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Polymeric microparticles composites with waste EPDM rubber powder

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Abstract. Polymeric materials filled with inorganic microparticles can be described as polymeric microparticle composites. These materials combine the various mechanical, physical and chemical properties of different phases. Waste microparticles can also be used as filler. Inclusion of these waste microparticles can optimize the required mechanical properties and decrease the price. This paper describes the possibilities of using recycled waste rubber powder in polymer composite systems. The aim of the experiment was to quantify the mechanical properties of epoxy resin (Glue Epox Rapid – with increased speed of hardening) and polyurethane (Sika Power – resin based on polyol) filled with recycled EPDM rubber powder (29 μm) gained from a Czech company and to describe the changes in the mechanical qualities with a changeable amount of microparticles. Composites were prepared with a different filler concentration of resins (5–35 volume percent). Cohesive and adhesive characteristics were chosen for the quantification of the system. Adhesive strength to the steel adherent was tested by means of lap-shear tensile strength. Cohesive strength was tested by means of tensile strength. Hardness was measured by the Shore D method. The described use of waste material is inexpensive and offers the possibility of recycling material. The application of waste EPDM powder in the area of resins is a benfitial way of material usage which should be preferred.

Key words: epoxy resin, lap-shear tensile strength, material utilization, tensile strength.

INTRODUCTION

The main damaging mechanism of reactive resin is the formation of isolated microcracks and their spreading. These microcracks often appear at the interface between particles and resin or in the area where air pores occur. An important aspect from the point of view of the strength of filled reactive plastics is adhesion defined by intermolecular forces at the interface between resin and soaked material. Cohesive characteristics are also very important; they define the strength of the mixture itself (strength at the interface between microparticles and resin). The optimal processes of hardening regarding the epoxy resin as well as the duration of the process are significantly affected by the soaking of the additive and theintermediate phase of the interaction according to Li et al. (2012). During the cross-linking process when reactive resin forms a matrix it is important to respect the technological requirements of the resin's producer – primarily to observe the prescribed hardening temperature and time. Adhesion can be observed both at the interface of the filling material and resin and on the boundary of the composite system and the adherent, to which the system is applied (Rudawska, 2008).

The utilization of rubber powder for optimizing the properties of epoxy resin is described by Schoberleitner et al. (2013). Subramaniyan et al. (2012) used recycled rubber particles for improvement of the mechanical properties of a hybrid composite – polyurethane resins filled with fibre (Kenaf). The utilization of recycled rubber along with fibres is described by Cerbu & Curtu (2011), who increased the impact resistance of the composite on the basis of epoxy resin with glass fibres and recycled rubber particles. Zhao et al. (2011) describe that waste rubber particles can be also used for thermoplastic materials (EPDM particles). The authors performed experiments to assess the effect of the particles on the mechanical properties of polypropylene. The results prove that it is possible to improve the tensile strength of filled polypropylene with 20 vol.% of EPDM particles, as well as the endurance against impact. Serenko et al. (2005) claim that the use of rubber microparticles in a polymer matrix leads to the formation of defects, i.e., microcracks, which grow in the direction of the system's tensile stress.

Mutual interaction between reactive resins, for instance in the form of epoxy or polyurethane resins, and additives on the secondary raw material basis forms new materials. These materials can have remarkable mechanical characteristics, whose definition is crucial for thedetermination of applied areas. The utilization of microparticle additives on the basis of reusable materials (secondary materials) has been discussed in the papers of many authors. It is an economically favourable and sensitive way of recycling that should be preferred among other methods.

The aim of the experiment is to describe the options for the utilization of anorganic microelements on the basis of reusable materials (EPDM of rubber powder) emerging during waste recycling in interaction with reactive resin. The following part of the experiment explores adhesive and cohesive characteristics in view of tensile strength and lap-shear tensile strength. The goal is also to verify the hypothesis about the influence of microparticle concentration in reusable material expressed in volume percentages on the resulting mechanical properties of resin.

MATERIALS AND METHODS

Preparation of test samples

The matrix was represented by the two-component epoxy resin Glue Epox Rapid and the two-component polyurethane resin Sika Power 7723. Epoxides are suitable for the field of agriculture, as they are resistant to degradation (Cierna & Ťavodová, 2013; Müller, 2013a; Müller, 2013b). Test samples were created with 5–35 vol.% (v_{pr}) of the filler (EPDM rubber powder) in the matrix. The filler was the EPDM rubber powder. This type of materials (secondary raw materials) are produced by Gumoeko, s.r.o. (Czech Republic), that specializes in recycling old and defective car and lorry tires and EPDM rubber used in cars (in accordance with the Waste Catalogue of the Czech Republic it is a non-hazardous waste). EPDM rubber (see Fig. 1) is used in the production of tubes intended for the distribution of liquids (fluids, brake fluid, etc.). EPDM rubber is very resistant to lasting deformation and also has a wide temperature range of use; it is resistant to soaking in addition to having a good resistance to polar fluids and mineral acids. Gumoeko, s.r.o. processes the waste on the technological line, which produces rubber granules fractioned to the required size with a sieve.

Figure 1. Product from the production line: EPDM rubber powder.

The resin and filler mixture was prepared by mechanical mixing. The formation of air bubbles during mechanical mixing was prevented by using an ultrasonic vat. The test samples were cast into forms made of silicone rubber and hardened according to the technological requirements of the resins' producer (see Fig. 2). The porosity was set based on the difference between the theoretical and real density which characterizes the quality of composite systems.

Figure 2. Models for forming, forms, test samples (for testing hardness, tensile strength, abrasive wear).

Laboratory tests

The standard CSN EN ISO 868 was used as a guide for determining the hardness of the composite systems. The hardness of test samples was also determined via the Shore D method. The dimensions of the tested specimens were 35 x 25 x 9 mm.

Test samples meant for determing cohesive strength by means of tensile strength were prepared according to the requirements of the standard CSN EN ISO 3167. Specimens were tested on a universal testing machine. The speed of cross beam motion was 6 mm min^{-1}. The settings for the tensile characteristics test were in accordance with the standard CSN EN ISO 527.

Overlapping assemblies were made for the lap-shear strength test in the boundary adherent-filled system according to the standard CSN EN 1465. The surface of the 1.5 mm thick steel sheets (S235J0), onto which the composite system (filled resin) was applied, was at first blasted using the synthetic corundum of the fraction F80 under the angle of 90°. In this way the average surface roughness of Ra = 1.44 ± 0.21 μm, Rz = 9.1 ± 0.34 μm was reached. Then the surface was cleaned and degreased using perchlorethylene. Surface preparation is important and should guarantee the good strength of the boundary adherent (Affatato et al. 2013; Novák 2011).

Two-body abrasion was tested on a rotating cylindrical drum device with an abrasive cloth (grain size P220; Al_2O_3 grains) according to the standard CSN 62 1466. On the drum device, the tested sample is in contact with the abrasive cloth, which covers 60 mm. During one drum turn of 360° the tested sample may have not been in contact with the abrasive cloth surface. The consequent impact of the tested sample with the drum simulates actual impact. The applied pressure force was 10 N. The mean of the tested samples was 15.5 ± 0.1 mm and their height was 20.0 ± 0.1 mm.

One-factor ANOVA, reliability level $\alpha = 0.05$ was used for statistical evaluation. The T-test was used for statistical comparison, while the zero hypothesis H_0 ($p > 0.05$) shows that the statistical sets of data are comparable.

RESULTS AND DISCUSSION

The optical analysis determined the average size of rubber powder particles to be 28 ± 16.6 μm, see histogram Fig. 3 (left). The size of most particles falls into the interval 20–30 μm (40%). The morphology of rubber EPDM dust particles is shown in Fig. 3 (right).

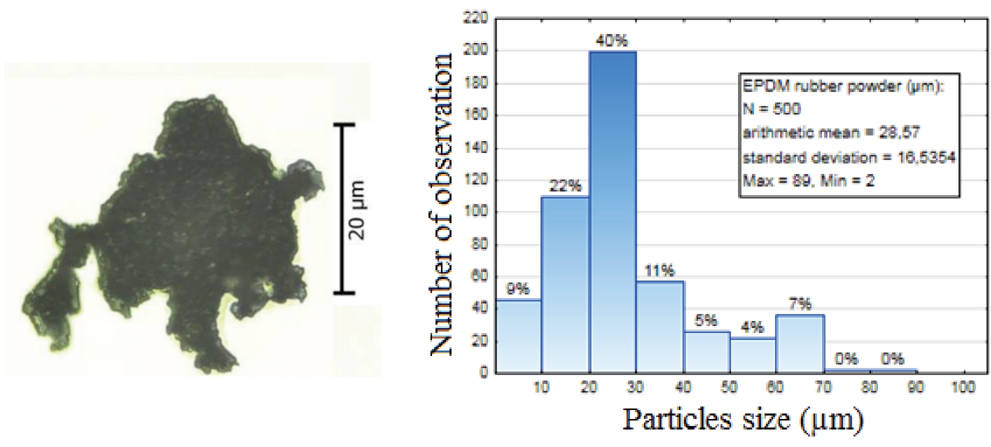

Figure 3. Histogram of the size of particles, EPDM rubber powder (right), morphology of a particle of EPDM rubber powder (left).

The lowest average porosity 5.03% was detected on the tested samples with resin Glue Epox Rapid (7.04% Sika Force 7723). Porosity and density of filled resin are shown in Table 1.

Table 1. Density and porosity of filled resins

Resin (EP/PU)	v_{pr} (%)	Density (g cm^{-3})	Porosity (%)
Glue Epox Rapid	5	1.15	5.34
Glue Epox Rapid	10	1.15	4.42
Glue Epox Rapid	15	1.15	5.06
Glue Epox Rapid	20	1.15	4.19
Glue Epox Rapid	25	1.14	6.22
Glue Epox Rapid	30	1.14	4.32
Glue Epox Rapid	35	1.14	5.67
Sika Force 7723	5	1.48	6.38
Sika Force 7723	10	1.46	8.69
Sika Force 7723	15	1.44	5.95
Sika Force 7723	20	1.42	8.90
Sika Force 7723	25	1.41	7.63
Sika Force 7723	30	1.39	6.27
Sika Force 7723	35	1.37	5.46

The hardness of the filled resin (Shore D) is shown in Fig. 4. While the ratio of EPDM rubber powder in the resin increased, the hardness decreased from about 11.2 to 78.7 ± 1.0 (Glue Epox Rapid), the hardness of the polyurethane resin Sika Force 7723 decreased from about 16.7 to 50.9 ± 2.4. The coefficient of variation related to the measuring did not exceed 4.8%.

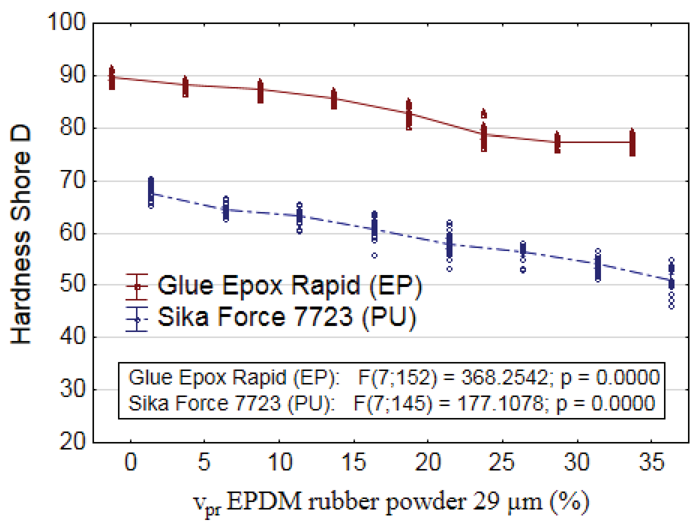

Figure 4. Influence of the EPDM rubber powder on resin hardness – Shore D.

The decrease in lap-shear strength was proved with increasing the percentage of EPDM rubber powder (see graphical illustration and results of ANOVA, Fig. 5) in the mixture but the presence of 5% EPDM powder did not lead to a statistically demonstrable decrease in shear strength, see the results of a statistical analysis in Table 2 (zero hypothesis H_0 confirms the hypothesis – there are no statistically significant differences between the compared sets of data, Glue Epox Rapid p = 0.38 and Sika Force p = 0.37). The higher percentage of rubber EPDM powder in these resins led to a decrease in hardness. The presence of rubber EPDM powder significantly increased the dispersion of measured values; this dispersion is revealed in the values of the coefficient of variation (up to 18% for Sika Force 7723).

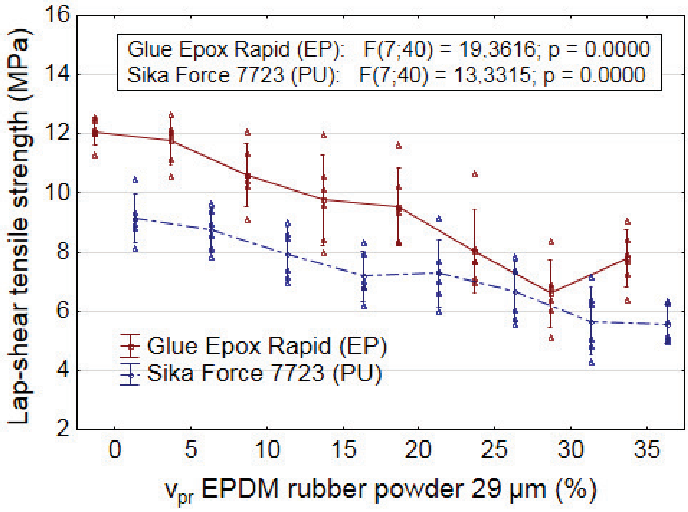

Figure 5. Impact of rubber EPDM powder on lap-shear tensile strength.

Table 2. Statistical analysis (T-test) – lap-shear tensile strength

T-test H_0; $\mu_1 = \mu_2$; ($p > 0,05$)				v_{pr} (%)			
Resin	**5**	**10**	**15**	**20**	**25**	**30**	**35**
0%: 5–35% / Glue Epox Rapid(EP)	**0.38**	0.01	0.00	0.00	0.00	0.00	0.00
0%, 5–35% / Sika Force 7723 (PU)	**0.37**	0.03	0.00	0.01	0.00	0.00	0.00

The used resins were characterised by cohesive failure. While the percentage of EPDM rubber powder (20–30%) increased, a predominate and special cohesive failure (SCF) occurred. The thickness of the layer filled resin between the adhesive and adherend increased with a higher percentage of EPDM rubber powder.

Tensile strength decreased verifiably while the percentage of EPDM rubber powder in the resin (see Fig. 6) increased. The strength of the resin Glue Epox Rapid decreased from about 36.61 MPa to 13.48 ± 2.39 MPa and the strength of the Sika Force 7723 decreased to the value 2.34 ± 0.78 MPa (3.49 MPa decrease). The coefficient of variation of the measurement increased with the inclusion of microparticles (filler) and reached the value of 33.5% (Sika Force 7723: 35%).

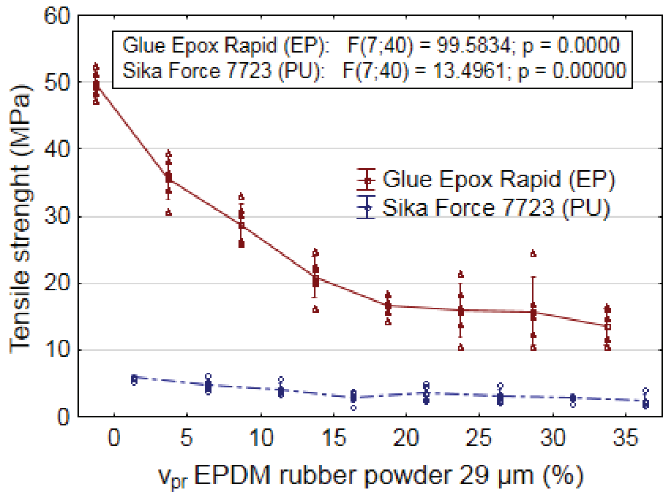

Figure 6. The influence of rubber EPDM dust on tensile strength.

The statistical analysis is shown in Table 3: there is a statistically significant difference between the compared sets of data in all cases. Abrasive wear resistance decreased when EPDM rubber powder was added (see Fig. 7).

Table 3. Statistical analysis (T-test) – lap-shear tensile strength

T-test H_0; $\mu_1 = \mu_2$; $(p > 0,05)$	v_{pr} (%)						
Resin	**5**	**10**	**15**	**20**	**25**	**30**	**35**
0%: 5–35% / Glue Epox Rapid (EP)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0%, 5–35% / Sika Force 7723 (PU)	0.02	0.00	0.00	0.00	0.00	0.00	0.00

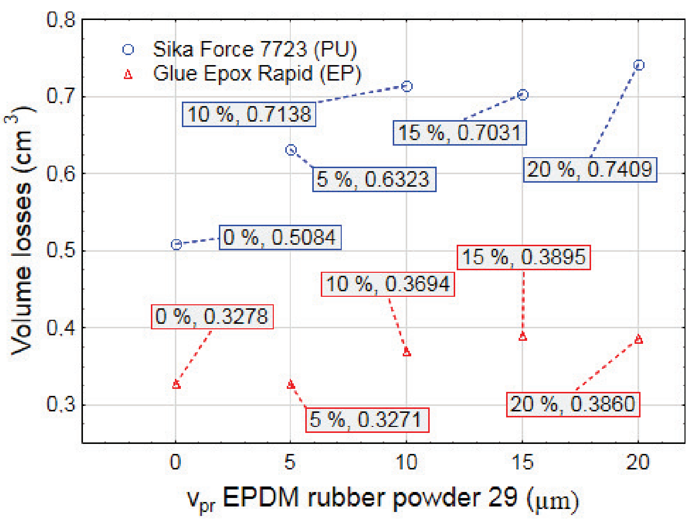

Figure 7. Abrasive wear resistance of test samples (volume losses) – abrasive cloth P220.

The experiment proved that the used epoxy polyurethane resins are able to form a new material with microparticle fillers on the basis of a secondary raw material. The viscosity of the used epoxy and polyurethane resins allowed to cast the samples without any difficulty. These conclusions are in compliance with the statements of many authors (Partridge, 1989; Müller, 2014) who confirmed the suitability of epoxy and polyurethane resins filled with different kinds of particles in their papers. Porosity was proved in the casted filled resins on the basis of their weight and volume (the difference between theorectical and real density). Porosity also became evident during the optical analysis of surface refraction performed with a stereoscopic microscope. The porosity of individual samples did not reach 10%. The higher values of porosity of the filled resins in question could be caused by the secondary characteristics of microparticles but may be also arise from the procedure with which the microparticle and resin mixture was prepared.

The occurrence of air bubbles could be decreased, for instance, with the use of vacuum for the preparation of filled resin. The low tensile strength of resin filled with the microparticles of rubber confirms the conclusion of Sereneko et al. (2005), who show that the use of rubber microparticles in the polymer matrix leads to the formation of defects, i.e., microcracks, which spread in the direction of the tensile force of the system. The defects were evident on the refraction surfaces in the surroundings of the rubber particles. The decrease in the tensile strength of the resin filled with rubber dust (EPDM) is confirmed by Schoberleitner et al. (2013). These conclusions were proved correct owing to the experiment that was performed.

CONCLUSIONS

The results of this paper provide a range of application areas for the products produced by companies involved in waste processing. The results can be also used by companies that did not offer their products to be used for the purposes of this experiment, as well as companies which use epoxy or polyurethane resins.

The use of secondary raw materials generally reduces the cost of resins (Valasek, 2014). The price of the Resin Glue Epoxy Rapid (15 EUR Kg^{-1}) may be reduced by 29% (i.e. 4.4 EUR) with a 35% inclusion of rubber particles. However, it is necessary to take into account the reduced mechanical properties described in this paper. The advantage in areas of application can be rubber's ability to dampen impacts. For example, in agriculture, Müller et al. (2013) refer to the possibility of using adhesive bonds (resin) filled with rubber particles to fix the functional areas of soil processing tools – rubber‘s ability to absorb impacts can be used, while the shear strength of the material is good. The experiment confirmed that filled resins with a 5% concentration of the filler in both epoxy and polyurethane resins have the same shear strength as unfilled resins.

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