INFLUENCE OF GLASS POWDER SIZE SORTING ON PROPERTIES OF COMPOSITE SYSTEMS*

K. Dědičová, P. Valášek

Czech University of Life Sciences Prague, Faculty of Engineering, Department of Material Science and Manufacturing Technology, Prague, Czech Republic

Glass powder ranks among the secondary raw materials, which can be used in the interaction with polymeric materials. In the present experiment the polymeric/epoxy particle composite with different sizes of glass powder particles is described. Such utilization of recyclable materials is environmental-friendly and should be preferred. The size of particles forming the filler of the described composites is one of the key characteristics affecting the mechanical properties. Due to the properties of the systems filled with glass powder, these materials can potentially be used in agriculture (renovations, adhesive bonding, cementing, etc.). In the experiment, glass powder was dimensionally sorted through sieves. Three fractions of glass powder with particles size of 0-30, 30-50, and 50-90 µm were created and utilized, the average particle size being 18.7, 38.7, and 72.6 µm, respectively. The interaction of the 18.7 µm particles did not lead to a statistically significant decrease of shear strength values in the interval 0-20 vol.%. The presence of glass powder, however, in all cases decreased tensile strength.

adhesion; agriculture; cohesion; epoxy resin; glass powder



doi: 10.1515/sab-2016-0005 Received for publication on August 20, 2015 Accepted for publication on October 15, 2015

INTRODUCTION

Epoxy resins are polymeric materials with macromolecular chains which contain more than one epoxy group, i.e. oxirane or ethylene oxide group. This group of structural adhesives is often used in agriculture either as adhesives or composite systems (K e j v a l, Müller, 2013; Müller, Herák, 2013). Epoxy resins with a dispersed particulate filler are mostly cured by polyamines while forming three-dimensional networks (in most cases without the excess pressure). This curing process is carried under normal (laboratory) temperature (Mleziva, 1993; Petrie, 2006). Particles have multiple functions in reaction resins. Particles influence (in some cases optimize) mechanical properties of resin and last but not least reduce costs. The resulting mechanical properties are given by a number of parameters, the most important being viscosity of resin, wetting of the filler with resin, nature of the linkages between resin and particles, etc. (Milton, 2002; Valášek, Müller, 2013a).

The described experiment is primarily devoted to the basic mechanical characteristics of epoxy resin filled with glass powder (GP), i.e. adhesion and cohesion. Adhesion is reflected on interfaces of both, the filler and resin, and the composite system and adherend to which the system is applied. Adhesion between the filler and the used resin is affected, among others, by morphology of particles and their size. Conclusions by Cheng et al. (2002) point to the fact that roughness of particles ranks among the most important parameters affecting adhesion of particles to matrix. Experiments performed by Z h a i et al. (2006) also show the influence of particles on the interface of the filled adherend and the system, where particles (particles of Al₂O₃, CaCO₃, SiO₂ were used in the experiment) can improve adhesiveness (adhesion) of epoxide to steel. From the viewpoint of cohesion

^{*} Supported by the Internal Grant Agency of the Faculty of Engineering (IGA), Czech University of Life Sciences Prague, Project No. 2015:31140/1312/3107.

(cohesiveness of a filled system), N a k a m u r a et al. (1992) described a crucial influence of particle size on strength and stated a decrease in tensile strength of polymers with increasing particle size (6–42 μ m). H o j o et al. (1974) formulated similar conclusions on the epoxy resin strength decrease with the increasing particle size by a mathematical relationship

$$\sigma_k = \sigma_m + k_p (V_p) d_p^{-1/2} \tag{1}$$

where:

 σ_k = composite breaking strength (MPa) σ_m = matrix breaking strength (MPa) $k_p(V_p)$ = constant as a function of the volume fraction of particles (-)

 $d_p = average particle size (mm)$

^P The aim of the experiment is to describe the adhesion of epoxy filled with different GP particle sizes to steel adherend (this type of material is commonly used in agriculture) by means of shear strength. Cohesion is described by tensile strength. Minimization of the composite system price through the inclusion of a secondary raw material – glass powder – is also one of the important issues dealt with in the present contribution. Effective handling of recyclable materials reduces the burden on the environment, costs, and saves primary raw materials.

MATERIAL AND METHODS

Matrix and filler

Filling reactive resins with a particulate filler is performed during the uncured state, depending on the required resulting properties. Preparation of filling mixtures is crucial with respect to the amount of pores contained in the material after curing. In experimental programs mixing with or without the use of vacuum can be applied. The resulting shape is then achieved, for example, by following casting into moulds with zero adhesion to moulded mixture or the system is applied directly to the adherend. After reaching the final shape the resin is cured according to the technological requirements. A two-component epoxy resin (Epoxy) Glue Epoxy Rapid F (DCH-Sincolor a.s., Karlovy Vary, Czech Republic) (density 1.00 g·cm⁻³) was used in the experiment. This epoxide exhibits high cure rate (9–10 min at 50 g of stiffed mixture, 23°C) and reduced sagging of the surfaces, glass transition temperature 59°C.

The resin was filled with GP (density 2.50 g·cm⁻³) made from recycled glass shards (classified as waste 20 01 02 – Glass according to the Waste catalogue of the Czech Republic), which are processed by the company AMT Příbram, s.r.o. Glass shards are pulverized by a ball mill and this secondary raw material is

then sieved by rotating sieve. The GP used (particles less than 90 μ m in size) is traded on the Czech market by Refaglass, a.s. The purchased GP was dried in the drying room (humidity lower than 1%) and then sieved using hand sieves with mesh sizes of 50 and 30 μ m (Fig. 1) to prepare different fractions of particle sizes. The different fractions were sizing 0–30 μ m, 30–50 μ m, and 50–90 μ m.

The composite mixture which was cured according to the manufacturer's requirement (at room temperature of $24 \pm 2^{\circ}$ C, humidity 40–50%) was prepared by mechanical mixing of GP and epoxy composite. The filler concentration was expressed by volume percentage and corresponded to 1, 2, 3, 4, 5, 10, and 20%. The test specimens for testing the tensile strength were cast in moulds made of two-component silicone rubber in accordance with the standard ČSN EN ISO 3167 (Plastics – Multipurpose test specimens). Tensile strength values describing the cohesive strength of the cast specimens were measured in accordance with ČSN ISO 527-1 (Plastics - Determination of tensile properties, Part 1: General principles) always on 6 specimens appropriate to the standard. The test was carried out on a universal testing machine LabTest 5.50ST (Labortech s.r.o., Opava, Czech Republic) (50 kN). Test speed (crosshead movement) corresponded to 6 mm min⁻¹. Hardness of the specimens was evaluated using Shore D scale (ČSN EN ISO 868).

Shear strength (adhesion to steel adherend) was determined in accordance with the standard ČSN EN 1465 (Adhesives – Determination of tensile shear strength of rigid adherends on overlapped specimens). Based on recommendations of T e n g et al. (2011) that the most appropriate treatment of adherends before the application of epoxy resins includes blasting, the surface of the adherend was blasted with corundum before applying the system (F80 at 90°C). After the blasting process, the surface of adherends was degreased and cleaned with perchlorethylen. The surface treatment of materials has been stated as crucial in many applications (N o v á k, 2011; D'A m at o



Fig. 1. Sieves used for glass powder particles size sorting into individual fractions

Table 1. Theoretical density and porosity glass powder (GP)/epoxy

GP (vol.%)	Theoretical density (g·cm ⁻³)
1	1.01
2	1.03
3	1.05
4	1.06
5	1.08
10	1.15
20	1.30

et al., 2014; R u d a w s k a , 2014; A f f a t a t o et al., 2015). As important factors describing the surface integrity were selected roughness parameters, which were determined by the profile according to ČSN EN ISO 4287 using a profilometer Surfest 301 (Mitutoyo America Corporation, Aurora, USA). Wavelength (cutoff) corresponded to 0.8 mm. During the cure process joints were loaded with 230 g · cm⁻². Thickness of the resin layer (gap) between adherends was evaluated using a stereoscopic microscope (SZP 11-T Zoom, Arsenal s.r.o., Prague, Czech Republic) via embedded software (Quick Photo Industry). GP and test specimens for each experiment performed are shown in Fig. 2.

The obtained data sets were evaluated by statistical methods, which were intended to indicate statistically significant changes from the perspective of the measured mean values of these sets.

RESULTS

Values for theoretical density, one of the basic characteristics of GP/epoxy composites, are shown in



Fig. 2. Glass powder/epoxy specimen for shear strength test (left), specimen for a tensile strength test (right)



Table 1. They are based on the theoretical densities of resin and GP – perfect wetting of the filler by epoxy is considered in the calculation.

GP was sieved on a production line in fractions with particle size below 90 μ m. This particle size represented the highest level of assessed intervals. GP particles were classified according to their size and each interval of particle size distribution was subsequently subjected to optical analysis on a stereoscopic microscope. Then the average size of particles was determined for the individual intervals – see histograms in Fig. 3. For each interval, the mean particle size corresponded to 18.7 ± 7.7 , 38.7 ± 7.2 , and $72.6 \pm 16.6 \mu$ m.

The presence of GP in all cases increased hardness (Fig. 4). Unfilled resins evinced Shore D hardness of 89.45 ± 1.25 . Hardness was the highest at 20% GP concentrations. The highest mean value of

Fig. 3. Dimensional analysis of glass powder particles sorted into individual fractions

Fig. 4. Hardness of glass powder/epoxy composites with different particles size



Shore D hardness was measured at 20% concentration (50–90 μ m), i.e. 91.38 ± 01.03. Coefficient of variation of measurements ranged 1.2–2.0%.

The impact of different particle sizes on the adhesive properties of the composite mixture was evaluated on steel adherend through shear strength. Prior to the system application on a surface, the surface parameters should be assessed. From this viewpoint basic roughness parameters Ra and Rz are particularly relevant (Fig. 5).

Unfilled resin exhibited shear strength of 11.49 ± 0.91 MPa (coefficient of variation was 7.9%) (Fig. 6).

In all cases except for 0–30 μ m/1% (an increase of 0.5% to 11.54 MPa) a slight decrease in shear strength values occurred due to the inclusion of the filler. The lowest measured shear strength was 9.48 ± 0.59 MPa (50–90 μ m/3%, a decrease of 17.5%, coefficient of variation 5.9%). As is visible from the statistical analysis (Table 2), in the case of decreasing values of shear strength, this decrease can be discussed as statistically



Fig. 5. Roughness parameters of steel adherends (S235J0) in the place of a joint

insignificant (due to the measured standard deviations), where the coefficient of variation of the measuring reached 15.8%. Only in the interval with particle size $0-30 \ \mu\text{m}$ the filled resin systems comparing to the unfilled resin systems do not evince any statistically significant decrease (hypothesis H₀) in shear strength (P > 0.05). In other cases, this statement is not fulfilled.

The analysis of failure type in the place of the joint was carried out by a stereoscopic microscope after testing according to ČSN ISO 10365 – Adhesives – Designation of main failure patterns. In all cases (concentration and particle size of GP) the failure was in the adhesive type (Fig. 7).

The dependence of cohesive characteristics on different particle sizes of GP was evaluated by tensile strength (Fig. 8). Unfilled resin reached tensile strength of 42.56 ± 2.64 MPa (coefficient of variation 6.2%).

In all cases the inclusion of GP particles resulted in a statistically significant decrease of tensile strength values of the systems. Higher concentrations of the filler led to a greater decrease of the value. The lowest value of -27.30 ± 2.86 MPa (coefficient of variation 10.5%) was measured in the system 50–90 µm/20%.

DISCUSSION

In terms of adhesion, we may partially agree with the conclusions of Z h a i et al. (2006), who describe the positive effect of particles on the adhesion of epoxy resin to the steel adherend, the optimum concentration of Al_2O_3 particles (60–100 nm) indicated by the authors was 2 wt.% (increase in strength from 3.6 to 7.8 MPa). The increase in adhesion was observed in only one case (0–30 µm/1%, an increase of 0.5%) and this increase was not statistically significant (see results of *T*-test). It should, however, be noted that this experiment describes the particle size in the order of

 Table 2. T-test: statistical comparison of shear strength (0 : 1, 2, 3, 4, 5, 10, 20%)

<i>T</i> -test H_0 : (<i>P</i> > 0.05)	Glass powder (vol.%)								
Particle size (µm)	1	2	3	4	5	10	20		
50-90	0.06	0.01	0.00	0.18	0.06	0.30	0.19		
30-50	0.41	0.03	0.29	0.08	0.01	0.15	0.02		
0-30	0.93	0.84	0.53	0.84	0.40	0.20	0.06		

Table 3. T-test: statistical comparison of tensile strength (0:1, 2, 3, 4, 5, 10, 20%)

<i>T</i> -test H_0 : (<i>P</i> > 0.05)	Glass powder (vol.%)								
Particle size (µm)	1	2	3	4	5	10	20		
50-90	0.01	0.01	0.01	0.01	0.00	0.00	0.00		
30-50	0.01	0.00	0.00	0.00	0.01	0.00	0.00		
0-30	0.01	0.00	0.01	0.00	0.01	0.00	0.00		

tens of micrometres, comparing to results with particle size in nanometres. We may partially agree with the results of D e k k e r s, H e i k e n s (1983), stating that the inclusion of glass spheres leads to good adhesion to the metal adherend – the authors describe a cohesive kind of disruption on aluminium adherends. The adhesive failure dominated in the experiment carried out on steel adherend. This shows that the weak point on the interface is the interaction. For example, the



Fig. 6. Lap-shear tensile strength of glass powder/epoxy composites with different particles size

optimum surface treatment of adherend could lead to an increase in strength at this interface.

In terms of tensile strength it is not possible to agree with the conclusions of K a h r a m a n a et al. (2008), who describe an increase in aluminium particles strength in the order of tens of micrometres. The inclusion of GP has always caused a decrease in tensile strength irrespective of the used particles size.

The experiment also did not confirm the increase in tensile strength by the inclusion of GP at a low concentration of 5% described by K u et al. (2010) and K u, W o n g (2012). The decrease in tensile strength can be caused by high porosity of the mixture, which originated only by moulding without the use of vacuum. The preparation is inexpensive and is frequently used in practice. This procedure can minimize the formation of air bubbles, which can then initiate the cracks formation. A decrease in tensile strength of thermoplastics due to the presence of glass sphere was described e.g. by N i c o l a i s, N i c o d e m o (1974), the strength of the unfilled matrix was always higher than the strength of the filled matrix; this fact was attributed to imperfect adhesion between the phases.

When applying GP into reactive resins or to other adhesives, their properties must be respected (Valášek, Müller, 2013b). For example, some epoxy resins differ in molecular weight and viscosity, which affects the preparation mixture and subsequent interaction between the resin and the filler (particles).



Fig. 7. Typical adhesive type of failure of test specimens (30-50 µm - left: 1%, 2%, 5%, 20%)

Fig. 8. Strength of glass powder/epoxy composites with different particles size



CONCLUSION

Inclusion of GP into reactive resins and adhesives is a method of utilization of secondary raw materials, which is inexpensive and sensitive to the environment. From this perspective, such a use of secondary raw materials should be preferred. Noteworthy results obtained in the experiments can be summarized as follows:

• The presence of GP increased Shore D hardness by up to 2.15%.

• The influence of GP particles size on shear strength was proved: a smaller particles size of $0-30 \ \mu m$ did not lead to a statistically significant decrease in the values of tensile strength.

• The inclusion of GP led to a decrease in tensile strength by up to 35.9%. A clear influence of particle size on tensile strength was not proved in the monitored intervals.

REFERENCES

- Affatato S, Ruggiero A, Merola M (2015): Advanced biomaterials in hip joint arthroplasty. A review on polymer and ceramics composites as alternative bearings. Composites Part B: Engineering, 83, 276–283. doi: 10.1016/j.compositesb.2015.07.019.
- Cheng W, Dunn PF, Brach RM (2002): Surface roughness effects on microparticle adhesion. Journal of Adhesion, 78, 929–965. doi: 10.1080/00218460214510.
- D'Amato RD, Caja J, Maresca P, Gómez E (2014): Use of coordinate measuring machine to measure angles by geometric characterization of perpendicular planes. Estimating uncertainty. Measurement, 47, 598–606. doi: 10.1016/j. measurement.2013.09.027.
- Dekkers MEJ, Heikens D (1983): The effect of interfacial adhesion on the tensile behaviour of polystyrene-glassbead composites. Journal of Applied Polymer Science, 28, 3809–3815. doi: 10.1002/app.1983.070281220.

- Hojo H, Toyoshima W, Tamura M, Kawamura N (1974): Shortand long-term strength characteristics of particulate-filled cast epoxy resin. Polymer Engineering and Science, 14, 604–609.
- Kahramana R, Sunarb M, Yilbas B (2008): Influence of adhesive thickness and filler content on the mechanical performance of aluminum single-lap joints bonded with aluminum powder filled epoxy adhesive. Journal of Materials Processing Technology, 205, 183–189. doi: 10.1016/j.jmatprotec.2007.11.121.
- Kejval J, Müller M (2013): Mechanical properties of multicomponent polymeric composite with particles of Al₂O₃/ SiC. Scientia Agriculturae Bohemica, 44, 237–242. doi: 10.7160/sab.2013.440407.
- Ku H, Wong P (2012): Contrast on tensile and flexural properties of glass powder reinforced epoxy composites: Pilot study. Journal of Applied Polymer Science, 123, 152–161. doi: 10.1002/app.34469.
- Ku H, Trada M, Cecil T, Wong P (2010): Tensile tests of phenol formaldehyde glass-powder-reinforced composites: Pilot study. Journal of Applied Polymer Science, 116, 10–17. doi: 10.1002/app.31424.
- Milton GW (2002): The theory of composites. Cambridge University Press, Cambridge.
- Mleziva J (1993): Polymers: manufacture, structure, properties and application. Sobotáles, Prague. (in Czech)
- Müller M, Herák D (2013): Application possibilities of adhesive bonds – Europe, Indonesia. Scientia Agriculturae Bohemica, 44, 167–171. doi: 10.7160/sab.2013.440307.
- Nakamura Y, Yamaguchi M, Okubo M, Matsumoto T (1992): Effects of particle size on mechanical and impact properties of epoxy resin filled with spherical silica. Journal of Applied Polymer Science, 45, 1281–1289. doi: 10.1002/ app.1992.070450716.
- Nicolais L, Nicodemo L (1974): Effect of particles shape on tensile properties of glassy thermoplastic composites. International Journal of Polymeric Materials, 3, 229–243.
- Novák M (2011): Surface duality hardened steels after grinding. Manufacturing Technology, 11, 55–59.

Petrie EM (2006): Epoxy adhesive formulations. McGraw-Hill, New York.

Rudawska A (2014): Selected aspects of the effect of mechanical treatment on surface roughness and adhesive joint strength of steel sheets. International Journal of Adhesion and Adhesives, 50, 235–243. doi: 10.1016/j. ijadhadh.2014.01.032.

- Teng JG, Fernando D, Yu T, Zhao XL (2011): Treatment of steel surfaces for effective adhesive bonding. In: Proc. 5th International Conference on FRP Composites in Civil Engineering (CICE 2010), Beijing, China, 865–868.
- Valášek P, Müller M (2013a): Composite based on hard-cast irons utilized on functional parts of tools in agrocomplex. Scientia Agriculturae Bohemica, 44, 172–177. doi: 10.7160/ sab.2013.440308.
- Valášek P, Müller M (2013b): Polymeric composite based on glass powder – usage possibilities in agrocomplex. Scientia Agriculturae Bohemica, 44, 107–112. doi: 10.7160/ sab.2013.440207.
- Zhai L, Ling G, Li J, Wang Y (2006): The effect of nanoparticles on the adhesion of epoxy adhesive. Materials Letters, 60, 3031–3033. doi: 10.1016/j.matlet.2006.02.038.

Corresponding Author:

Asc. prof. Ing. Petr Valášek, Ph.D., Czech University of Life Sciences Prague, Faculty of Engineering, Department of Material Science and Manufacturing Technology, Kamýcká 129, 165 21 Prague 6-Suchdol, phone:+420 224 383 262, e-mail: valasekp@tf.czu.cz