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Effect of rubber powder from waste tyre rubbers on mechanical properties of one-component polyurethane putty

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Abstract. The utilization of adhesives in technical practice is varied. Adhesives serve for a creation of strength bonds on the one hand, and on the other hand e.g. for cementing. The aim of the research is a modification of one-component polyurethane putty RPS 45 used in automotive industry to increase strength properties in an adhesive bond. An interaction between a filler in the form of rubber powder micro-particles and one-component polyurethane adhesive was investigated by means of SEM analysis. Sealing is a primary property of this putty. Sealing putties usually reach very small strength which can be increased by an admixture of the filler. In order to keep elastic properties, micro-particles of the rubber powder gained from tyre recycling process were used as the filler. An aspect of a loading speed of the adhesive bond is essential at the practical application at which the adhesive bond can be failed in adhesive or cohesive layers. The adhesive bond can be perceived in terms of its function as a complex of three layers, i.e. an adhesive bonded material, the interaction between the adhesive and the adhesive bonded material and the adhesive layer itself. There are often states in the practices when the adhesive bonds are exposed to the loading which can be either a static or a dynamic one. That is why the research is focused not only on the evaluation of the influence of the modification of the one-component polyurethane adhesive, but also on the influence of the loading speed of the adhesive bond. Tested speeds set on a universal testing machine Zwick/Roell Z150 were 2, 50 and 100 mm min^{-1}. The results of mechanical tests proved a positive influence of the filler on the strength σ_m higher by 42.68 ± 6.96% and the elongation at break ε_b higher by 12.2 ± 20.95%. On the contrary, the stress at yield σ_y was decreased.

Key words: Loading speed, particle filler, strength, stress at yield, elongation, SEM, recycling.

INTRODUCTION

The technology of adhesives is constantly in high demand. It enables bonding of diverse materials, creating light structures and complex constructions (Pohlit et al., 2008). Adhesive bonds are often applied in industries such as aircraft industry, car manufacturing and electric industry to decrease weight, the concentration of voltage and to facilitate manufacturing (Mancusi & Ascione, 2013).

For the matrix we used a polyurethane putty, which is used in the automotive industry and has excellent shock-absorbing properties. Polyurethanes belong to the group of polyesteramides. The experiment featured soft polyurethanes, which solidify thanks to air humidity on being expressed from a hermetically sealed tube (Ducháček, 2015). Putties in general have good elastic properties. However, they reach very small strengths. The subject of study is increasing the strength of polyurethane putty with a filler made from rubber powder extracted from tyres trough the recycling process.

Rubber granules can be used as fillers in composite materials with various matrix basis (Sienkiewicz et al., 2017). It is assumed that the rubber particle acts as an absorbing 'toughening' processes (Mona, et al., 2015).

The dynamic increase of used tyre waste is a serious environmental issue. Recent news points to a significant progress in tyre recycling. This means that tyres no longer pose a threat as hazardous waste but an environmentally friendly source where the extracted granulation product can be used to make new polymeric composites. (Sienkiewicz et al., 2017).

In order to preserve the elasticity, the rubber powder is a suitable modifier (Quan et al., 2018). Polymers are basic materials for creating the matrix for composites. Resilience and toughness of the polymeric matrix depends on the orientation of nanofibers in the polymer (Ekrem & Avci, 2018). As reinforcing stiffeners, the composites use continuous fibres but also various kinds of short reinforcement elements (Cho et al., 2006). In the course of research, the polyurethane matrix used rubber powder from recycled tyres as a reinforcing particle element.

The properties of the composite with reinforcement particle elements depend on the material but also on the volume ratio of the particle filler, the size of the particles and the homogeneousness of particle distribution in the volume and the adhesive properties between the matrix and the particles (Míšek, 2003). To understand the effect of particle size in the composite, the mechanical properties of the composite must be established (Cho et al., 2006). They are the tensile strength, stress at yield, and strain at strength. The relation between particle size and mechanical properties was studied by many authors (Knapníčková et al., 2014; Valášek & Müller, 2014; Müller, 2015). Studies showed that tensile strength of the polyester composite with glass balls increases with the decreasing size of the glass balls (Cho et al., 2006). The polymer matrix is generally of a lower rigidity than the inorganic particles, however, the toughness depends on the tension transfer between individual particles and the polymeric matrix (Shao-Yun et al., 2008).

The limiting factors for the strength of adhesive bonds are defects in adhesive caused by production process, air bubbles, foreign bodies, grease and dirt as well as generally insufficient preparation of the glued surfaces (Ribeiro et al., 2016). To ensure the strength of the adhesive bond, it is most important to treat the surface by e.g. sandblasting for bonding steel, titanium, titanium alloys, aluminium alloys, the polymer and the composite (Rudawska et al., 2016).

The aim of this research was to establish the kind of interaction between the filler in the form of rubber powder and the polyurethane putty and how this interaction affects the mechanical properties of the adhesive. Also, the relations between the filler particle size, the filler volume ratio, and the mechanical properties were the focus of this study.

MATERIALS AND METHODS

The subject of study was the modification of a single-component polyurethane putty RPS 45 with a filler of rubber powder from recycled tyres. The modification of the single-component polyurethane putty was studied while changing the concentration and grain size of the filler. Rubber powder was chosen to establish the relation between the microparticle size of the reinforcing elements and the mechanical properties. The rubber powder with maximum dimensions of 0–400 μm is labelled as AGP4 and the powder with maximum dimensions of 0–800 μm is labelled as AGP8.

The filler concentration in the polyurethane putty was 5, 10 and 15 wt.%. Adding the rubber microparticles created a composite adhesive with polyurethane basis. The effectiveness of tension transfer between microparticles was measured by SEM analysis and observing the tension curve during mechanical tension tests.

Adhesive bonds were created in accordance with ČSN EN 1465 (the equivalent of BS 1465), which describes testing the single-lap adhesive bonds. To examine the strength of the adhesive bond we used carbon steel S235J0 of thickness 1.5 ± 0.1 mm. The bonded material consisted of two test bodies with dimensions of 100 x 25 mm and the modified putty was applied creating a single-lap adhesive bond at length of approx. 12.5 ± 0.25 mm. The single-lap bond was immediately weighted right after bonding for 12 hours to allow the glue to harden and solidify. The surface of test bodies was treated by sandblasting by Garnet MESH 80 (ČSN ISO 8501-1) and degreased in an acetone bath. Roughness parameters were measured with a portable profilometer Mitutoyo Surftest 301. A limit wavelength of the cut-off was set as 0.8 mm. The surface roughness at the grit blasted adhesive bonded material, i.e. structural carbon steel S235J0 was Ra = 1.76 ± 0.18 μm, Rz 11.22 ± 0.84 μm.

To establish the mechanical properties of the modified polyurethane putty, three factors were studied. They were the strength (σm), stress at yield (σy) and strain at strength (εb) with filler concentrations of 5, 10 and 15 wt.%. To find out about the relation of mechanical properties depending on the loading speed, these factors were measured at the speeds 2, 50 and 100 mm min^{-1}.

Adhesive bonds were tested by a static tensile test. Next, we evaluated the influence of concentration and grain size of the filler on the properties of the modified single-component polyurethane putty RPS 45. Mechanical tests (according to DIN EN 1465) were carried out on a universal measuring device for tensile testing Zwick/Roell Z150 with evaluation software testXpert II. The samples were tested in individual series. The types of disruptions of adhesive bonds were assessed according to ISO 10365.

To follow the interaction between the single-component polyurethane putty and the filler powder made from recycled tyres, was used a scanning electron microscope TESCAN MIRA 3 GMX (SEM), which examined the break surfaces and the interaction of the adhesive bond. The preparation of the test sample was done by gold-plating on the machine Quarum Q150R ES in argon vacuum. The samples were measured with a microscope TESCAN MIRA 3 GMX in nitrogen vacuum and the images were taken with acceleration voltage (HV) of 5.0 kV at a distance of approx. 15 mm.

The recorded values were processed by means of statistical analysis. To compare the recorded data statistically, we used Anova (Analysis Of Variance). By means of the Anova F-test we established p-values, which will make it possible to compare the differences of tested sets. The null hypothesis H_0 was set to a state when there is no statistically significant difference between the median values of the data sets being compared: $p > 0.05$

RESULTS AND DISCUSSION

The result of statistical testing is evident from Table 1. Filler concentration i.e. microparticles of rubber granulate, had significant influence on the strength and strain at strength of adhesive bonds. The strength of the adhesive bond was increased by adding filler up to 42.68 ± 6.96%. There was an increase on the strain at strength up to 12.2 ± 20.95%. The hypothesis H_0 was not confirmed i.e. is statistically significant difference between the strength and strain at strength of adhesive bond according to adhesive bonds with filler and without filler (matrix). Similar statistical results were obtained on stress at yield of tested variants AGP4–50 mm min^{-1}, AGP4–100 mm min^{-1}, AGP8–2 mm min^{-1} and AGP8-100 mm min^{-1} i.e. a significant influence of stress at yield was determined, depending on adhesive bonds with filler and without filler.

The stress at yield for adhesive bonds AGP4–2 mm min^{-1} and AGP8–50 mm min^{-1}, there was not statistically significant difference between adhesive bonds with filler and without filler i.e. the hypothesis H_0 was confirmed.

Table 1. The results of statistical testing for mechanical properties – parameter p (comparison of adhesive bond with no filler (matrix) and adhesive bond with filler concentrations 5–15 wt. % rubber powder)

Filler	Loading speed (mm min^{-1})	Strength σ_m (MPa)	Stress at yield σ_y (MPa)	Strain at strength ε_b (%)
AGP4	2	0.0000	0.5577	0.0000
	50	0.0000	0.0000	0.0000
	100	0.0004	0.0000	0.0000
AGP8	2	0.0000	0.0141	0.0000
	50	0.0002	0.0822	0.0001
	100	0.0015	0.0202	0.0000

Effect of the modification on the tensile strength is shown in Fig. 1 by the percentage difference between the strength of the adhesive bond without filler and adhesive bond with filler concentrations 5, 10 and 15 wt.% at loading speeds 2, 50 and 100 mm min^{-1}. The Fig. 1 shows that the highest increase in the tensile strength is found on adhesive bond with the filler concentration 10 wt.% AGP4 at loading speed 2 mm min^{-1} up to 42.68 ± 6.96%. The course of the stress points that tensile strength is horizontal at the filler concentration 5 and 10 w.% and decreases at the filler concentration 15 wt.%. From this it can be concluded that the filler concentration 15 wt.% of adhesive bond is approaching the critical volume concentration (Míšek, 2003).

The Fig. 1 shows that modification of adhesive has positive influence on the tensile strength with the filler concentrations 5, 10 and 15 wt.% AGP4 at loading speeds 2 and 50 mm min^{-1} and with the filler concentration 5 wt.% AGP4 at loading speed 100 mm min^{-1}. Positive influence with the filler concentrations 5, 10 and 15 wt. % AGP8 at loading speed 2 mm min^{-1} and with the filler concentrations 5, 10 wt.% AGP8 at loading speed 50 mm min^{-1}. This implies that the particle size affects the tensile strength i.e. decreasing filler particles increase the tensile strength. The influence on the increase in strength has a particle size filler 400 µm (AGP4) compared to a particle size filler 800 µm (AGP8). At loading speed 100 mm min^{-1} is a large drop in concentration 10 wt.% AGP8 – 17.17 ± 10.08% i.e. there is not significant increase at modification of adhesive bonds for loading speed 100 mm min^{-1} with filler AGP8.

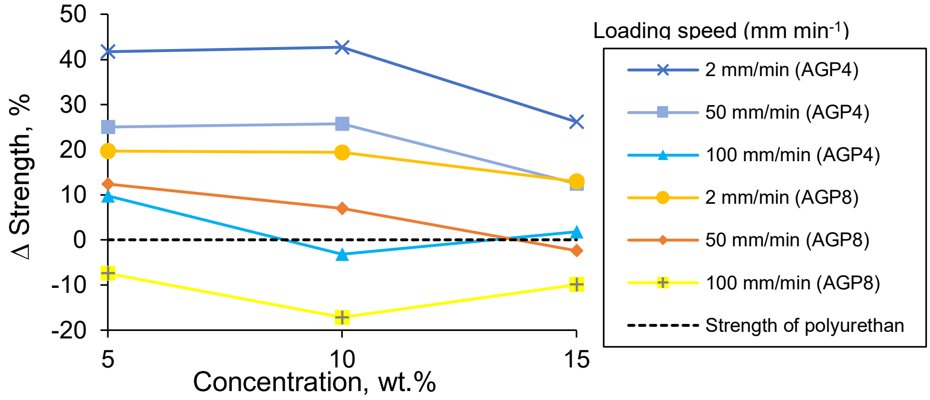

Figure 1. Percentage difference between strength of adhesive with no filler and strength of adhesive with 5, 10 and 15 wt.% concentration of filler AGP4, AGP8 on loading speed 2, 50 and 100 mm min^{-1}.

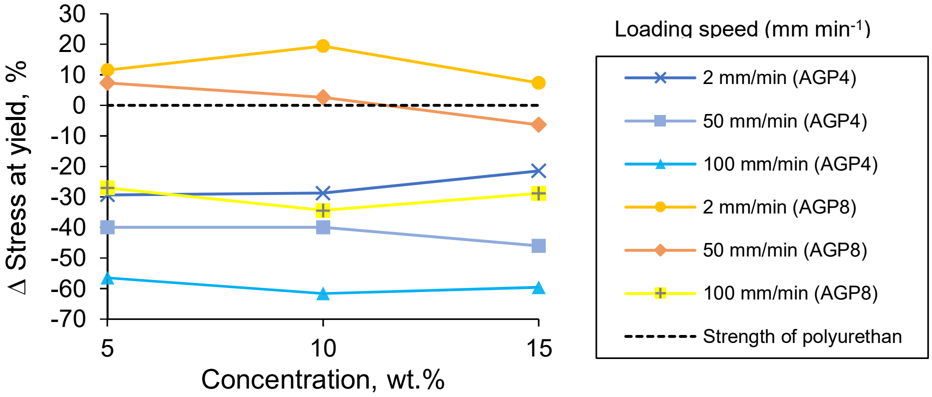

Figure 2. Percentage difference between stress at yield of adhesive with no filler and stress at yield of adhesive with 5, 10 and 15 wt.% concentration of filler AGP4, AGP8 on loading speed 2, 50 and 100 mm min^{-1}.

Effect of the modification on the stress at yield is shown on Fig. 2 by the percentage difference between the stress at yield of the adhesive bond without filler and adhesive bond with the filler concentrations 5, 10 and 15 wt.% at loading speeds 2, 50 and 100 mm min^{-1}. In general, modification of adhesive bond with filler AGP4 has negative influence on the stress at yield. The biggest drop on the stress at yield – 61.65 ± 6.99% is with the filler concentration 10 wt.% AGP4 at loading speed 100 mm min^{-1}. The stress at yield was increased with the filler concentrations 5, 10 and 15 wt.% AGP8 at loading speed 2 mm min^{-1} in maximum up to 19.37 ± 5.70%. This implies that particle size 0.8 mm (AGP8) has biggest influence on tress at yield at loading speed 2 mm min^{-1}.

Effect of modification on strain at strength is shown on Fig. 3 by the difference between strain at strength of adhesive bond without filler and adhesive bond with the filler concentrations 5, 10 and 15 wt.% at loading speeds 2, 50 and 100 mm min^{-1}. Fig. 3 shows that influence on strain at strength at filler AGP8 is without significant difference between concentrations. The influence on strain at strength has filler AGP8 with concentration 15 wt.% at loading speed 2 mm min^{-1} up to 3.3 ± 16.95%. The influence on strain at strength has filler AGP4 at loading speed 2 mm min^{-1} with concentration 15 wt.% at maximum increase up to 12.2 ± 20.95%. Particle size 400 μm (AGP4) will stay better in the matrix which increase strain at strength (Fig. 3.). Increase strain at strength is also given by flexibility segments of adhesive bond.

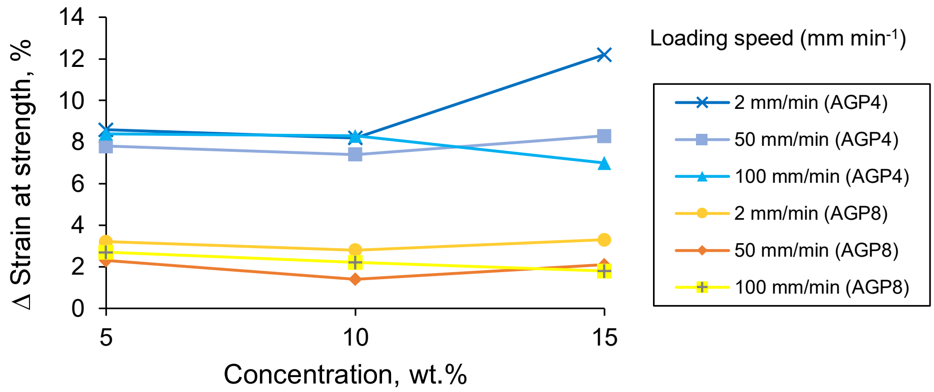

Figure 3. Percentage difference between strain at strength with no filler and strain at strength of adhesive with 5, 10 and 15 wt.% concentration of filler AGP4, AGP8 on loading speed 2, 50 and 100 mm min^{-1}.

After tensile test on fracture surface is possible to determine interaction between filler and polyurethane matrix with SEM analysis (Fig. 4, A, B). Fig. 4 Shows location with good wettability of particle filler and matrix i.e. polyurethane putty.

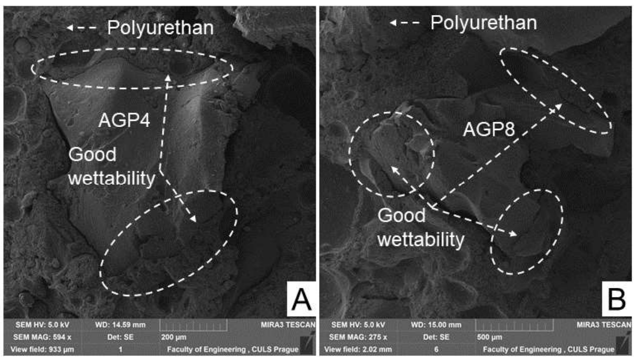

Figure 4. SEM images of fracture surface after strength test of adhesive bonds with filler AGP4 (secondary electrons): A: filler AGP4 (size of particle 0,4 mm) (MAG 594 x), B: filler AGP8 (size of particle 800 μm) (MAG 510 x).

This low interaction of wettability at the microparticle AGP and polyurethane (matrix) interface is not visible throughout the perimeter (Figs 5 and 6). It can be assumed that this is not a lower microparticle AGP wettability, but rather the deformation of the elastomeric microparticle AGP and delamination from polyurethane (matrix). Microparticle AGP and matrix have delamination in some locations i.e. producing of low interaction. If there was bad wettability, it would be low interaction around the perimeter at microparticle AGP and matrix.

Fig. 5 and Fig. 6 shows different distribution of AGP in matrix depending on the concentration of filler. Fig. 5C, Fig. 6C shows contacting the microparticles AGP with concentration 15 wt.% i.e. microparticle are not fully separated by the matrix. At concentration 10 wt.% (Fig. 5, C; Fig. 6, C.) is visible, that microparticle are fully separated by the matrix.

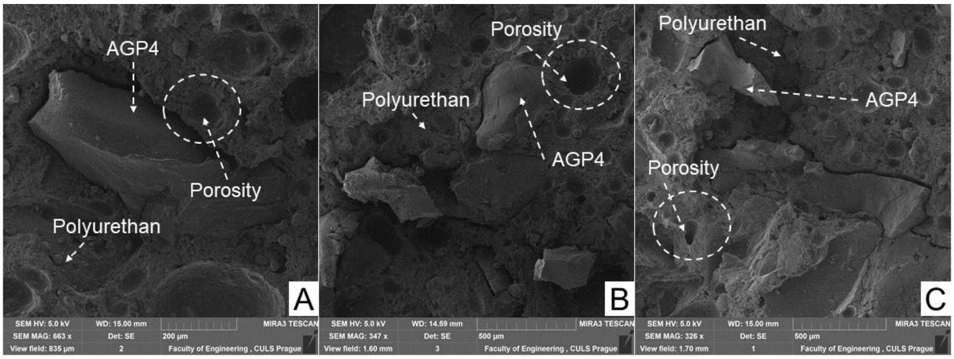

Figure 5. SEM images of fracture surface after tensile strength test of adhesive bonds (secondary electrons): A: Concentration 5 wt.% of filler AGP4 (MAG 663 x), B: Concentration 10 wt.% of filler AGP4 (MAG 347), C: Concentration 15 wt.% of filler AGP4 (MAG 326 x).

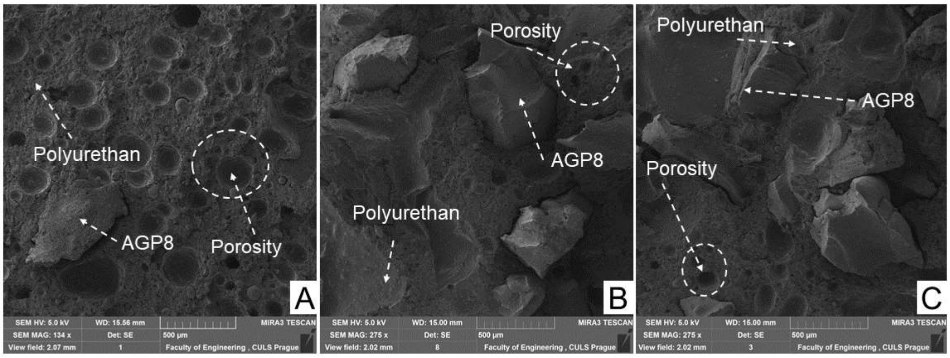

Figure 6. SEM images of fracture surface after tensile strength test of adhesive bonds (secondary electrons): A: Concentration 5 wt.% of filler AGP8 (MAG 134 x), B: Concentration 10 wt.% of filler AGP8 (MAG 275 x), C: Concentration 15 wt.% of filler AGP8 (MAG 275 x).

The research shows that increasing the loading speed increases strength, stress at yield and strain at strength. Maximal strength of adhesive bond is 2.129 ± 0.125 MPa with concentration 5 wt.% AGP4 at loading speed 100 mm min^{-1}. Maximal stress at yield is 0.49 ± 0.18 MPa without filler at loading speed 100 mm min^{-1}. Maximal strain at strength is 14.8% ± 20.9% with concentration 15 wt.% AGP4 at loading speed 100 mm min^{-1}. This implies that the highest value achieves the adhesive bond at loading speed 100 mm min^{-1}.

The most significant influence of modification on strength is up to 42.68 ± 6.96% with concentration 10% AGP4 at loading speed 2 mm min^{-1}. The stress at yield is most influenced by modification up to 19.37 ± 5.70% with concentration 10 wt.% AGP8 at loading speed 2 mm min^{-1}. The strain at strength is most influenced by modification up to 12.2 ± 20.95% with concentration 15 wt.% AGP4 at loading speed 2 mm min^{-1}. This implies that modification of one-component polyurethane putty has most influence at loading speed 2 mm min^{-1} with concentrations 10 and 15 wt.%. It can be agreed with the statement that waste tire rubbers are attractive group of materials due to their preparation only from rubber wastes what means sustainable and clean recycling (Sienkiewicz, 2017).

In the statistical results was confirmed the influence of filler on strength and strain at strength i.e. is statistically significant difference between the median values of strength and strain at strength, parameter: $p < 0.05$. Statistically significant difference was not confirmed on stress at yield with concentration AGP4–2 mm min^{-1}, parameter: $p = 0{,}5577$ and AGP8–50 mm min^{-1}, parameter: $p = 0{,}0822$. At rest variants is statistically significant difference on stress at yield, parameter: $p < 0.05$.

CONCLUSIONS

The modification of the single-component polyurethane putty in the form of a rubber powder is highly beneficial in terms of the strength and strain at strength. The highest increase of the strength is by 42.68 ± 6.96% at AGP4 filler with concentration 10 wt.% at the loading speed 2 mm min^{-1}. The strain at strength increased by 12.2 ± 20.95% at AGP4 concentration 15 wt.% at the loading speed 2 mm min^{-1}. The modification has its strongest impact on RPS 45 polyurethane putty at the loading speed 2 mm min^{-1}.

Fracture surface of the adhesive bond switched from the cohesive one to the adhesive one, which shows in the thin boarder layers between the bonded material and adhesive with the AGP4, AGP8 fillers. The results of the experiment proved a positive impact of adding the rubber AGP particles in the adhesive. That is why the following research will have to concentrate on the border between the bonded material and the adhesive to remove this thin boarder layer, i.e. for the adhesive bond not to show any adhesive type of damage.

The use of the rubber filler coming from recycled tyres has a positive impact on the environment. The research shows a way how to recycle the used tyres and thus how to relieve the environment of the burden. There is also the economical factor at play where using the recycled material decreases the price of the adhesive.

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