SZENT ISTVÁN UNIVERSITY

THE CONDITIONS OF ELASTOMER BONDING DURING MANUFACTURING HYBRID PARTS FOR THE AUTOMOTIVE INDUSTRY

Thesis of PhD work

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CONTENTS

LEGEND

Signage used in the study:

s_{min}: Minimum rotor torque [Nm]
s_{max}: Maximum rotor torque [Nm]
t_{02}: Time required for 20% vulcanization [min]
t_{09}: Time required for 90% vulcanization [min]
t_{s2}: Scorch time [min]
M_{1-5}: Tensile test specimens
R_a: Average surface roughness [μm]
R_y: Depth of asperity [μm]
R_z: Roughness height [μm]
S_v: Depth of valleys measured from median line [μm]
S_z: Roughness height 3D [μm]
S_a: Average surface roughness 3D [μm]
σ: Standard deviation
ω: Angular velocity [1/s]
m: Mass [kg]
F_t: Loading force [N]
k_f: Shaping strength [N/mm^2]
φ: Rate of deformation [%]
W: Deformation work [J]
D: Diameter [mm]
t: Time [s]
V: Volume [m^3]
P: Power [kW]
E: Elasticity modulus [N/mm^2]
h: Liquid column height [m]
T: Temperature [K]
T_c: Critical temperature [K]
g: Gravitational acceleration [m/s^2]
L: Length of extrudate [m]
ρ: Density [kg/ m^3]
G_L: Mass of extrudate of length L [kg]
A: Cross-section of tool orifice [m^2]
V_t: Tool feed volume [cm^3]
V_v: Change of volume per revolution [cm^3]

Material signage used in the study:

NR: natural caoutchouc
NBR: acrylonitrile – butadiene copolymer
CR: chloroprene rubber
EPDM: ethylene – propylene – diene terpolymer
SBR: butadiene – styrol copolimer
SI: silicone rubber
Fe-235: general steel
GN-50: steel shot
S-140: steel grain
C4C (EN10263): steel wire
R155OF1: natural caoutchouc based rubber mixture
EKF-24: corundum
1.2312: hot forming tool steel
1.2767: pre-hardened hot forming tool steel

1. INTRODUCTION, OBJECTIVES

Requirements for state-of-the-art machine components applied in industry stipulate that they are to work at high technical standards, without failures, and for a long time. This can only be achieved if each component built in is produced with the required technical parameters at a constant quality as demanded at planning already. My thesis work is intended to provide technological specifications on rubber and metal joints to rubber industry specialists based on scientific experiments, measurements and calculations and proven research results.

The objectives of my thesis work are as follows, in an itemized fashion:

1. To optimize the pre-treatment technology parameters of steelwork to be bound to a rubber body (type of spraying material, impact of surface roughness, influence of microtopography, etc.).

2. To describe the mathematical correlation between the pressure within the vulcanization mould and the rubber-metal bond force generated.

3. To present the connection between vulcanization speed and the tensile force to be measured on products.

4. To examine the storage life of caoutchouc mixtures and related quality changes.

5. To quantify the suitability of caoutchouc mixtures for rubber and metal bonding.

6. Component analytics survey of processes at the rubber and metal interface.

7. Possibilities of increasing the strength of crosslinking systems produced by vulcanization.

2. MATERIAL AND METHOD

In this chapter, procedures developed for examining rubber and metal connections are presented together with hardware and software tools to survey the pressure conditions of the mould hollow. Finally, model tests are presented in the system I examined.

2. 1. Impact of steelwork surface pre-treatment

Tests were intended to identify surface characteristics of steelwork in contact with rubber to maximize the rubber and metal bonding created. Model tests were performed first by EKF-24 quality corundum spreading material and an injection sprayer, then by applying GN 50 steel shot and a centrifugal sprayer. In respect of surfaces produced by interventions through various technologies and materials, the average surface roughness R_a and spatial surface characteristics S_v (distance between the lowest point measured on the tested surface of the steelwork and the median plane) were measured, and a 3D microtopography map was produced.
During manufacturing, the surface roughness of steelwork was kept at a constant value of 20 μm in order to be able to easily produce Sv=34 μm roughness – as optimized in the pre-treatment technology – by mechanical treatment afterwards. Cold heating combined with cold extrusion was selected for steelwork production technology because it was demonstrated by destruction tests and microsection surveys that this was the procedure to achieve the highest rate of shaping within the allowable deformation range.
As a first step, test specimens equipped galvanically with a zinc chromate layer were treated by EKF-24 corundum at 25º angle of incidence and 35 cm spraying distance. Spraying time was varied in 5 steps while pressure changes of the compressed air as well as the plane and spatial characteristics of the surface roughness produced were measured. Surfaces were also pre-treated by a centrifugal sprayer with test settings similar to the above, to be followed by adhesive treatment of the steelwork and specimen vulcanization. Afterwards they were subjected to tensile tests and tensile forces were measured.

2. 2. Testing for the impact of mould hollow pressure

Measuring instrument design

A GEFRAN type pressure sensor was connected to the tool, emitting 0-10 V analogue signals to a MOXA Logic E1240 signal receiver. The recording unit was a MODBUS TCP device to produce a structured text file. The software

applied transcribes results from TCP into a CSV format, enabling their handling in excel. The pressure measurement instrument required for measurements was designed expediently to be applicable in measurements regarding both the traditional compression technology and injection moulding technology as well, at the same time to enable useful volume to be changed within 13.5% in any period of the vulcanization cycle.
The rheological characteristic curve of the mixture applied in the production of test specimens was specified by a S 100 Monsanto rheometer; tensile strength and specific strain by a tensile test machine; to be followed by testing for mixture density.

Measurements by compression technology

Pressure conditions within the mould hollow were controlled by modifying the intial material quantity. The weight of the rubber mixture built in was measured by assay scales, to be followed by test vulcanization while recording tool temperature changes and the course of clamping pressure. Vulcanized specimens were subjected to tensile tests after 24 hours of rest and tensile forces were represented in function of the mould hollow pressure produced.

Injection moulding measurements

Mould hollow pressure mesurement tests were performed on an injection press as well. During the tests, injection pressure was constant but the pressure profile within the hollow was changed by an adjustment screw built in the mould. Various levels of pressure were produced this way, and after vulcanization – following 24 hours of rest – tensile forces were measured by a tensile test machine. Results were included in a table and evaluated according to the rules of mathematical statistics.

2. 3. Correlations between rheological features and the tensile force

The storage and use of rubber mixtures is discussed, among others, by national standard DIN 53500 and international standard ISO 1826. The different standards stipulate storage time at 4 weeks, but they do not discuss the impact of storage on the changes of rheological features, nor the impact of characteristic parameter changes (ts_2, t_{02}) of a given mixture on the strength of the rubber and metal bonding. In the course of my work, the mixture examined was stored for 21 weeks at a storage temperature of 20ºC and 40% humidity. In the course of storage, samples were taken from the basic material first on a weekly basis and subsequently on a biweekly basis, and vulcanization curves were produced by rheometer and evaluated. Tensile specimens were also produced from the samples, subjected to tensile tests.

2. 4. Component analytics survey

Electron microscopic stylus instrument measurements and characteristic X-ray emission tests were performed on account of morphological descriptions and to produce 1D and 2D lateral component maps in the environment of the boundary layer. The measurement was intended to verify whether the composition of the mixture is enriched by the components studied as referenced in the literature; and a further objective was to establish how the composition of sulphur changes numerically in surroundings of the boundary layer. The specimen was a cylindrical rubber and metal component of 25 mm diameter, cut into half longitudinally, whose metal component was Fe-235 general steel and its rubber component was natural caoutchouc-based mixture R155OF1, tested several times already; the contact area was treated by a Chemosil 211+411 combination binder. In order to perform tests, 2 mm thick pieces of 6x10 mm^2 were sawed out of the sample. The surface to be examined of the sample was washed by ethanol of analytical purity (Ethanol 96%) to remove scraps from sawing. The envisaged testing method also required that the surface to be examined of the sample should be coated by an approx. 10 nm thick gold layer as well.

2. 5. Profilometer measurements

Surface tests by stylus instrument (SEM) were performed for the purpose of 2D morphological testing; profilometer measurements were completed using a lateral scan method, in 3 and 5 mm length, to determine 1D depth parameters. As a complementary test, optical microscopic interferometry contrast images were produced.

3. RESULTS

3. 1. Impact of surface roughness characteristics on tensile strength

Results from the application of EKF-24 corundum

On the basis of the tests it was established that the impact of the rubber and metal connection on tensile strength is less characterized by average surface roughness ”R_a” than by microtopographic testing, whose progress clearly follows changes in tensile strength (Figure 1).

Table 1. Correlations between 2D surface roughness, spraying time, and tensile force

No.	Spray-ing time [s]	Ra [µm]	Ry [µm]	Rz [µm]	Rq [µm]	M 1	M 2	M 3	M 4	M 5	Tensile force average [N]	σ	2 σ
1	3	4.78	35.62	29.63	6.05	3184	3135	3304	3205	3200	3207	55	110
2	5	5.1	42.45	31	6.53	3100	3308	3420	3352	3300	3295	107	214
3	8	4.07	29.5	25.82	5.15	3422	3206	3316	3400	3305	3336	77	154
4	15	4.4	31.07	26.97	5.52	3588	3434	3434	3456	3409	3478	64	128
5	30	4.48	31.49	26.2	5.52	2963	3074	3213	3010	3000	3065	88	176

Table 2. Correlations between 3D surface roughness, spraying time, and tensile force

No.	Spray-ing time [s]	S_q [µm]	S_v [µm]	S_z [µm]	S_a [µm]	M 1	M 2	M 3	M 4	M 5	Tensile force average [N]	σ	2 σ
1	3	7	27	61	5.08	3184	3135	3304	3205	3200	3207	55	110
2	5	7	27.55	60.5	5.04	3100	3308	3420	3352	3300	3295	107	214
3	8	7	30.18	54.5	5.4	3422	3206	3316	3400	3305	3336	77	154
4	15	7	34.18	59.08	5.4	3588	3434	3434	3456	3409	3478	64	128
5	30	8	27.84	56.78	5.98	2963	3074	3213	3010	3000	3065	88	176

Results were evaluated as follows: a 5% error range was defined in the negative direction from the maximum value of the curve showing the course of the tensile force, which the tensile force generated should fall within. Then the S_v sections associated with the 5% sections of the curve were projected to the S_v

axis, wherefrom optimized microtopography indices could be read directly. Thereby a roughness range describing the surface (31 μm <Sv<34 μm) was identified where the bond force was at its maximum. On the basis of the tests I performed it can be stated that the tensile strength of cylindrical rubber products can be kept within an 5% error range by applying a R155OF1 caoutchouc mixture in the testing system in compliance with the steps and criteria of the optimized manufacturing technology presented. It should be noted that these results are valid only in case of plain plated steelwork and injection moulding.

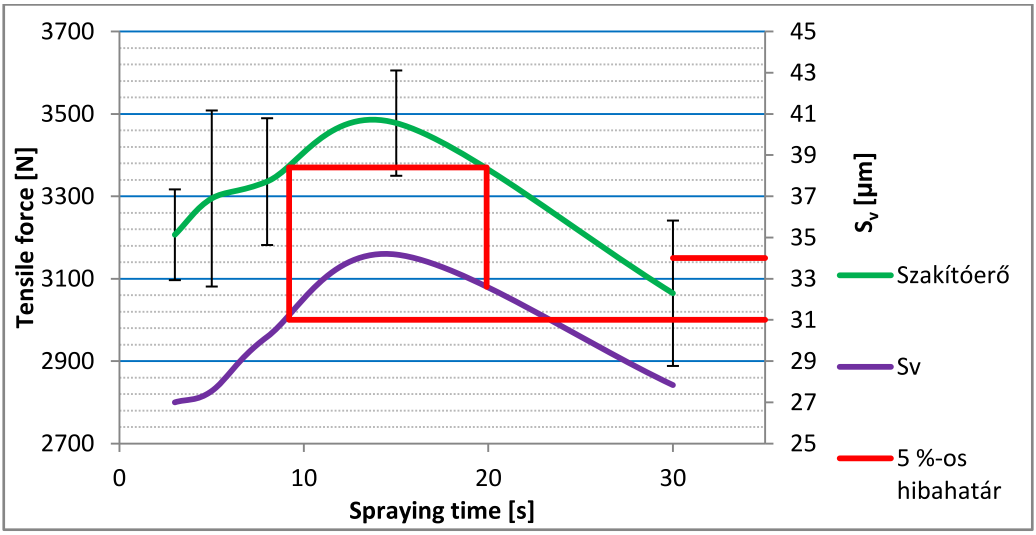

Figure 1. Interpretation of error limits for corundum as spraying material

Results from the application of GN-50 steel shot

My experiments were continued by changing metal pre-treatment technologies and mechanical spraying was performed by applying GN-50 steel grain in a closed centrifugal spraying cabin. In the course thereof, another 50 pieces of steelwork were treated, out of which 25 tensile specimens were vulcanized. A Mitutoyo measuring machine was used for specifying the 2D characteristics of the surface, with settings of DIN Pc5 1990 0.8x5. Measurement results are shown in Tables 3-4 and Figure 2. Based on the results it was stated, similarly to the series of measurements with corundum, that the impact of the rubber and metal connection on tensile strength is less characterized by average surface roughness ”R_a” than by microtopographic testing; therefore the 3D surface characteristics of sprayed surfaces were determined in case of steel grain spraying material as well, whose progress clearly follows changes in tensile strength (Figure 2).

Table 3. Correlations between 2D surface roughness, spraying time, and tensile force

No.	Spray-ing time [s]	Ra [µm]	Ry [µm]	Rz [µm]	Rq [µm]	M 1	M 2	M 3	M 4	M 5	Tensile strength average [N]	σ	2 σ
1	3	5.57	45.6	35.65	7.16	2500	2530	2670	2610	2450	2578	79	159
2	5	6.69	49.81	39.76	8.47	2750	2760	2700	2710	2800	2730	37	73
3	8	7.53	58.84	43.83	9.4	3550	3530	3400	3700	3670	3545	108	216
4	15	7.47	48.93	40.82	9.14	3670	3690	3200	3401	3480	3490	181	363
5	30	6.01	42.58	35.07	7.48	3600	3610	3560	3200	3400	3493	157	313

Table 4. Correlations between 3D surface roughness, spraying time, and tensile force

No.	Spray-ing time [s]	S_q [µm]	S_v [µm]	S_z [µm]	S_a [µm]	M 1	M 2	M 3	M 4	M 5	Tensile force average [N]	σ	2 σ
1	3	7.2	27.12	57	5.7	2500	2530	2670	2610	2450	2578	79	159
2	5	7.12	27.78	55	5.57	2750	2760	2700	2710	2800	2730	37	73
3	8	5.96	33.45	36.6	4.82	3550	3530	3400	3700	3670	3545	108	216
4	15	6.27	31.11	40.5	5.02	3670	3690	3200	3401	3480	3490	181	363
5	30	6.82	29.23	51.2	5.41	3600	3610	3560	3200	3400	3493	157	313

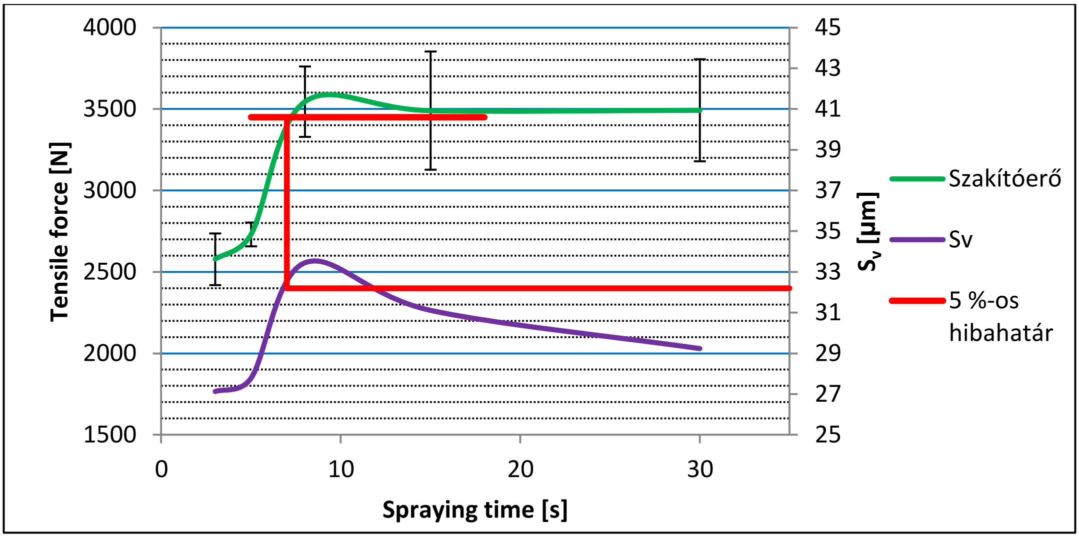

Figure 2. Evaluation of measurement results

Results were evaluated similarly to the previous section. It can be observed in Figure 2 that the numerical value of the S_v index number to characterize surface microtopography starts to decrease if spraying time is increased over a certain limit (9 s). Profilometer tests were performed to explain this phenomenon. Figure 2 shows the values associated with the 5% error limit of the curve representing the course of tensile force. The roughness range to describe the surface can be identified from the figure as 32 μm$<S_v<$34 μm, where the bond force is at its maximum. It can be stated that surface pre-treatment by EK-24 corundum and GN 50 steel grain yield identical results. The practical significance of this is that considerable productivity improvements can be achieved by applying the spraying times specified in the course of machinery operation in addition to the fact that energy and wages costs can be minimized by reducing cycle times.

3. 2. Profilometer test results

Profilometer measurements were completed using a lateral scan method in 3 and 5 mm length on mechanically pre-treated surfaces to determine 1D depth parameters. The significance of these measurements lies in the fact that the average surface roughness R_a became constant as the spraying time was increased, in spite of the fact that the treatment was continued. On the other hand, it can be observed that the S_v figure to characterize microtopography tended to decrease with the extension of spraying time. In the course of surface analysis by profilometry, it was intended to be verified whether the ”asperity features” of the surface really change as spraying time is increased. If it is so, it means that – in line with my assumption – the extension of spraying time over a certain limit will actually lead to a reduced tensile force. The results presented refer to measurements within 24 hours following treatment of Fe-235 steelwork by EKF-24 corundum at room temperature and 45% relative humidity.

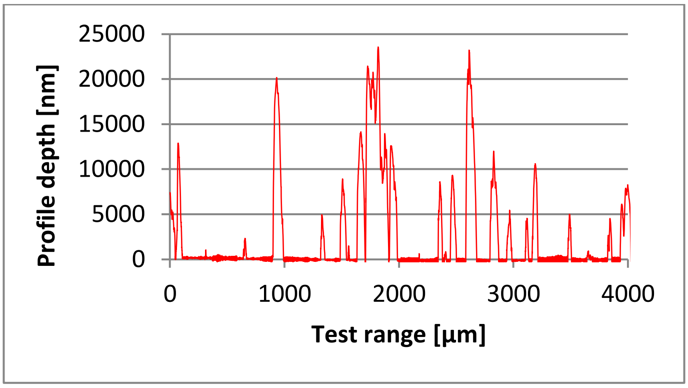

Figure 3. 8 s profile image as measured

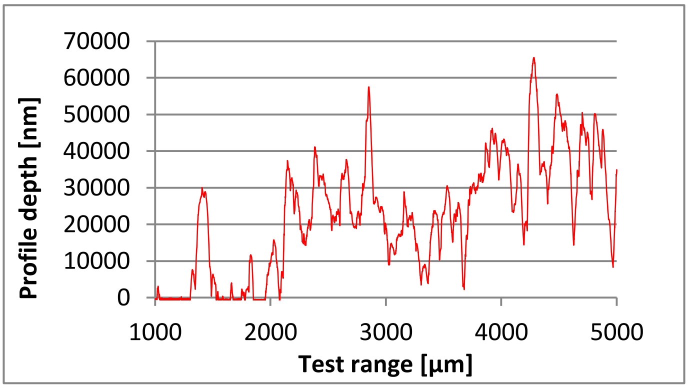

Figure 4. 15 s profile image as measured

Profilometer measurements are consistent with electron microscopic observations: lateral roughness frequency increases slightly – though not significantly in proportion to spraying time; however, the tendency of normal rms roughness frequency (perpendicular to the surface) is not clear-cut. Figures 3-4 show the sqared deviations of the scans of specimens treated for various lengths of time in a discretionally selected range. By studying the technological details of steelwork adhesive treatment and rubber coating, it is assumed that surface morphology changes consequent upon spraying can be associated with tensile strength through actions of forces resulting from the tensile force applied to the rubber and through internal structural changes. My initial assumption was verified by profilometric images as the largest distance of peaks and valleys can actually be detected in the case of surfaces treated for periods between 8 s and 15 s. In the knowledge thereof, correlations between 3D images and tensile strength can be explained. It can be observed that the surface of rupture is not the rubber and metal interface, giving rise to the assumption that rupture is determined by macroscopic correlation distances (of 0.1 to 1 mm order of magnitude) within the rubber layer. These are probably of thermodynamic nature and can be linked to the impact of heat – dissipated due to high degrees of mechanical stress – on mechanical properties. Tensile strength highly depends on temperature, which can also be influenced by the good thermal conductivity of the steelwork. The steelwork can stabilize the temperature of the surroundings of the boundary layer – with thickness thereof depending on the thermal conductivity of the boundary layer; in other words, the heat dissipated is carried away and the rupture will occur within the rubber layer. The reasons how the thermodynamic properties (heat dissipation, thermal conductivity, tensile strength versus temperature function) of the boundary layer and its surroundings are determined by surface roughness are not yet clear; in addition, potential structural changes during the application of the rubber coating should also be taken into consideration. Besides, the external physical parameters of tensile tests (e.g. temperature, rate of increase of tensile force), and their stability can also play an important part in measurements.

3. 3. Impact of mould hollow pressure on metal bonding

Results of pressure measurements by compression technology

In the course of this experiment, rubber bodies were vulcanized on the pieces of steelwork pre-treated for an optimum surface roughness, followed by measurements of the tensile force generated. Different pressure levels were generated in the vulcanization mould nest by charges of varying weights. Table 5 shows pressure levels in the nest caused by the clamping force in case of different rates of overfill and Figure 5 shows the course of pressure in time.

Table 5. Compression technology

Number	Rate of overfill	Weight of initial rubber mixture [g]	Pressure at t_{02} [bar]	Force [N]
1	**3**	**10.3**	50	1100

2	**10**	**11**	55	1670
3	**20**	**12**	60	2080
4	**35**	**13.5**	55	1700

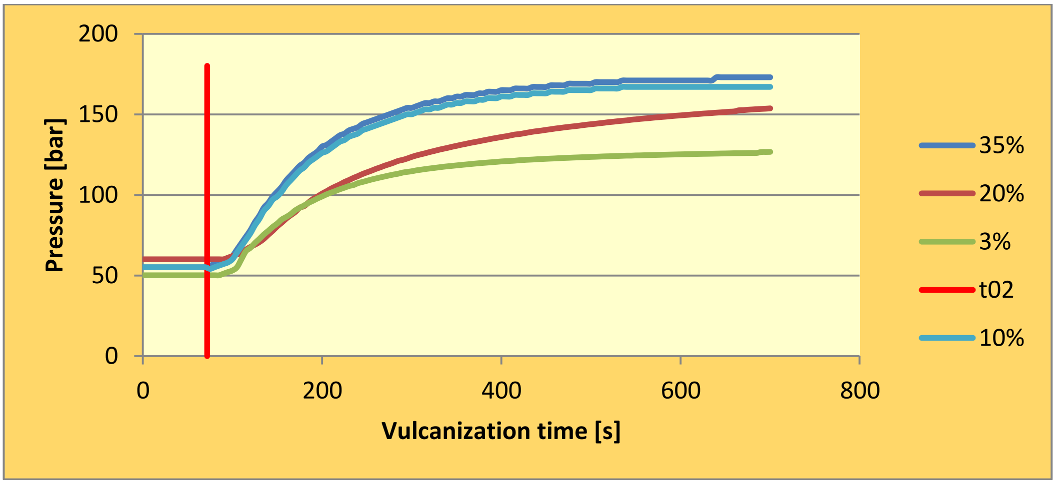

Figure 5. Pressure measured at t_{02} in case of compression technology

Results of pressure measurements in case of injection moulding

Table 6 shows pressure levels in the injection press of vulcanization at different experimental settings.

Table 6. Impact of mould hollow pressure on tensile strength

Mould pressure [bar],(t_{02})	Tensile force [N]	Tensile force [N]	Tensile force [N]	Tensile force average [N]	σ	2σ	Variance
70	2650	2956	3250	2952	300,02	600,04	90012
80	4330	3327	3152	3603	635	1270	403225
90	4263	3555	4364	4061	440	880	193600
100	3731	3960	4249	3980	260	519,16	67381
110	3973	3901	4366	4080	250	500	62500
115	4363	4003	4000	4122	208	416	43264

Figure 6 shows correlations between mould pressure measured at t_{02} and the tensile force generated.

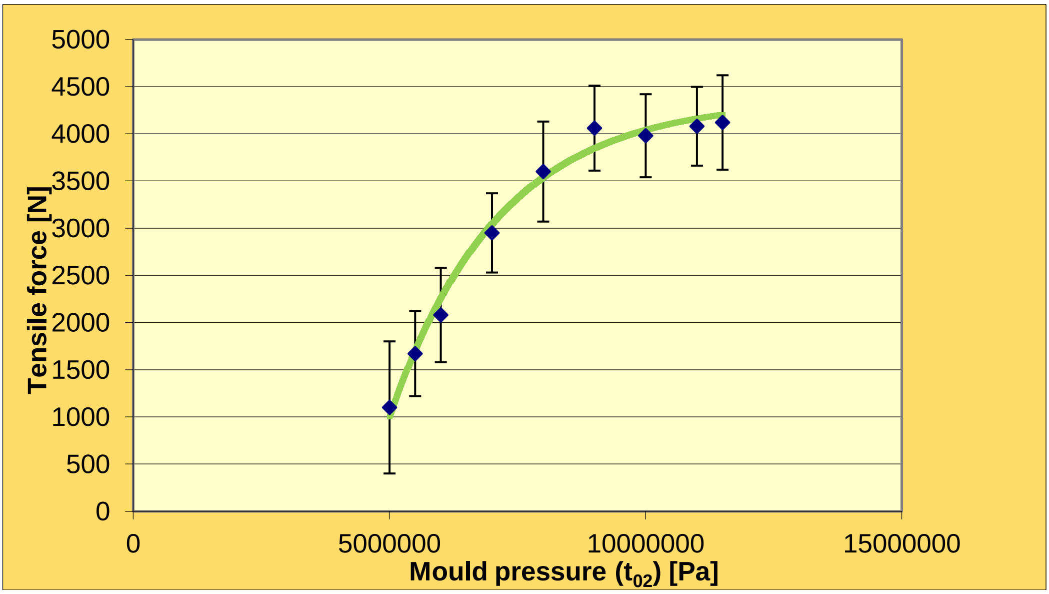

Figure 6. Correlations of initial mould pressure and tensile force

Verification of the correctness of the mathematical model

In order to verify my zero hypothesis, namely that this phenomenon is described by a saturation curve, it was put to the test by statistical methods. A statistical test was performed by using a test function. Appropriateness of the test function was declared on the basis of the test function value corresponding to the table. Decision therefor was made at a significance level *p=10%*.
The mathematical form of the saturation curve to describe the phenomenon is as follows:

$$f(x) = a \cdot (1 - e(c + b \cdot x)) \quad (1)$$

where:
- a,b,c represent parameters wothout any physical content;
- x means pressure.

3. 4. Impact of changes in rheological characteristics on bond strength

Key success factors to the success of rubber and metal bonding include not only properly treated steelwork, an appropriate rubber mixture, and adherence to the production technology, but other factors as well, such as the age of the rubber mixture, for instance. My experiments focussed on changes of certain investigated rheological features of the mixture by ageing and on the impact of changes in these values on the size of the tensile force generated.

Figure 7 shows the results in a graphic format.

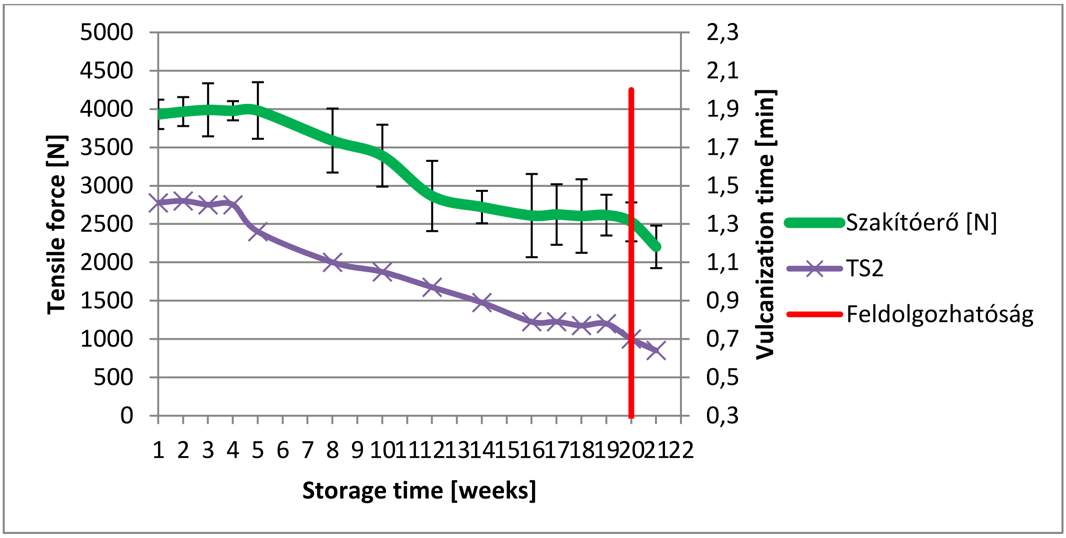

Figure 7. Changes of tensile force and ts_2 in function of storage time, at 20 °C

It can be stated as a result that the mixture can be stored without considerable reduction in strength for 4 weeks, as referenced in the standard. It is remarkable, however, that changes in the rheological feature indicated by ts_2 (scorch point) follows tensile force changes with good approximation.

3. 5. Component analytics survey of the rubber and metal boundary layer

A rubber and metal connection system depends on the simultaneous adequacy of several parameters, therefore processes in the boundary layer – that is, the interface of metal and adhesive and the interface of adhesive and rubber – must also be examined. To this end, one-dimensional component distributions perpendicular to the rubber and metal boundary layer were examined. The diagram produced by the X-ray equipment in the course of testing shows relative X-ray intensity on the vertical axis and various components examined on the horizontal axis. Based on the test results it was established that no material composition modifications are produced along the interface, therefore development experiments with nanofibers can be productive.

3. 6. Rubber spring tests

Modelling and testing rubber as a structural material poses a highly complex mathematical problem. Rubber industry testing is further complicated by the fact that measurement results highly depend on deformation speed, specimen shape, temperature, etc. For these reasons, different standards have been developed to determine nearly each of the characteristic features numerically, setting out the most important test parameters, respectively. Tensile stress and and strain tests are referenced by the DIN 53504 and ISO 37 standards. Two devices were used in the course of my work: a LLYOD LR30K insrument for static tests and an INSTRON device for dynamic heat chamber tests. Thermal tests were required because the machine component examined works in a broad temperature range in operational conditions. Negative temperatures were ensured by applying liquid nitrogen. For tests in the positive temperature range a heat chamber of electric heating was available for use.

Figure 8 and 9 show rubber spring test results. The test refers to the material qualities and geometry described in the experimental system presented by me.

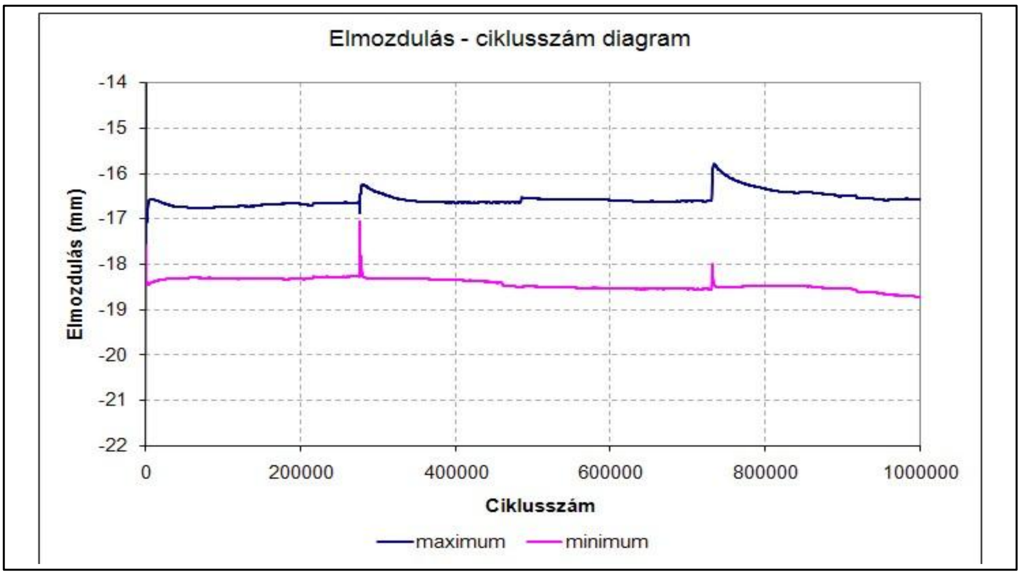

Figure 8. Displacement versus cycle number diagram

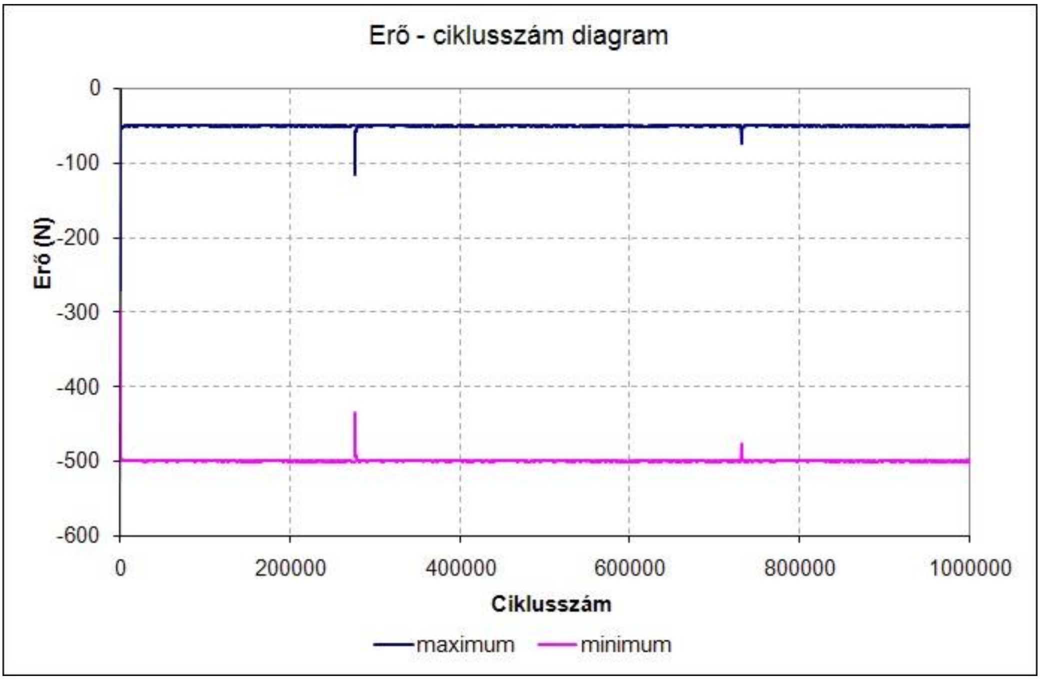

Figure 9. Force versus cycle number diagram

The two ”protrusions” in the diagrams are present because of liquid nitrogen cylinder replacement. It should be noted that cylinder replacement caused 15 minutes of interruption in the process of testing; however, the temperature did not change considerably in the heat insulated testing chamber in the meantime. With a view to the relatively large size of test specimens and therefore their significant thermal capacity, the final result of the experiment was not modified notably by the interruption. It can be established from the curves that the rubber springs produced in the course of an optimized production process during my work went through as many as 1 million fatigue cycles as expected during their lifetime without any damage even at -40 ºC. Figure 10 shows static hysteresis loops during dynamic fatigue at different fatigue cycles.

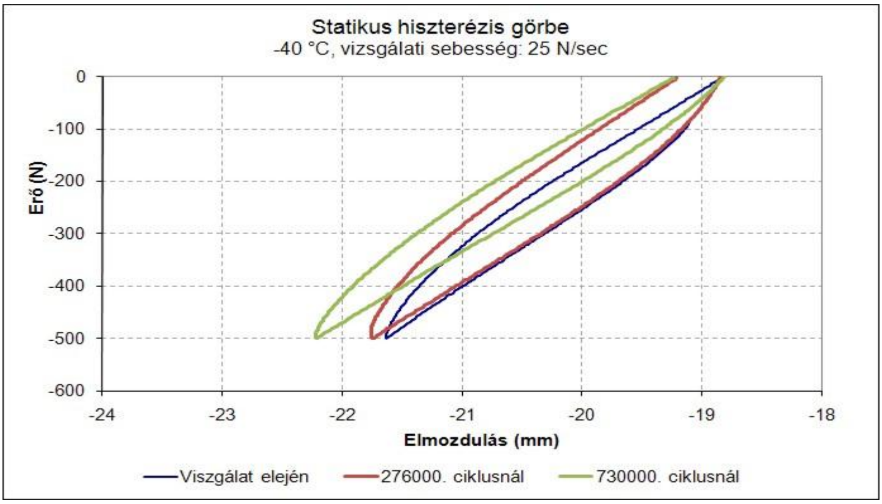

Figure 10. Static hysteresis loop in different states of fatigue

Following an analysis of hysteresis loops, it can be established that the rubber component got somewhat softened after the fatigue process, which can be explained by the partial rupture of cross bonds characteristic of crosslinking systems. However, this does not cause a problem of operation and as it could be observed, it does not significantly affect the metal bonding, either, since the tensile force reached 95% of the figure after production even after dynamic fatiguing in the heat chamber.

4. NEW SCIENTIFIC RESULTS

1. It was established by microtopographic analysis that the impact of the rubber and metal connection is not properly characterized by two-dimensional ”R_a” (average surface roughness). Therefore the spatial characteristics of sprayed surfaces pre-treated by GN 50 steel grain and by EKF-24 corundum, respectively, were specified at a 25º angle of incidence, and a 35 cm spraying distance. On the basis thereof it was established that the emerging adhesion strength of rubber and metal is connected to the spatial microtopography index ”S_v” of the steelwork (distance between the deepest point of the surface and the median plane). In respect of the rubber and metal bond strength examined, the optimum roughness range is 31 $\mu m < S_v < 34\ \mu m$.
   It was established on the basis of my experiments that in case of EN10263 steelwork, the rubber and metal bond strength cannot be associated with the type of spraying material. Bond strength is only affected by the spatial morphology of the surface shaped.

2. A complex measurement system was developed for determining the bond strength of the metal and rubber connection by which it was demonstrated in case of a real technological process that the mould pressure measured at 20% vulcanization of the rubber mixture (t_{02}) is linked to the strength of the bond produced at 155 ºC vulcanization temperature. The interconnection between the mould pressure measured at 20% vulcanization, considered as a rheological feature, and the tensile strength developed can be described by a 3-parameter saturation function in the form of $p_{fv}=a\bullet(1-e^{(c+b\bullet x)})$, where a, b, and c are parameters with no physical content and x is the pressure.
   It was demonstrated by tests using a measurement tool with variable volume in the course of the vulcanization cycle that rubber and metal adhesion is independent of the course of the pressure profile: it is only affected by mould pressure measured at t_{02}.
   A connection was established, with compression technology applied, between the weight of the billet to be placed in the vulcanization nest and the tensile force. The billet quantity placed in the mould can be increased effectively up to an excess 20% of mass weight; afterwards, flash formation in the parting plane will lead to unwanted pressure fluctuations, resulting in the uncertainty of tensile strength and an increased standard deviation thereof.

3. It was demonstrated by vulcanization experiments that in case of mixtures with various crosslinking speeds, the tensile strength is not independent of the vulcanization speed of the mixture in the range 0.7 min$<t_{s2}<$1.4 min. A linear correlation was found between the rheological index examined and the adhesion force developed after test vulcanization.

4. It was demonstrated by measurements that in accordance with the applicable standard requirements, the mixture can be stored for four weeks without suffering any change in quality. It was established that in case of the caoutchouc based mixture examined, at 20ºC of storage temperature the scorch point characterized by t_{s2} is in a nearly linear relationship with the bond strength produced. In the knowledge thereof, the usability of mixtures and the limits of their applicability can be identified by simple measurement and calculation methods.

5. It was established in the experimental system that the irregularity of $t_{s2}>0.7$ min is required but not sufficient for producing rubber and metal products.

6. Electron microscopic tests were applied to describe the surface of steelwork in contact with rubber, and characteristic X-ray emission measurements to track material structure changes in the surroundings of the boundary layer. Based on 1D and 2D lateral component maps, sulphur and chlorine were demonstrated to segregate considerably near the boundary layer. It was established on the basis of lateral component maps that the maximum total sulphur content of mixtures suitable for developing rubber and metal bonding can be 4%.

7. In respect of the optimized production technology it was established that in the event of destruction produced by tensile tests the surface of rupture represents an internal contraction of the rubber layer and not of the rubber and metal interface. This is primarily of a thermodynamic nature, which can be associated with the impact of heat – dissipated due to high degrees of mechanical stress – on mechanical properties.

5. CONCLUSIONS AND PROPOSALS

In the course of my work, I have gathered a great deal of information on the behavior of caoutchouc mixtures and components with rubber and metal bonding woth a lot of benefits both in theory and practice. The technology of metal pre-treatment was quantified in the experimental system examined; this makes up for a deficiency in the special field concerned. Experiments were used to determine the function which produces a correlation between the pressure within the mould hollow and the tensile force developed. This is also an important result as in the knowledge thereof the manufacturing safety of rubber and metal products can be improved considerably and the standard deviation of the tensile strength of the bond established can be minimized. In the course of component analytics surveys, the characteristics and component composition of the bond zone were determined. In the knowledge thereof it was demonstrated why significant nanotechnology developments in the past decade had failed to yield results in the structural reinforcement of rubber products. Actually, inert carbon nanotubes cannot form chemical bonds with crosslinking structures made up of sulphur bridges connecting carbon chains, therefore there is no impact to increase tensile strength. Based on my results, I will conduct further promising research on which nanostructures are capable to establish chemical bonds with any of the components of the crosslinking structure described. Rubber industry companies make considerable financial sacrifices to determine the usability periods of caoutchouc mixtures stored. However, analyses widespread in practice do not provide correct correlations between lifetime and any of the mechanical properties produced. As the substance under discussion keeps on losing its quality features as time goes by, and as they are extremely influenced by storage conditions, it contitutes a great help for technicians to quantify the limits of usability. In my thesis, a correlation is presented whereby the rheological index indicated by ts_2 and named as scorch point correlates with the size of the tensile force of rubber and metal, developed in the course of production. The economic crisis of our days and the increasing market competition as a consequence thereof enforce all companies to optimize their production processes, to minimize scrap production, and to supply a numerical classification of basic material quality. This can only be achieved if there is a measurable parameter for each work process mentioned to qualify the subprocess concerned. The new scientific results defined in the course of my work are intended to provide a theoretical basis for this endeavor.

6. SUMMARY

At the start of my studies I wanted to answer the following question: How can the manufacturing safety of parts with metal-rubber bond used in the aviation industry be increased? To achieve this, I had designed experiments and measurements to examine the boundary surface between the rubber and metal components which are very different from each other in terms of physical features. I collected the data and then I evaluated them respecting the rules of mathematical statistics. During my work I used some operational measurement units; and I relied on not only the measurements of university institutions but also those of research institutes. For the measurement of mold cavity pressure, I developed a variable volume measurement tool. I connected a GEFRAN pressure sensor to this tool so that I could manage and process the results with the help of computer software.

When manufacturing rubber vibration absorbers or other rubber-metal parts in an industrial environment, rubber blend is bound to the metal part via applying a layer of chemically produced binding material. The process starts with degreasing the metal parts, followed by the mechanical preparation of the metal. This can be done using corundum or steel grits; depending on the material. Apart from coating the adhesives according to the correct technology, the strength of the binding is also dependent on the rubber blend being used. The binding abilities of the mixture are also determined by the hardness of the mixture as well as the type of elastomer used.

I analyzed the extent of mechanical preparation regarding metal parts with the help of spraying trials. I created different surface roughness values by using different spraying materials and different spraying times; calculating an average surface roughness; and then treating the metal parts with adhesives and vulcanizing the samples. Then I carried out a tensile test and measured the tear strengths. At the set-up of the experiment, I observed the references available from the literature (Pék, 2000).

I used the Kelvin model to model the rubber vibration absorber. During the measurements of the surface preparation, I sprayed the surface of the 23 mm diameter cold-formed Qst-37 metal parts (with M6x18 mm threaded rod) with corundum, and then I measured 2D and 3D surface properties on the samples and analyzed the micro-topography. Then I treated the samples with two-layered adhesive, and then I carried out trial vulcanization using an R155OF1 natural caoutchouc based rubber blend. After manufacturing, the samples were put through a static tear test, and then I showed the results in tables and charts.

The pressure measuring tool to be used for the measurements was planned to suit my purposes; so that it could be applied both at the traditional press technology and at injection molding, while making it possible that useful volume can be adjusted within the 13.5% range any time during the vulcanization cycle. First I used press technology, applying different volume overcharges at trial vulcanizations, while measuring changes of the pressure during the whole process. Then I started using injection molding with varying injection pressure, and then I evaluated the samples according to their tear strength. After evaluating the results I observed that although the final pressure is similar at both technologies, a remarkable difference can be seen at the beginning of the process. Finally, I wanted to find an answer to the following question (examining the technologies one by one now to make comparisons): How does the pressure at the cavity influence the strength of the bond at t02 which is considered the fundamental rheological property?

With the help of modified injection doses and injection pressures the mold cavity pressure also changed – by measuring this pressure I observed that tear strength is independent from the extent of overcharge; it is only dependent on the initial cavity pressure. The initial cavity pressure measured at t02 as typical rheological parameter and the resulting tear strength change according to the pfv=a•(1-e(c+b•x)) 3-parameter saturation function.

Rubber-to-metal bonding is dependent on the appropriateness of several parameters at the same time- This is why processes at the boundary layers (between the metal and the adhesive as well as between the adhesive and the rubber) also had to be observed. This was analytically clarified by observing one dimension element distribution perpendicularly recorded at the rubber-to-metal boundary layer.

The sample was a 25 mm diameter cylindrical rubber-metal part halved lengthwise. I took a sample with 60 mm2 area with 2 mm thickness for examination. To prepare the sample, I removed the sawdust via washing the piece with analytically clean (96%) ethanol. The method of examination also involved coating the surface of the sample with a layer of about 10 nm thick gold.

It was determined that element distributions at the environment between rubber and metal parts disclose limited information regarding manufacturing technology and/or aging processes (such as transport phenomena) – the primary reason for this is the roughness of the boundary environment at the cutting surface. This is also essential from a measurement technology point of view, as the scanning electron beam is statistically affected at the tear which leads to broader element distribution, so I examined two dimension element distributions in the environment between the rubber and metal part with the help of an electron microscope. Profilometer measurements supporting further surface analysis are consistent with electron microscope observations; the frequency of lateral roughness increases (although not significantly) together with spraying time. The tendency of normal (perpendicular) roughness, however, is not unequivocal.

The changes of surface morphology occurring because of spraying in relation to tensile strength can be linked to the forces and structural changes by the tensile strength on the rubber layer. It can be observed that at optimized manufacturing technology, the surface of tear is not the boundary between the metal and the rubber part which leads to the consequence that the attributes of tear are determined by macroscopic (0.1-1 mm) correlation distances. These are likely to be of thermodynamic nature and are related to the effects of heat dissipated due to significant mechanical stresses on mechanical properties. Tensile strength is highly dependent on which might also be influenced by good thermal conductivity of the metal part. The metal part might stabilize the environment of the changing thickness of the conductive boundary which means that the dissipated heat is conducted and tear takes place within the rubber layer. The way surface roughness determines the thermodynamic attributes (thermal dissipation, thermal conductivity, and tensile strength-temperature function) of the boundary and its environment is still not clear; and potential structural changes occurring when applying the rubber layer should also be examined. In addition both the external physical parameters of tear (such as temperature or the incremental speed of the tensile strength) and the stability are also very important factors of the measurement.

During the rheological examinations, I used the Monsanto S100 measuring tool at the rubber blend. I prepared a 40 kg sample of the blend, and I stored it in a 20 ºC warehouse. The first measurement took place on 6 March 2012 and then I cut out 1.6 kg of the sample every week, and I carried out rheological examinations and tear tests at the vulcanized samples. With the help of rheological and vulcanization measurements, I pointed out that when using blends of different curing speeds, the tear strength measured is not independent form the vulcanization speed of the blend in the ts2 = 0.7-1.4 min range, in case of the R1550F1 blend.

The results of experiments carried out on preparation of the metal parts clearly show that the Ra average surface roughness is not suitable for describing the strength of the rubber-to-metal bond. This is because no clear relation between the spraying time (and thus the variable surface roughness) and the strength of the bond can be shown. However, it is an important measurement result that there is a measurable parameter typical for the 3 dimension surface (Sv) whose changes can be related to the changes of the tear strength.

The curve observed in the mold cavity is similar to the Monsanto curves; the maximum pressure can be observed at full curing. In the light of the results, the strength scaling of the vulcanizing tools can be carried out safely. Pressure values are valid at pressings with 50 kN closing force and max. 5 min closing time.

The results of the element distribution analysis show that the chlorine is enriching on both sides of the border layer, and the quantity of the iron and carbon don't change significantly. The chlorine is enriching due to the evaporation of the binding material which is worth knowing so that we can specify the maximum permitted tool-opening timeframe, since if it is too long, then the evaporation goes into the atmosphere instead of the border layer, which is also weakening the bond. It would also be useful to examine the sulfur, silicon and sodium ratios in the future so that it could be determined whether further sulfur bridges form in the boundary layer, and how much polluting and additional materials will accumulate in the examined zone.

7. MOST IMPORTANT PUBLICATIONS RELATED TO THE THESIS

Reffered articels in foreign languages:

1. **Renner T.** – Pék L. (2011): Comparing strength properties of natural and synthetic rubber mixtures, Sustainable Construction and Design Volume 2, 2011, pp. 134-141. ISSN 2032-7471

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3. Barányi I. – **Renner T.** – Kalácska G. – Baets P. (2013): Influence of surface preparation on roughness parameters and tensile strength of steel/rubber bonded shock absorber parts, Applied Surfice Science, (under review)

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4. **Renner T.** – Pék L. (2009): Természetes és szintetikus kaucsukkeverékek szilárdsági tulajdonságainak összehasonlítása, Műanyag és Gumi 46/12, A9-A12 o. HU-ISSN 0027-2914

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6. **Renner T.** – Pék L. (2011): Gumi-fém kötés optimalizálása repülőgép-ipari hibrid alkatrészek gyártásánál, Műanyag és Gumi 48/12, 473-475 o. HU-ISSN 0027-2914