RECYCLATION OF WASTE MICROPARTICLES IN INTERACTION WITH POLYMERIC MATRIX – MULTIPHASE COMPOSITE

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Abstract. A composite is a material consisting of two and more phases. The paper describes the composite system with the polymeric matrix – the epoxy resin filled with two various types of inorganic micro-particles based on the waste – Al_2O_3 and the glass powder. The interaction of microparticles and the polymeric matrix creates resulting mechanical properties which are unwound from the percentage representation of the microparticles and their mutual relation. The paper deals with the possibility of the primary microparticles (raw materials) substitution by the secondary microparticles (waste). It comes to the material recyclation which should be preferred. As the experiment results show the inclusion of the microparticle fillers increased the wear resistance of 68 % at keeping the constant strength of overlapped bonds to the detriment of 37 % decrease of the tensile strength.

Keywords: tensile and shear strength, waste utilization, wear resistance.

Introduction

The mutual interaction of the polymer and the microparticle filler creates the material which is different by its properties from the unfilled material. The optimization of namely the polymer mechanical properties extends their application area. The resulting properties of the filled systems are influenced by physical, mechanical and chemical properties of the used filler and the polymer, their mutual relation, the filler orientation and its distribution in the matrix (polymer). In the sphere of the filled polymeric materials-polymeric composite systems the reactoplastics represented by epoxy, polyester and other types of resins are commonly used as the matrices. The possibility to fill is extended also to other groups of polymeric materials – thermoplastics and elastomers [1; 2]. Provided it is dispersed more types of particles in the polymeric materials which differ with their mechanical – physical properties we speak about the multiphase (multi-component) composite systems.

Meng a Kee [3] optimized the modules of elasticity of the three-phase composite system with the polymeric matrix where they dispersed nanoparticles of wood powder and clay particles. The example of multi-phase composites can be also a combination of fibre and particle reinforcements. Alavi and Ashraphi [4] increased the tensile properties of the polyester composite with glass fibres (E-glass) by adding 0.2 wt % (weight percent) Al_2O_3 of a size 50 µm. Yang and Dai [5] carried out a similar experiment and optimized the tensile and bending strength of the PA6 filled with particles of talc by glass fibres. They set the optimum ratio of phases as 70:5:25 (PA66/Talc/Glass fibres).

Wang and Jijang [6] used particles of SiO_2 to optimize the mechanical properties of epoxy resin, they noticed a significant difference of these properties relating to the composite preparation at the same time. The composites filled with 1 wt % SiO_2 and prepared by mechanical mixing have of 7.9 % better bending properties than the unfilled composite. So long as was the particle filler dispersed by the ultrasound, this improvement increased to a value 9.7 %.

5 wt % of hard inorganic particles of Al_2O_3 of size 48-100 µm increased significantly the wear resistance of phenolic resins according to Satapathy et al. [7]. Using Al_2O_3 for increasing the wear resistance is mentioned also by other authors. Increased wear resistance of composite systems can be used according to Müller [8; 9] in a sphere of a renovation of machine functional areas.

For improving the strength characteristics of some polymers the micro-particles of glass powder can be used. E.g., authors Ku and Wong [10] describe the strength increase of epoxy resin filled with 5wt % of glass powder with sizes 11-18 µm.

The filler can also decrease the price besides the change of the matrix properties. In case of using the waste particle fillers it comes to their material recyclation which is inexpensive and should be preferred. It comes to significant savings of costs for production of these systems at the same time. Valášek et al. [11-13] state filling epoxy resins with waste particles which were taken away from a process of mechanical treatment of material surfaces (grit blasting) and from a process of material machining (milling and turning). Using chips from the machining process is possible owing to the fact that at modern machining ways the arisen chips do not have to be always polluted by a processing liquid [14]. The inclusion of these fillers led to increasing the wear resistance.

The aim of this experiment is to verify the hypothesis that it is possible to create a composite system with sufficient cohesive strength by various ratio combinations of two inorganic waste micro-particle types the properties of which can be modified on the basis of the percentage representation of single phases. From the references it follows that the given amount of glass powder can slightly increased the system strength characteristics [6]. On the contrary, Al_2O_3 decreases in most cases the strength characteristics and it increases the abrasive wear resistance. The size of Al_2O_3 particles influences significantly the speed of the strength characteristics fall-smaller particle sizes ease the strength fall which is proportional to the filler concentration in the matrix [7; 11]. The aim of the experiment is to describe the mechanical properties (hardness, abrasive wear resistance, tensile strength, shear strength) of the composite with various percentage and ratio representation of Al_2O_3 and glass powder in the epoxy matrix.

Materials and methods

The stated resin Eco Epoxy 1200/324 was filled with the glass powder produced by the firm Refaglass s.c. of the particle size smaller than 90 µm (a middle dimension 47 µm) and with the waste Al_2O_3 F800 of the grain sizes 6 ±1 µm. The particles of Al_2O_3 were used for grit blasting of common carbon steel. The waste filler did not show a character of dangerous waste.

The mixture of the filler and the epoxy resin was prepared by mechanical mixing. The mixture was cast into silicone rubber forms which corresponded by their shape and sizes to the requirements of single standards. The testing samples were prepared with different volume percentages of the filler (15 and 30 %). The filler concentration was set on the basis of the hypothesis that higher concentration will lead to better abrasive wear resistance. The ratios of Al_2O_3 (F800) and the glass powder (GP) (F800:GP) were following at single concentrations: 1:1, 1:5 and 5:1.

An important first-class quality of the composite system – porosity (P) was calculated according to the equation (1):

$$P = \frac{\rho_{The} - \rho_{Rea}}{\rho_{The}} \cdot 100 \tag{1}$$

where P – porosity, %;
ρ_{The} – theoretical composite density, g·cm^{-3};
ρ_{Rea} – real composite density, g·cm^{-3} [2].

As a guide for the hardness determination of the composite systems the standard CSN EN ISO 2039-1 [15] was used. The tested specimen dimensions were of 35 x 25 x 9 mm. The ball from hard metal of 10 mm diameter was used. The tested specimens were loaded using the force of 2.452 kN for the duration of 30 s (HBW 10/250/30).

The testing samples determined for the specification of the cohesive strength by means of the tensile strength were prepared according to the requirements of the standard CSN EN ISO 3167 [16].

The setting of the tensile characteristics was carried out in accordance with the standard CSN EN ISO 527 [17]. For the lap-shear strength description in the boundary adherend –filled system overlapped assemblies were made. The surface of 1.5 mm thick steel sheets, onto which the composite system was applied, was at first blasted using synthetic corundum of the fraction F80 under the angle of 90º. In this way the average surface roughness of R_a = 1.36 ± 0.31 µm (R_z = 9.1 ± 0.24 µm) was reached. Then the surface was cleaned and degreased using perchlorethylene and prepared to the composite mixture application.

The two-body abrasion was tested on a rotating cylindrical drum device with the abrasive cloth of the grain size P220 (Al_2O_3 grains) according to the standard ČSN 62 1466. The mean of the testing specimens was 15.5 ± 0.1 mm and their height was 20.0 ± 0.1 mm. The mass decreases were measured on analytic scales weighing on 0.1 mg. The volume decreases were calculated on the basis of the found out volume and the density of the composite systems.

A statistical evaluation of the results was carried out by means of a program Statistica – one factor ANOVA, reliability level $\alpha = 0.05$, for statistical comparison of the values the Tukey's HSD test was used (in vertical columns there are designated identical sets of data).

Results

The composite systems were hardened in accordance with the data stated by the producer (7 days, 23 ºC). After passing the stated time the hardness test was carried out and the porosity *P* was set, see Tab. 1. When comparing the densities it was calculated with the values stated by the producer (Epoxy = 1.15 g·cm^{-3}, F800 = 4.00 g·cm^{-3} and GP = 2.55 g·cm^{-3}). The highest reached mean value of the hardness 16.91 ± 0.63 corresponded to the composite with 30 % 1:1. From the measured results it clearly follows that the average values of the hardness are higher at the composite with a more saturated matrix (30 %) – in average it came to 10.8 % increasing of the hardness compared with the composites with 15 %. Various ratio representations of the fillers did not have a significant influence on the system hardness. The results reflect till a given measure a presumption that higher ratio of the corundum which is of higher hardness than the glass powder leads to more significant increase of the composites hardness (the hardness according to Mohs scale: glass powder = 6-7, corundum = 9).

Table 1

Ratio of filler and matrix, density and porosity

Material (F800:GP)	ρ_{The} g·cm^{-3}	ρ_{Rea} g·cm^{-3}	Porosity %	Hardness HBW 10/250/30
1:1 15 %	1.47	1.42	3.23	14.15
1:1 30 %	1.79	1.68	6.20	16.91
1:5 15 %	1.40	1.35	3.67	14.39
1:5 30 %	1.64	1.55	5.44	15.70
5:1 15 %	1.54	1.46	4.89	14.95
5:1 30 %	1.93	1.79	7.19	16.22
GP 15 %	1.34	1.26	6.72	15.06
GP 30 %	1.53	1.45	5.88	15.92
F800 15 %	1.58	1.45	8.23	16.04
F800 30 %	2.01	1.81	9.95	16.86

The abrasive wear resistance was evaluated on the basis of volume losses (owing to the different density of single materials, see Tab. 1). The mean values of the volume losses together with variation coefficients are visible in Fig. 1. Higher filler concentration (30 %) decreased the volume losses more significantly than the concentration 15 %. The filled systems showed always smaller volume losses than the unfilled epoxy adhesive (0.3432 ± 0.0285 cm^3). The smallest mean volume loss 0.2081 ± 0.0064 cm^3 was recorded at the material 1:1 30 % and the material 5:1 30 % (0.2370 ± 0.0302 cm^3). The presence of glass powder in the composite matrix increased the tendency of the systems to the wear compared with the materials with higher ratio of corundum.

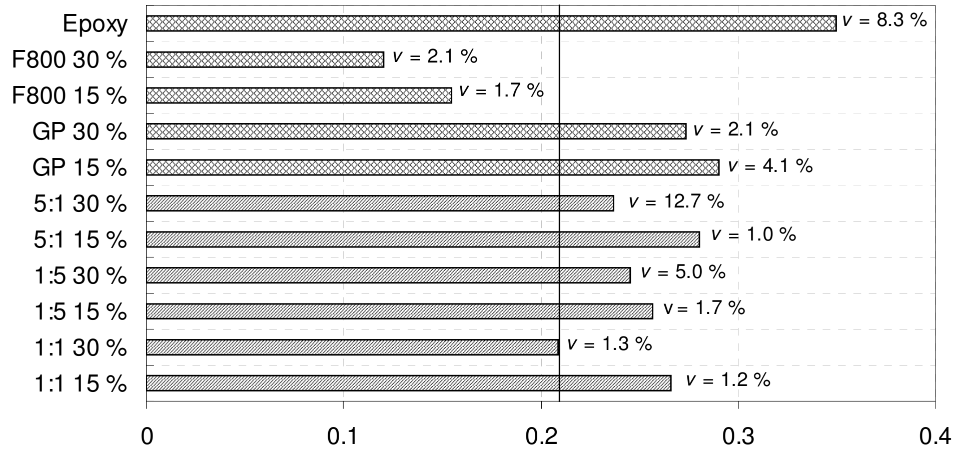


Fig. 1. **Volume losses in cm^3**

The shear strength of the composite systems compared with unfilled resin (11.65 ± 0.42 MPa) is visible in Fig.2. The highest shear strength was reached at the filled systems with 15 % of the filler (1:1 – 12.10 ± 0.47 MPa, 5:1 – 12.01 ± 0.32 MPa, 1:5 – 12.17 ± 1.10 MPa) – this increase of the shear strength compared with resin without the filler was negligible from the point of the standard deviation size (see Fig. 2 – Turey's HSD Test, graphical presentation). However, from the results the shear strength increase of the multicomponent systems is evident compared with the systems which had only corundum particles in the matrix.

Material		Mean (MPa)	agreement	
30%	F800	10.06	*	
30%	5:1	10.17	*	*
15%	F800	10.35	*	*
30%	1:1	11.38	*	*
30%	GP	11.46	*	*
15%	GP	11.54	*	*
Epoxy		11.65	*	*
30%	1:5	11.68	*	*
15%	5:1	12.01	*	*
15%	1:1	12.10		*
15%	1:5	12.17		*

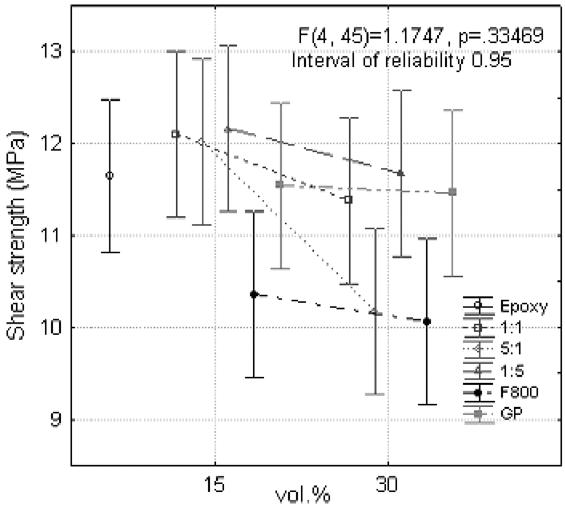


Fig. 2. **Tukey's HSD, tensile shear strength**

The main types of the bond failure (CSN ISO 10365) were evaluated at the places of the bond fracture of the overlapped testing samples (places of adhesive bond) [18]. At the multi-component systems the special cohesive failure (SCF) was the most often type of the failure, as well as at the systems with glass powder (see Fig. 3). Only the systems with high ratio of corundum (5:1) showed in some cases the adhesive failure (AF) or a combination of the adhesive and cohesive failure (ACFP). The systems with the inclusion of only the corundum particles showed the adhesive failure. Pores were observed by the stereoscopic microscope in the place of the adhesive bond fracture. Their presence is described by the porosity which influences both the shear strength and the tensile strength by indisputable way. The joint width of the multicomponent systems was defined by the applied system in the place of the adhesive bond (without using distance wires as well as at remaining systems). The joint thickness measuring was carried out on the stereoscopic microscope when the joint width ranged in the interval from 0.16 mm (1:5 15 %) to 0.24 mm (11:1 30 %).

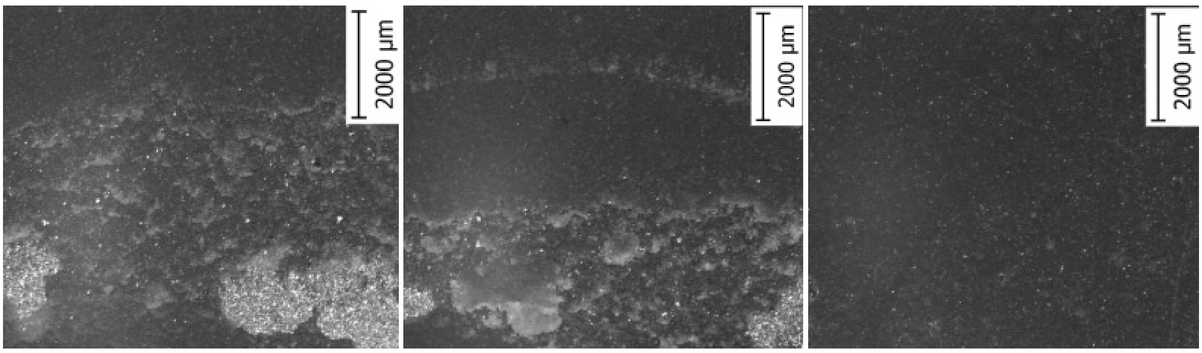
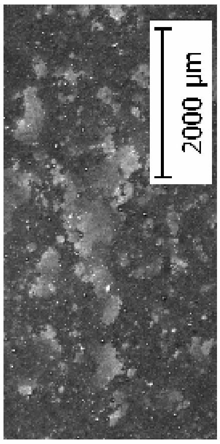


Fig. 3. **Adhesive bond failure:** (from left: 1:5 15 % SCF, 1:5 30 % SCF, F800 30 % AF)

All filled systems had significantly smaller tensile strength than the resin without the filler (45.73 ± 0.95 MPa). From the measured values it is obvious that higher corundum content in the matrix deteriorated the tensile strength compared with the tensile strength of the systems with higher ratio of glass powder. The statistical comparison of the data sets for single measurements and the graphical presentation of the results together with the typical failure area are depicted in Fig. 4.



Material		Mean (MPa)	agreement			
30%	F800	18.69	*			
30%	1:1	22.70	*	*		
15%	5:1	23.11	*	*		
30%	5:1	23.36	*	*		
15%	F800	24.65	*	*	*	
30%	1:5	27.01		*	*	
15%	1:1	27.28		*	*	
30%	GP	28.01		*	*	
15%	1:5	28.64		*	*	
15%	GP	30.96			*	
Epoxy		45.73				*

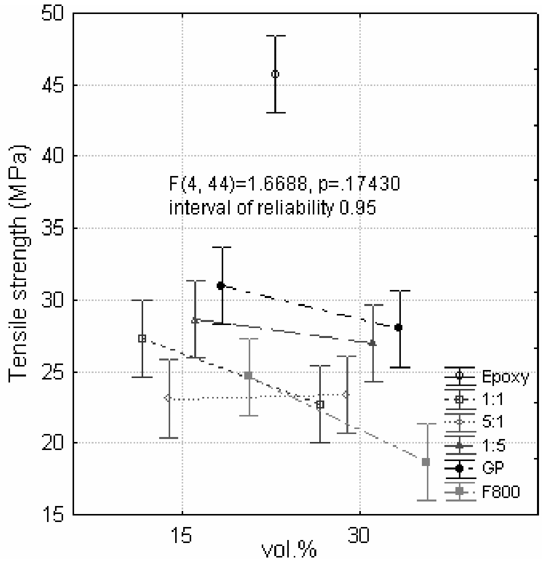


Fig. 4. **Failure area, Tukey's HSD test, tensile strength**

The elongation values (*A*) are sketched in Diagram 5 where the characteristic curves for the tensile strength and the shear strength of multicomponent systems are combined. Higher representation of corundum at the tensile strength decreased the elongation values. At the tensile shear strength the elongation of the overlapped samples is formed from the great majority by the elongation of the adherends (metal sheets). The used metal sheets show approximately $A = 1.84$ % for the force value 4000 N and $A = 0.97$ % for 3000 N. The maximum loading capacity of the adherends is approximately 11 500 N at $A = 46$ %. At the destructive testing of the overlapped adherends the bending moment rise was not eliminated. The filled systems showed the elongation till 2 %.

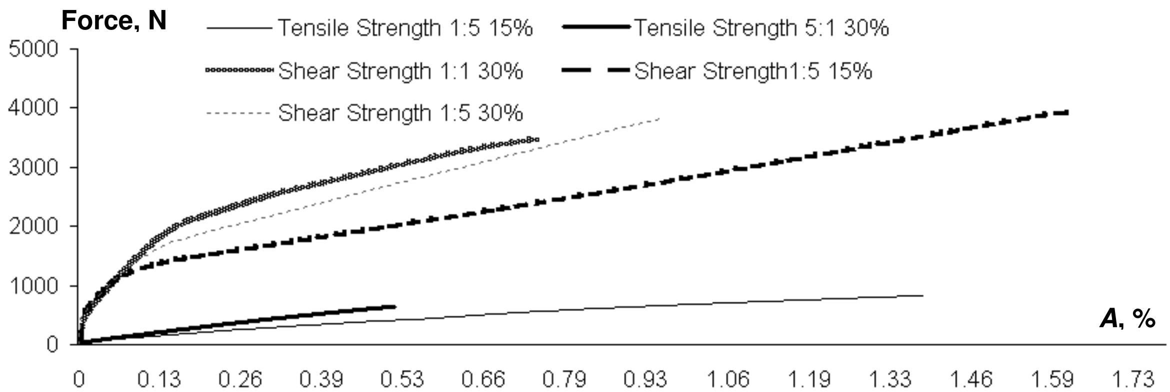


Fig. 5. **Elongation of composite systems**

Discussion

The results proved the presence of pores in the tested systems. The chosen methodology of the testing sample preparation was selected in following the practice when it is not possible to think about using the vacuum and mechanical mixers at the composite systems based on waste when their usage would increase the costs. According to the results of Wang and Jijang [6] the particle dispersion by the ultrasound as the example could increase the observed characteristics order of percentage units. From the results the presumption coming from the studies [7; 8; 11] was proved that corundum optimizes the wear resistance but it influences the tensile and adhesive characteristics in a negative way. On the contrary, glass powder did not increase the wear resistance so significantly as corundum, however it had not such a great negative influence on the cohesive and adhesive characteristics. The hypothesis about the possibility to optimize the mechanical properties by means of mutual ratio of various filler types was confirmed. However, it is necessary to mention that it is possible to increase the hardness, the abrasive wear resistance at keeping the shear strength by the chosen filler types but with significant decrease of the tensile strength (compared with the resin without the filler).

Conclusion

The results of the carried out study – the comparison of composite multicomponent systems with the unfilled epoxy resin can be summed up from the mechanical properties point of view as following:

- The composite system hardness increased as much as of 54 % (1:1 30 %).
- The volume losses of the composites decreased as much as of 68 % (F800 30 %), respective of 40 % (1:1 30 %).
- The shear strength increased compared with the resin without the filler maximum of 4 % (1:5 15 %), however for systems with higher representation of corundum it came to 13 % (5:1 30 %), respective 14 % fall (F800 30 %), when evaluating the shear strength it is necessary to take into regard the high standard deviation.
- The tensile strength decreased minimum of 32 % (GP 15 %), respective of 37 % (1:5 15 %) compared with the resin without the filler.

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