area size of the alternative filler. In the case of elastomeric systems (ES) containing the filler (EG) (figure 1), an increase in minimum and maximum torque values corresponding to the increase in the values of the specific surface area of alternative filler can be observed. Since the minimum torque indicates the stiffness of the elastomeric blend, it can be seen that a larger specific
surface area size of the filler EG (higher surface activity) led to the increase of the stiffness of the blend at the beginning of the vulcanization process. The maximum torque results of polymer systems ES/EG show a similar course to the minimum torque. The highest value of the minimum and maximum torque was achieved in the case of polymer system 4ES/EG with a highest filler specific surface area size (11.2 m² g⁻¹). With increasing the specific surface area size of the alternative filler, the particle distribution per unit weight increases. A larger number of particles may cause a reduction in the mobility of the elastomeric chains in the matrix, resulting in an increase in stiffness [13].

**Figure 1.** Values of minimal ($M_L$) and maximal torque ($M_H$) of elastomeric polymer systems ES/EG.

In the case of thermosetting polymer systems (TS) containing the filler (GW) (figure 2), an increase in maximum torque values with the increasing the specific surface area size of alternative filler can be observed. However, in the case of the resultant minimum torque values, this trend was not confirmed. The results obtained for the determination of rheological properties of the TS/GW polymer systems show large differences between the values of minimum torque (values range from 0.50 to 0.68 dNm) and the maximum torque (values range from 193.34 to 200.92 dNm), which corresponds to the specific properties of the thermosetting polymer matrix.

**Figure 2.** Values of minimal ($M_L$) and maximal torque ($M_H$) of thermosetting systems TS/GW.
Curing characteristics studied include scorch time \((t_{0.2})\) and optimal cure time \((t_{90})\) [14]. 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 [15]. Optimum cure time \((t_{90})\) is the time required for the torque to reach 90% of the maximum achievable torque and relates to the time which is necessary for the cured rubber to achieve optimal properties [16].

The graphical representation of measured values of scorch time \((t_{0.2})\) and optimum cure time \((t_{90})\) for ES/EG elastomeric system is in figure 3 and resulting values of curing characteristics for the thermosetting system TS/GW with the content of relevant type of alternative filler with the various specific surface area size are graphically processed in figure 4. In the case of ES/EG elastomeric systems it can be observed that the scorch time \((t_{0.2})\) values increased with increasing specific surface area size of the alternative filler used for preparation of the ES/EG systems. The increase in the scorch time from the technological point of view can be considered as positive, because the longer scorch time ensures perfect filling of the mould even for shape-complicated or bulky articles. From the economical point of view an increase in the scorch time is a negative phenomenon, because the time required for the production of the product increases and thus increases the costs of production. Also from the resulting values of optimal curing time \((t_{90})\) for ES/EG elastomeric systems an increase in optimal curing time values with the increasing the specific surface area size of alternative filler EG can be observed. The highest values of both curing characteristics studied showed the system 4ES/EG containing alternative filler EG with the largest specific surface area \((11.2 \, \text{m}^2 \, \text{g}^{-1})\). The extension of the optimal curing time due to an increase in the specific surface area of the EG filler is related to the content of \(\text{SO}_4\) groups in the alternative filler that are involved in the vulcanization process. It is important to emphasize that an increase in the specific surface area of the filler results in a higher number of \(\text{SO}_4\) groups that may be present in the vulcanization process. Increasing the availability of \(\text{SO}_4\) during the vulcanization process leads to the formation of multiple cross-links, thereby extending the optimal curing time.

![Figure 3. Values of scorch time \((t_{0.2})\) and optimal curing time \((t_{90})\) of polymer systems ES/EG.](image-url)

In the case of thermosetting polymer systems TS/GW it can be observed, that the specific surface area size of filler GW in polymer bland has no clear effect on the scorch time \((t_{0.2})\) or the optimal curing time \((t_{90})\). The lowest values of both vulcanization characteristics (scorch time and optimum curing time) were measured for the polymer system 2TS/GW containing a GW filler with a specific surface area size of \(0.7 \, \text{m}^2 \, \text{g}^{-1}\). While the highest values of the scorch time and also of optimum curing
time has reached the system 4 TS/GW with the addition of GW filler with the highest specific surface area size (2.2 m² g⁻¹).

Figure 4. Values of scorch time ($t_{90}$) and optimal curing time ($t_{90}$) of polymer systems TS/GW.

3.3. Physical and mechanical properties
The physical and mechanical parameters of prepared vulcanized elastomeric systems ES/EG containing the alternative filler EG with various specific surface area size have been studied. The selected physical and mechanical properties (tensile strength, elongation at break and hardness) were tested and evaluated and the effect of the specific surface area size of alternative filler on these parameters was examined. The results from the measurements of physical and mechanical properties of prepared vulcanized elastomeric systems ES/EG are summarized in Table 3 and their graphical processing is given in Figure 5.

Table 3. Physical and mechanical properties of vulcanized elastomeric systems ES/EG.

| System labeling | Tensile strength (MPa) | Elongation (%) | Hardness (ShA) |
|-----------------|------------------------|----------------|---------------|
| 1ES/EG          | 15.93 ± 0.95           | 433.05 ± 12.96 | 61.06 ± 0.27  |
| 2ES/EG          | 16.53 ± 0.64           | 435.88 ± 11.81 | 62.40 ± 0.29  |
| 3ES/EG          | 17.41 ± 0.82           | 438.77 ± 9.66  | 62.80 ± 0.31  |
| 4ES/EG          | 18.04 ± 0.64           | 446.76 ± 8.04  | 63.00 ± 0.31  |

Based on comparison of obtained values of physical and mechanical parameters, an increasing trend of tensile strength, elongation at break and also hardness values of prepared vulcanizates with the increase of specific surface area size of used EG alternative filler can be observed. This increasing trend is evidence that the alternative filler EG is directly involved in the vulcanization process. The particle size and thus specific surface area size of the filler also affects tensile strength and hardness values of the vulcanizates. Since the particles are smaller, their specific surface area, as well as their number per unit of weight is higher, it is possible to ensure a more even distribution and thus better dispersion of the filler particles in the system of polymer blend.
4. Conclusion
Two kinds of alternative waste-based fillers (EG and GW) coming from industry have been presented in the paper and their applications into two various types of polymer composite systems used in the automotive industry have been described. Various fractions of both types of fillers with the particle size (>40 µm, 40–32 µm, 32–25 µm, <25 µm) have been prepared by sieve analysis and the specific surface area size of various fractions of alternative fillers was investigated. The first type of alternative filler (EG) obtained from flue gas desulfurization in energetics in the various fractions has been applied into elastomeric composite system (ES) for tire production as a substitution of commonly used carbon black filler. Another type of alternative filler (GW) obtained by treating the waste from glass production was applied to the multi-component thermosetting polymer matrix commonly used in the friction composite system for clutch facing production. The series of two types polymer systems (ES/EG and TS/GW) with the addition of four various fractions of alternative fillers have been prepared and the influence of specific surface area size of alternative fillers various fractions on the rheological properties and vulcanization characteristics, as well as physical and mechanical properties of newly prepared polymer systems have been investigated. Based on the obtained results, it can be concluded that there was the effect of the alternative fillers specific surface area size on the selected properties of the prepared polymeric systems. Mainly in the case of ES/EG elastomeric systems containing alternative filler EG from energetics an increase in all rheological properties (minimum and maximum torque) and also in curing characteristics with increasing specific surface area size of the alternative filler used for preparation of the ES/EG systems can be observed. The same trend was confirmed by the measured values of physical and mechanical parameters of the elastomeric system ES/EG. An increase in the tensile strength, elongation at break and hardness values of the vulcanized elastomeric systems ES/EG was observed depending on the increase in the specific surface area of the EG filler used. In both types of polymer systems – elastomeric (ES) and also thermosetting (TS) the highest values of scorch time and optimal cure time were reached using the alternative fillers (EG or GW) with the highest specific surface area size.
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