QUASI-STATIC TESTS ON POLYURETHANE ADHESIVE BONDS REINFORCED BY RUBBER POWDER

Martin Tichy, Viktor Kolar, Miroslav Muller, Petr Valasek
Czech University of Life Sciences Prague, Czech Republic
artintichy@tf.czu.cz, muller@tf.czu.cz, valasekp@tf.czu.cz

Abstract. Waste from tires is a global issue. New recycling methods allowed to create rubber powder from tire waste. This research shows a possibility of this rubber powder to reduce the impact of waste tires on environment. Polyurethane adhesive reinforced by rubber powder creates an interesting composite, which can be used across all fields of industry. Adhesive bonding is a progressive technology of bonding various materials. This research is one part of the study on reinforced polyurethane adhesive by rubber powder, which shows the influence of microparticles on mechanical properties. This research follows interactions of rubber powder microparticles and polyurethane adhesive in quasi-static fatigue on mechanical properties. Quasi-static test of adhesive bonds simulates real conditions in practice. The quasi-static test of adhesive bonds was set on 200, 500 and 1000 cycles. The influence of strength and elongation on reinforced polyurethane adhesive in the quasi-static test was compared with the results from the static mechanical tests. The interactions of rubber powder microparticles, polyurethane adhesive and adherend were analysed by SEM in three layers. Polyurethane adhesive properties are good sealing and adhesion to various materials, i.e. suitable for filler modification. The weaknesses of polyurethane adhesive are low strength and high price. Reinforcing by rubber powder is effective for polyurethane adhesive, because it does not limit the sealing properties, increases the strength of bonds and can reduce the price. The modification of polyurethane adhesive by rubber powder was in various concertations 5, 10 and 15 wt. %. The quasi-static tests prove increasing influence of rubber powder on mechanical properties by percentage difference. The strength of reinforced polyurethane adhesive increased by 17 % and the elongation positively decreased by 6 %.

Keywords: quasi-static fatigue, recycling, elongation, microparticles, SEM.

Introduction

The adhesive bonding technology currently represents one of the relevant technologies in the material bonding process, it has wide application in automotive, agriculture production, aerospace etc. fields [1;2]. The progressive trend in adhesive bonding is modification of adhesive by various fillers, e.g. a filler based on recycled products [3]. The filler modification by recycled products improves the mechanical properties of adhesive and decreases the weight, price and impact on environment [4].

In the research polyurethane adhesive was used, which is used in automotive sphere for its good shock-absorbing properties. Its disadvantage is the low strength characteristic, e.g. tensile strength. For these reasons the study is based on modification of polyurethane adhesive by rubber powder to improve the mechanical properties.

The worn-out tyres or tyre waste is serious problem for their impact on environment. Reuse of the tyre waste in the form as rubber powder could lead to considerate alternative for environment. Rubber powder as a product form the tyre waste recycling process can be used in adhesives as fillers [5;6].

The adhesive bonding technology uses fillers, which are particles [7;8] and fibres [9] in various dimensions. Based on the results of the research by various authors, it follows that mechanical properties of the particle composite depends on the particle dimensions and concentration in the matrix [8;10]. The strength of adhesive bond depends on the physical and chemical factors, e.g. wettability, cohesion and adhesion, also on the technology factors, e.g. surface treatment, roughness of the surface structure [11;12], further on the construction factors, e.g. type and dimension of bond, type of stress etc. [13]. Significant factors, which influence the quality of adhesive bonds, are the surface treatment before adhesive application and homogenous [14;15] and constant adhesive layer [16].

The cyclic stress has a major impact on the durability of adhesive bonds. This stress, resp. cyclic material fatigue, is the most destructive form of mechanical stress. It is an irreversible process that occurs even with small stress [17]. Cyclic stress of adhesive bonds represents most frequent cause of degradation failure in practice [3]. The strength is influenced not only by the filler, but also by the stress between the particle and matrix, i.e. the effective stress distribution between the particles and matrix by good adhesion [8;10;18]. This effect increased the strength of adhesive bonds.

Electron microscopy (SEM) is used to evaluate the mechanical properties and overall quality of adhesive bonds [19].

New recycling methods allowed to create rubber powder from tire waste. This research shows a possibility of this rubber powder to reduce the impact of waste tires on environment. Polyurethane adhesive reinforced by rubber powder creates an interesting composite, which can be used across all fields of industry.

The use of the tire waste in adhesive has positive impact on environment. The research points on the next usage of unused tire waste, which can be used for modification of the mechanical properties, cost reduction and the decreasing of environmental impact.

Polyurethane putty has good sealing properties and adhesion to various materials, i.e. it is applicable for filler modification. On the other hand, it has low strength and high price. Rubber powder is suitable for modification, because does not inhibit the sealing and increases the strength of polyurethane putty.

The research on the mechanical properties of polyurethane adhesive bonds reinforced by rubber powder at quasi-static load is continuation of the previous research. The previous research deals with the effect of rubber powder from waste tyre rubber on the mechanical properties of one-component polyurethane putty (adhesive). The previous research was focused on the mechanical properties of reinforced polyurethane adhesive with concentration of rubber powder at static tensile test with various loading speeds. The results of the previous research proved the best value at the loading speed 2 $mm \cdot min^{-1}$ and positive increase of the mechanical properties by adding rubber powder [20].

The influence of rubber powder in polyurethane adhesive on the strength and elongation was compared with the results of static mechanical tests. The interaction of adhesive bonds was followed up by SEM analyse in three layers, i.e. between polyurethane putty, rubber micro-particles and adherend.

Materials and methods

For the research one-component polyurethane adhesive Roberlo RPS 55 was used. This adhesive is used in automotive for its fast hardness, good sealing and good adhesion on various materials. The polyurethane adhesive was modified by rubber powder from recycled tyres to increase the mechanical properties of adhesive bond.

The rubber powder was used in two sizes to find out the characteristic between the microparticle size and mechanical properties of adhesive bond. The rubber powder marked as AGP4 had the maximal size 0–400 μm and AGP8 had the maximal size 0 to 800 μm. The concentrations of rubber powder in polyurethane adhesive were set to 5, 10 and 15 wt. %.

For single lap bond structural carbon steel S235J0 was used with the size 100 ± 0.1 x 25 ± 0.1 x 1.5 ± 0.1 mm. The surface of bonded steel was sandblasted by MESH 80 according to CSN ISO 8501-1. The bonded samples were degreased by acetone. The surface parameter was measured by the profilometer Mitutoyo Surftest 301 to Ra = 1.76 ± 0.18 μm, Rz 11.22 ± 0.84 μm. The single lap bond has the length 12.5 ± 0.25 mm in accordance to CSN EN 1465 (equivalent BS 1465). The curing time of adhesive was set on 12 hours with static load 745 ± 5 g.

The mechanical properties of bond with modified adhesive were tested on the universal test machine LabTest 5.50ST. The adhesive bond was tested on the tensile strength (σ_m) and the elongation (ε) at quasi-static fatigue. The quasi-static area of the tensile test was set to 200, 500 and 1000 cycles with the loading speed 2 $mm \cdot min^{-1}$. The interval of the pulsing tensile strength was set to 5 % and 30 % static shear tensile strength (σ_m).

The interactions between polyurethane adhesive and microparticles of rubber powder were followed by scanning electron microscope TESCAN MIRA 3 GMX (SEM).

The measured values were processed with statistical analyses Statistica. For statistical comparation of the measured values multi-factor analysis of Anova was used. For Anova analyses T-test was set with p-values: $p > 0.05$.

Results and discussion

The statistical analyses tested the difference of the strength and elongation of filler AGP4 and AGP8 according to the number of the loading cycles. The statistical results are given in Table 1. The hypothesis H_0 shows a state, when there is no significant difference between the measured values: $p > 0.05$. The hypothesis H_0 was not confirmed in elongation of modified polyurethane with AGP4, i.e. there is influence on the number of the loading cycles. Also, the hypothesis H_0 was not confirmed in the strength at 500 cycles of AGP4. The hypothesis H_0 was not confirmed in the strength of AGP8, i.e. there is no difference during the increasing the number of the cycles.

Table 1

Statistical results of the dynamic quasi-static test of mechanical properties – parameter $p > 0.05$ (the difference of strength and elongation of filler AGP4 and AGP8 according to the number of loading cycles)

Number of cycles	AGP4		AGP8	
	Strength, σ_m	Elongation, ε	Strength, σ_m	Elongation, ε
0	0	0	0	0
200	0.282817	**0.000146**	**0.044581**	0.092610
500	**0.015604**	**0.000146**	**0.015542**	0.710255
1000	0.534652	**0.000146**	**0.001144**	0.655922

Influence of the quasi-static tensile stress on the strength is represented as the difference between the static and quasi-static tensile stress of modified polyurethane adhesive by 5, 10 and 15 wt. % rubber powder with sizes AGP4 and AGP8. The graph in Figure 1 illustrates the influence of the quasi-static tensile stress on the strength (σm) of adhesive bond. The graph illustrates how the quasi-static tensile stress changed the strength compared to the strength in the static tensile stress. Figure 1 confirms the statistical statutes of AGP4 filler strength (Table 1), where the peeks are on 500 cycles.

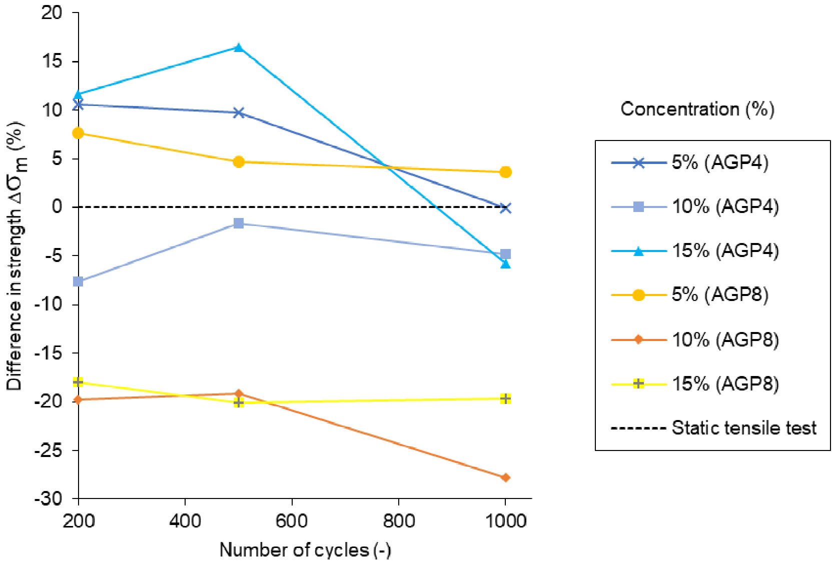

Fig. 1. **Percentage difference between strength (σ_m) of adhesive at static tensile test and dynamic tensile test with number of cycles 200, 500 and 1000. Modification of adhesive 5, 10 and 15 wt. % concentration of filler AGP4, AGP8**

The graph (Fig. 1) illustrates significant increase of the strength up to 16.50 % with rubber powder concentration 15 wt. % size AGP4 at 500 cycles, i.e. the strength increases to 1.405 MPa (Table 2). On the other hand, the modified adhesive with rubber powder size AGP8 decreases on strength, especially with concentration 15 wt. % at 500 cycles decreases up to -20.09 % on 0.863 MPa (Table 3). This effect is due to the fact that the microparticle AGP4 with smaller size 0 to 400 µm has better adhesion ability in the matrix. This effect also proves that modified adhesive with rubber powder AGP4 has the self-toughening process in quasi-static area.

Table 2

Results of the strength (σ_m) and elongation (ε) of adhesive bond with concentration AGP4 400 μm) at quasi-static test

Phys. Qty.	Filler concentration	Concentration 5 % AGP4				Concentration 10 % AGP4				Concentration 15 % AGP4			
	Number of load cycles	**0**	**200**	**500**	**1000**	**0**	**200**	**500**	**1000**	**0**	**200**	**500**	**1000**
σ_m	**Average, MPa**	1.355	1.499	1.487	1.354	1.364	1.26	1.341	1.298	1.206	1.347	1.405	1.137
	Standard deviation, MPa	0.093	0.103	0.061	0.092	0.095	0.133	0.058	0.105	0.078	0.147	0.147	0.141
	Variation coefficient, %	6.86	6.87	4.10	6.79	6.96	10.56	4.33	8.09	6.47	10.91	10.46	12.40
ε	**Average, MPa**	11.19	5.07	5.16	5.82	10.81	8.86	5.61	6.56	14.79	5.72	4.87	5.53
	Standard deviation, MPa	1.80	0.73	0.82	0.72	0.74	10.44	0.74	0.87	3.14	0.99	0.52	0.758
	Variation coefficient, %	16.07	14.45	15.86	12.33	6.48	117.90	13.24	13.21	20.95	17.28	10.70	13.703

Table 3

Results of the strength (σ_m) and elongation (ε) of adhesive bond with concentration AGP8 (800 μm) at quasi-static test

Phys. Qty.	Filler concentration	Concentration 5 % AGP8				Concentration 10 % AGP8				Concentration 15 % AGP8			
	Number of load cycles (-)	**0**	**200**	**500**	**1000**	**0**	**200**	**500**	**1000**	**0**	**200**	**500**	**1000**
σ_m	**Average, MPa**	1.144	1.231	1.198	1.185	1.141	0.915	0.922	0.824	1.08	0.886	0.863	0.868
	Standard deviation, MPa	0.067	0.115	0.146	0.152	0.064	0.186	0.212	0.138	0.098	0.124	0.126	0.108
	Variation coefficient, %	5.86	9.34	12.19	12.83	5.61	20.33	22.99	16.75	9.07	14.00	14.60	12.44
ε	**Average, MPa**	5.81	8.15	8.30	8.33	5.39	8.12	5.91	6.03	5.87	5.54	5.01	5.024
	Standard deviation, MPa	1.16	0.67	1.07	0.88	0.50	7.06	0.54	0.66	1.01	0.68	0.53	0.47
	Variation coefficient, %	20.69	8.26	12.85	10.52	9.26	86.93	9.21	10.86	16.95	12.33	10.64	9.33

Influence of the quasi-static tensile stress on the elongation is represented as the difference between the static and quasi-static tensile stress of the modified polyurethane adhesive by 5, 10 and 15 wt. % rubber powder with sizes AGP4 and AGP8. The graph in Figure 2 illustrates decrease of elongation at the quasi-static tensile stress compared to the static tensile stress. This effect confirms that the potential of the absorption ability of rubber powder is not completely used at static tensile stress. The decrease is especially at concentration 15 wt. % size AGP4 at 500 cycles up to -5.92 % on 4.87 % (Table 3). This decrease has positive influence on the strength of adhesive and confirms the self-toughening process and absorption ability of microparticles in the modified adhesive.

On the other hand, in the previous research in static tests, the plastic deformation was increased when the strength was increased by microparticles AGP4 of modified polyurethane adhesive [20]. This fact confirms the incomplete use of AGP 4 rubber microparticles.

The distribution of the microparticle filler in the matrix is shown in Fig. 3 and Fig. 4. Fig. 3 and Fig. 4 show the surface after the quasi-static test of adhesive bond with the porosity and anchoring the microparticle filler in the matrix. Fig. 3 shows good distribution of the filler AGP4 at concentration 5, 10 and 15 wt. %. The fillers AGP8 with concentration of 10 wt. % and 15 wt. % are not completely separated between themselves (Fig. 4). The results proved that the distribution of filler AGP4 in the adhesive bond has positive influence on the mechanical properties.

The results confirm increasing of the strength with increasing the concentration of rubber micro-particles AGP4 in cycling fatigue at 200 and 500 cycles. On the other hand, the micro-particles AGP8 in adhesive increase the strength only at 5 vol. %. This is given by the differences of dimensions of micro-particles which have different distribution in adhesive. The smaller dimension of micro-particles has better distribution and it increases the mechanical properties of composite.

The research confirms the incomplete use of rubber microparticle AGP4 at static load. The research therefore shows that the rubber microparticles AGP4 are suitable for quasi-static stress. This is given by increasing the strength of the modified adhesive at quasi-static stress and good distribution of filler in the matrix. The microparticles AGP8 are not suitable for quasi-static stress for bad distribution in the matrix, but on other hand, are suitable for static stress for the deformation resistance by a larger dimension of microparticles, which confirms the previous research [20].

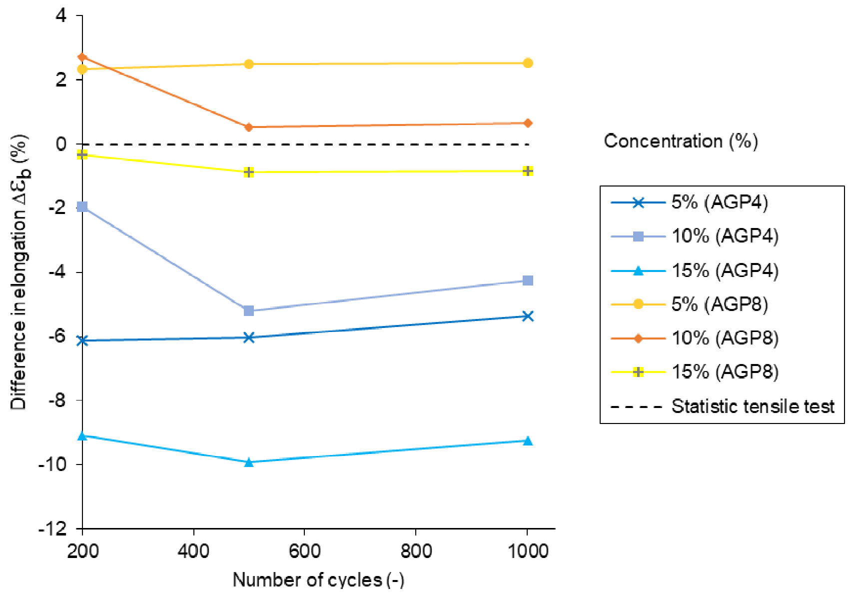

Fig. 2. **Percentage difference between elongation (ε) of adhesive at static tensile test and dynamic tensile test with number of cycles 200, 500 and 1000. Modification of adhesive 5, 10 and 15 wt. % concentration of filler AGP4, AGP8**

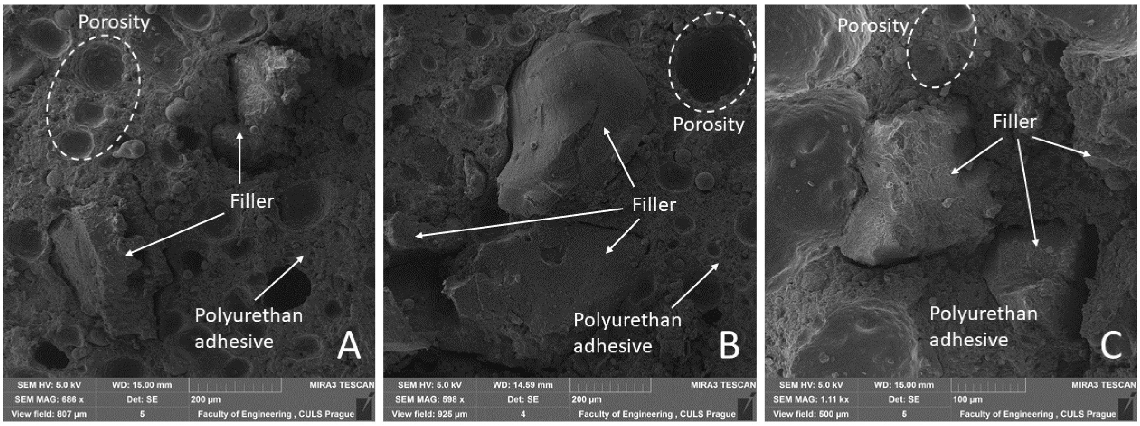

Fig. 3. **SEM images of surface after quasi-static test of adhesive bonds (secondary electrons):** A – filler AGP4 concentration 5 wt. % (MAG 686 x); B – filler AGP4 concentration 10 wt. % (MAG 598); C – filler AGP4 concentration 15 wt. % (MAG 1.11 kx)

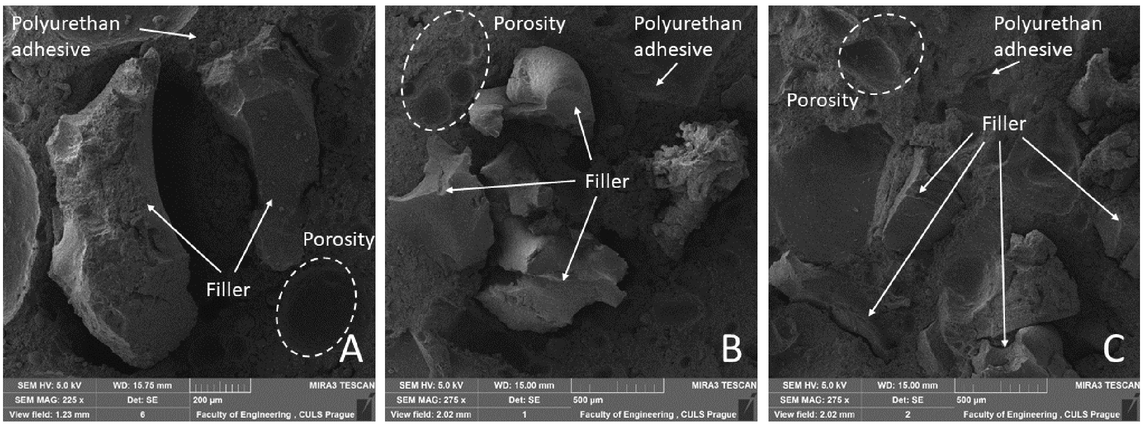

Fig. 4. **SEM images of surface after quasi-static test of adhesive bonds (secondary electrons):** A – filler AGP8 concentration 5 wt. % (MAG 225 x); B – filler AGP8 concentration 10 wt. % (MAG 275 x); C – filler AGP8 concentration 15 wt. % (MAG 275 x)

Conclusions

1. The results confirm significant strength increase at 1.405 MPa up to 16.50 % at concentration 15 wt. % AGP4 at 500 loading cycles.
2. The elongation positively decreases at 4.87 % up to -5.92 % at concentration 15 wt. % AGP4 at 500 loading cycles. This means that the rubber microparticles AGP4 with dimensions 400 μm are more resistance to quasi-static stress than the rubber microparticles AGP8 with dimensions 800 μm.
3. The results confirm absorption capacity of rubber microparticle AGP4 at quasi-static test. It follows, that this application improves the mechanical properties. This is given by better distribution of rubber microparticles in the matrix, which was confirmed by SEM analyses.
4. The research points to the possibility of use waste to modify the adhesive bond properties, especially waste from worn-out tires in rubber powder form. This fact could lead to decreasing impact on the environment from tire waste. The use of the waste has also positive economical factor and could reduce the cost of the adhesive.

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