

Polymer Materials and Its Properties

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1. Introduction

The technological process of rubber blend preparation plays an important role in the product quality, and mainly in traffic security. Nevertheless, after more than two hundred years of tyre production, the technology of rubber blend mixing is still a current and intensively developed process. The principle of rubber blend preparation in mechanical mixing is implemented by screw mechanism and extrusion of blend manipulated in such way. The success of the whole technology depends on proper mechanical construction of the masticator's components for every mixture. Nowadays the polymer materials used in rubber or automotive industry are submitted to new research activities by the miscellaneous angle of vision. Of course the final purpose is to provide the best required properties. Tire as a composite imply a lot of materials which have quite disparate properties and are able to appear as unit – consequently they are up to required standard. For example in areas of safety characteristics as an (wet road holding, tire grip, stability), the achievement of high speeds, low power consumption (rolling resistance), low noise level, comfort, attractive design and the tendency of increase lifetime (abrasion resistance, ozone and heat ageing) of these products with a purpose of economical and protection the environment. The interest in polymer materials and its application rising, e.g. in Audi A6 there is represented mass percentage contribution of polymer materials nearly 14 % on the present.

2. Mixing aspects

There are common a lot of factors influence the final properties of article in manufacturing process. These baseline impacts occur in case of quality and kind of deliver chemicals, particle size, its concentration, particle morphology, its specific surface. Consequently these chemicals are mixing. The main base of rubber mixture is a caoutchouc, according as natural or synthetic. By caoutchouc relates the term of plasticizing – this represents the process of reduction the molecular length of caoutchouc and occur from the elastic state to the plastic state during this time. After the caoutchouc feeding into the masticator or calender (figure 1) occur to the heat generation and stress transmission on the polymer chains in consequence of frictional forces between the machine components and visco-elastic material.

Thus the caoutchouc plasticizing is mechanical – chemical process characterizing degrade of caoutchouc which leads to structure change and consequently change on mechanical and physical – chemical properties of caoutchouc.

Abnormal plasticizing is accompanied by bad mechanical properties of vulcanizates, decrease fatigue and ageing resistance. Process of plasticizing follows large noise in consequence the shear stress of caoutchouc masticated between rotors and mixing chamber wall.

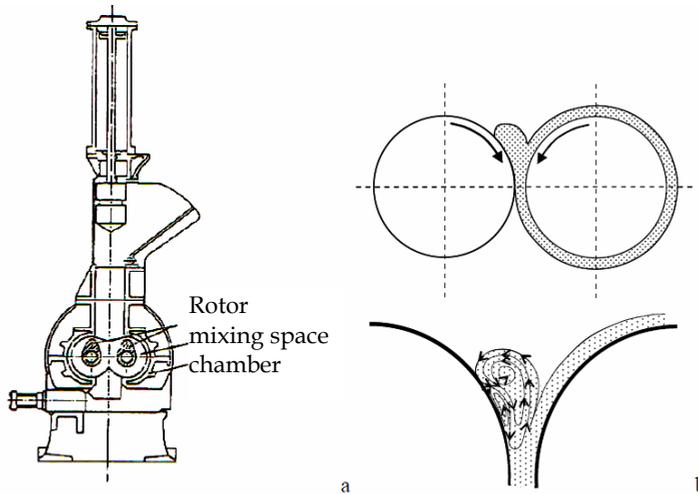


Fig. 1. Schema of masticator (a) and calender (b)

The efficiency of mechanical tearing of caoutchouc molecules decreases by temperature and consequently is process of plasticizing delayed. A rare behavior of temperature dependency of minimal efficiency is observed by temperature scope of 115 - 120 °C on figure 2. There is occurred decrease efficiency of mechanical tearing of molecules in case on the left side and rising effect of heat oxidizing degradation of polyisoprene chains in case of right side.

Maximal plasticizing efficiency is achieved by temperature of 55 °C or temperature over 140 °C by case of natural caoutchouc. Lower temperatures are used by calender plasticizing, higher temperatures are characterized for masticators.

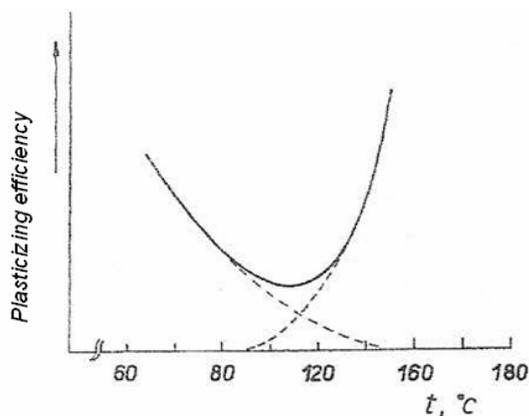


Fig. 2. Plasticizing efficiency temperature dependence

At higher temperatures occur to radical creation by bonds refracting which is necessary chemical stabilized. Long storage of this treated caoutchouc results in re-meshing and viscosity rising in consequence of un-stabilization. Chemical chain plasticizing and stabilization practically ends by carbon black feeding. There is occurred only physical chain reduction in consequence of re - mixing (reprocessing). Only natural caoutchouc is practically plasticizing. Synthetic caoutchouc and caoutchouc with constant viscosity isn't necessary to plasticize. Altogether the physical plasticizing is first mixing step of each mixture but this effect isn't as large as plasticizing of straight caoutchouc. The oils decrease the plasticizing effect in mixtures.

Temperature influence on plasticizing efficiency

The quality of caoutchouc plasticizing process in masticator affected following factors: dimensions of masticator, geometry of rotors, the dimension between rotor and chamber wall, state of machine filling, stress on the upper stop element, rotor speed, caoutchouc temperature, kind and concentration of plasticizing agent, time of plasticizing.

Mixture preparation and especially its mixing is one of important processes in rubber industry because following mixtures processing, products properties and producing economy largely dependence on mixtures quality.

Besides caoutchouc rubber mixture contains next approximately 10 chemicals (additions), table 1. Each chemical has specific role and therefore mixing purpose must provide the best homogeneity of mixture (most uniform distribution of chemicals in the whole caoutchouc mixture).

Compound of mixture	PHR *
Elastomers - natural and synthetic caoutchouc, respectively their ratio	100
Fillers - active and inactive	0 - 200
Softeners	0 - 40
Activators of vulcanizing	0 - 40
Stabilizers - antioxidants, antiozonants a protective wax	0 - 9
Vulcanizing agents	0,3 - 50
Accelerators of vulcanizing	0,3 - 4
Assistant rubber additives - plastic and adhesive agents	0 - 10

* PHR - parts per hundred rubbers (means elastomers - caoutchouc)

Table 1. Standard recipe for rubber mixture

After the caoutchouc plasticizing is coming the next step - blending - together the plasticizing there is a preliminary step of mixing where are the separate additions (caoutchouc and fillers) moulded by rotors or calender into a coherent mass. The blending action is described as a carbon black wetting by caoutchouc together an air voids expelling which was internally incorporated along with chemicals. Before blending process with powder fillers occur to a large deformation of caoutchouc follow by bond chain tearing (plasticizing). This conditioned material is able to flow in the chamber of masticator during all the mixing process round. The process of blending has two parallel mechanisms. Primarily occurs to caoutchouc formation follow by its surface rising with consecutive filler wetting by caoutchouc matrix. In the second mechanism is caoutchouc sharply deformed in consequence of bonds tearing, during which time occurred to transmission of tearing forces on adjacent chains. Bonds tearing allow rapid agglomerates coating by caoutchouc.

During the initializing stage of carbon black blending process in consequence of high shear stress created in masticator chamber thereafter of polymer pressure which coated the agglomerates are these smashed. Separate agglomerates are air filled by creation of weakly, partly composites. Caoutchouc is gradually embossed to agglomerates what causes air elimination.

The progressive carbon black wetting by polymer can be observed in case of machinery indirectly as an immediate loss of power the engine which specifies shear stress between mixture and rotor. Where this time period is the time of carbon black incorporation (so called the incorporation time - BIT).

On macroscopic scale the dispersion of filler into a polymer matrix shows the following stages:

- The filler smears into striations following the deformation pattern of the polymer
- Agglomerates up to 10 to 100 micrometer in size appear
- Agglomerates are continuously broken and aggregates with an average size of 100 nanometers till 0.5 micrometers appear
- Smaller aggregates and primary particles appear on the expense of larger aggregates and agglomerates

Figure 3 illustrates the transition from large agglomerates into smaller aggregates and primary particles, and gives an indication of their dimensions.

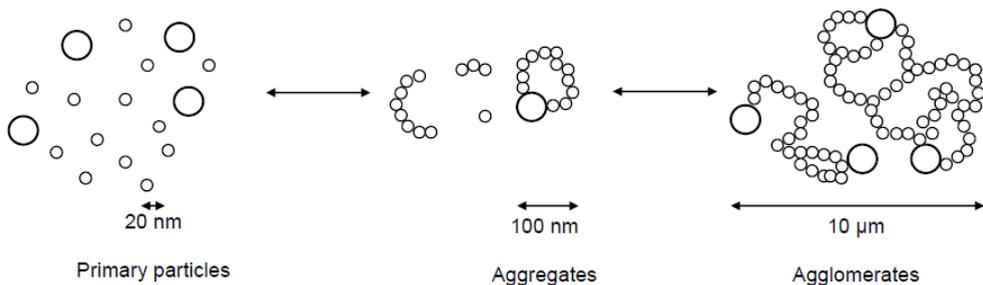


Fig. 3. The filler aggregation and dispersion

Based on these phenomena, Yoshida described mixing as a three step process: transposition, insertion and breaking of the disperse system. During transposition the system is subjected to stretching deformation by shearing forces, which increases the interface between the disperse phase and the matrix, and results in a gradual insertion of the disperse phase into the matrix. The particles of the dispersed phase are disrupted by shearing forces, and the size of agglomerates and aggregates is reduced. The degree to which the filler finally has to be dispersed depends on the quality requirements of the compound: the higher the degree of dispersion, the better the properties. But there is a lower limit to the aggregate size as the properties deteriorate with very small aggregate sizes and an increasing amount of primary particles.

A more refined model of dispersive mixing separates the process into four different steps:

- Incorporation
- Plasticization
- Dispersion
- Distribution

In the initial stages of mixing before incorporation starts, two processes take place: The first process involves large deformations and subsequent relaxation of rubber domains, during which filler aggregates are sandwiched between rubber layers. The second mechanism is based on the disintegration of the rubber into small particles, which are blended with the filler agglomerates and finally seal them inside.

Incorporation

The incorporation of the filler is subdivided into two phases: formation of a rubber shell around the filler particles followed by filling up the voids within the filler agglomerates, in other words between the filler aggregates. It includes a subdivision step: breaking of large agglomerates into smaller entities.

Mastication and plasticization

Mastication and plasticization take place during the whole mixing process and result in a change of the rheological properties of the compound, especially a viscosity decrease of the polymer matrix by degradation of the elastomer chains. Figure 4 gives a schematic view of the viscosity changes during mixing and the contributions of temperature increase and polymer breakdown to the viscosity decrease.

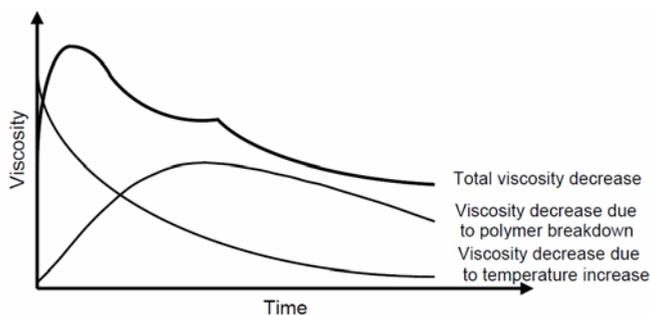


Fig. 4. Contributions of polymer breakdown and temperature increase to the viscosity decrease

Dispersion

At the end of the incorporation stage the majority of the filler is present as agglomerates. They act as large, rigid particles, whose effective volume is higher than that of the filler alone due to rubber trapped inside the filler voids and the rubber immobilized on the surface. The bound and occluded rubber increases the rate of dispersive mixing by increasing the effective radii of the filler particles: larger effective radii lead to higher stress during mixing. The filler agglomerates are successively broken to their ultimate size, mainly by shear stress. Parallel with the reduction of the agglomerate size the interface between the matrix and the filler is increased, and the filler particles are distributed homogeneously throughout the rubber matrix. When the filler agglomerates decrease in size, the occluded rubber concentration is reduced. The viscosity of the compound decreases and finally reaches a plateau region. In general, the average particle size reaches a minimum value and a further energy input does not result in a reduction of the size of the filler aggregates any more, as the mixing and dispersion efficiency is decreasing with reduced viscosity of the compound.

Distribution

In the distributive mixing step particles are spread homogeneously throughout the polymer matrix without changing their size and physical appearance. The thermodynamic driving force for this process is the entropy increase of the blend.

Figure 5 illustrates the different mixing stages with respect to filler subdivision, incorporation, dispersion and distribution.

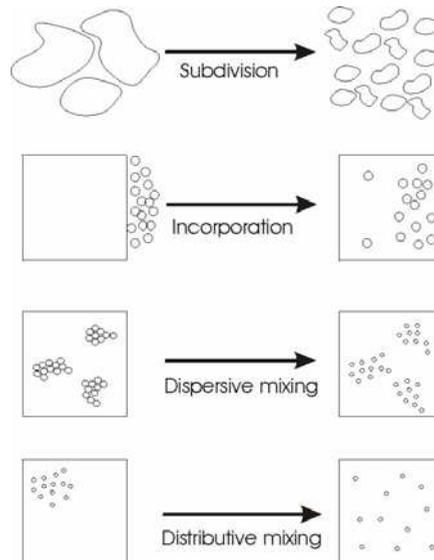


Fig. 5. Illustration of the different mixing stages for filler-polymer systems

An optimal dispersion is one that evenly distributes carbon black throughout the polymer down to the smallest carbon black unit, the aggregates. A poorer dispersion results in larger agglomerates, figure 6.

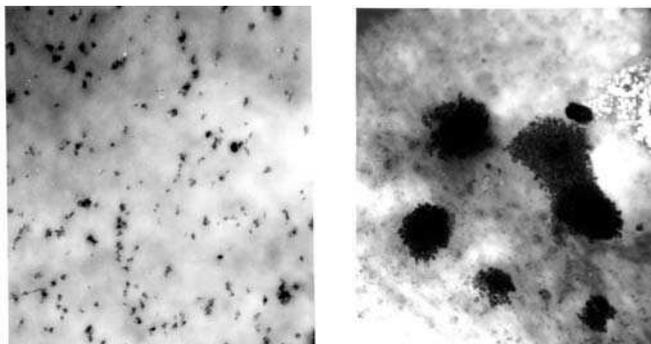


Fig. 6. Scheme of aggregates and agglomerates

The stage of dispersion characterized the process efficiency demands the higher energy consumption than blending process. Generally the dispersion stage is evaluated in

according to methodic of CABOT Company. By using of this methodic is possibly to determine the quantify of un-dispersed carbon black and following particle size is possible to merge the mixture into six different dispersion qualities accordance to figure 7.

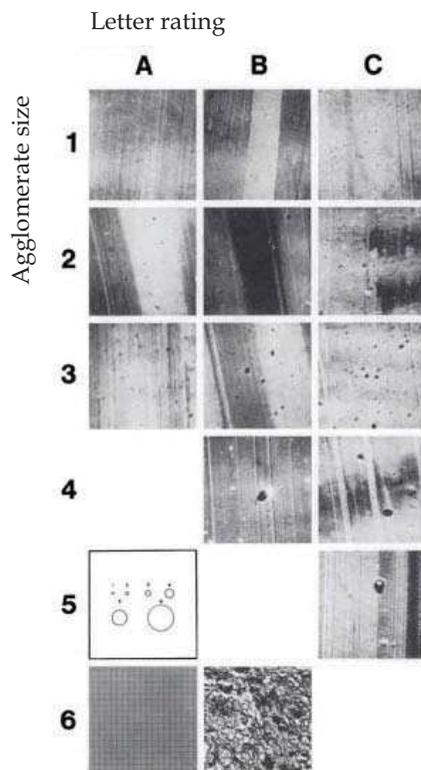


Fig. 7. Quality ranking of dispersion

The behavior of energy consumption the masticator is characterized by two marked maximums. The first maximum is created by caoutchouc feeding and ram down mixing. The second is characterized by fillers feeding (carbon black or white fillers). First peak relates by caoutchouc tearing and raising the active surface, the second marked the agglomerates creation of bond caoutchouc - filler. By sequential agglomerates smashing, the energy consumption decrease and the stage of filler dispersion accrue (mixing uniformity of primarily units). The mixture properties are changed by increased filler dispersion. We can allege that Mooney viscosity decrease by improved filler dispersion. Dispersion filler have different chemical contain, morphology (shape), density, color, hardness, specific surface and other physical - mechanical properties. The morphology of dispersion fillers can be regular (spherical, fibrous, platy) or irregularly, figure 8.

On behalf of observing purposes the mixing process were created various models studies which are able to ordered stage dispersion in rubber mixture e.g. through the particle flow in masticator. Similarly rotor design, slit dimension and chamber profile affected the mixing process and therefore these parameters are optimizes by producers.

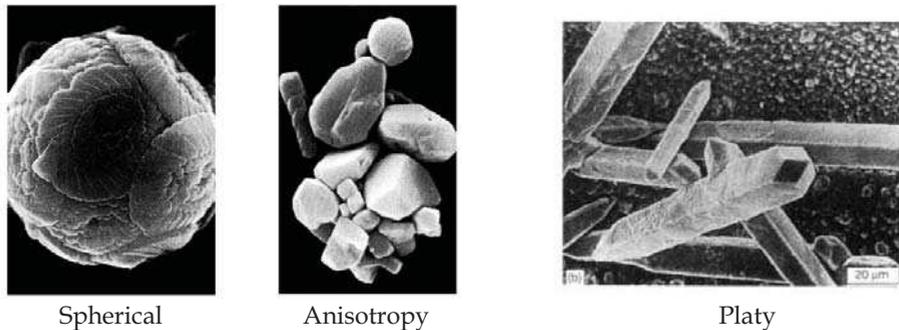


Fig. 8. The particle shape of dispersive fillers

Last step inducing the mixing process is the homogenization and viscosity reduction. For a good uniformity is necessary excellent filler distribution in the whole volume of mixture. This effect is possibly to achieve by becomingly processed mixing settlement together the time step of particular components feeding.

For the first degree preparation of mixture (without the vulcanizing agents) are apply two ways of mixing:

- Conventional,
- Upside - down.

By using of a conventional mixing occurs to filler incorporation into caoutchouc matrix at first. Mixing time is longer and follows to temperature increase during mixing. The final temperature can reach the value of 160°C. Owing to the achievement of high stage of filler homogenization and consecutive achievement of necessary processed properties are feeding oils in the final mixing phase.

In order to dispersive degree increase together homogeneity improvement are used so called processing additives (PA) in manufacturing process. At the same time these additives minimize the energy state of process. However is possibly to feed PA only in the first degree of mixing before fillers feeding. The processing additives also decrease viscosity of mixture, but the efficiency isn't the case of softeners. To achievement of a minimal tolerance in case of viscosity is important for the next processing operations - e.g. extrusion, calandering.

The UPSIDE-DOWN method of mixing uses the reverse practice and there is realize by high feeding of softeners and big particles of fillers. Primarily are feeding the fillers, then are mixed softeners and last chemicals added into masticator are caoutchouc.

However this method isn't very useful for the mixtures includes high-activated fillers (high structural carbon black, active SiO₂) or mixtures the high contains of soft mineral filler and oil together polymer with a high viscosity.

The second mixing stage is characterized by vulcanizing agents mixing off. Time of its adequate dispersion and homogeneity achievement considering physical properties is shorter than mixture preparation in the first stage. The maximal temperature for finishing of mixing process is much below (max. 120 °C) owing to the possibly reaction of sulphur with caoutchouc. The decrease of viscosity is not so high than the first mixing stage.

Besides the vulcanizing agents is convenient to adding the vulcanization inhibitors and retarders in the second stage of mixing process needs for consequently repeated processes linked to mixture warming - profile extruding, multi calandering, returnable wastes

processing. The progressive methods enable mixing of the first and second stage in the same line equipment.

Figure 9 shows a generalized torque-time profile of a mixing cycle for a carbon black compound, which is characterized by two torque maxima. The first torque maximum corresponds to the point when all ingredients so far added to the compound are forced into the mixing chamber and the ram reaches its final position. Time and height of the maximum depend on the composition of the compound, the fill factor of the mixing chamber, the activity and structure of the filler as well as the bound rubber fraction. The region between the start of the mixing cycle and the first minimum is the region, in which mainly mastication of the polymer takes place and dispersion starts. In the next zone dispersion and distribution of the additives including the filler occurs, and a second torque maximum is observed. This torque maximum corresponds to the incorporation of the filler: the agglomerates are wetted by the polymer, entrapped air is removed and the compound reaches its final density. Filler dispersion and polymer breakdown result in a fast torque decrease after the second peak down to a dispersion degree above 90%, and the kinetics can be described by a first order law: The rate of agglomerate breakdown is proportional to the concentration of the agglomerates. This period of steep torque reduction is followed by a period of a slower torque decrease, during which polymer breakdown and dispersion occur to a very limited degree, shearing is reduced and homogenization starts.

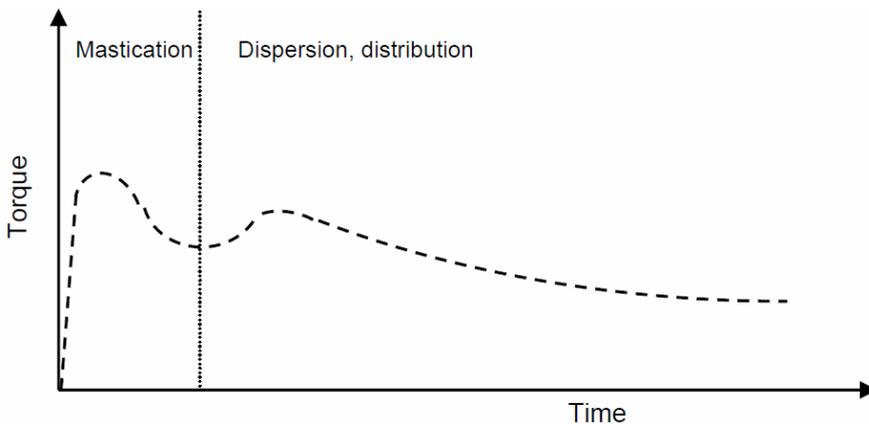


Fig. 9. Generalized torque-time profile of a mixing cycle

The carbon black construction of units and particles influences the final properties. Base particles have approximately sphere morphology, the furnace carbon black have a more complicated construction. Elementary sphere particles are coupled into big formations, called as primary structural aggregates which created chains or 3-D branched formations. The aggregation of elementary particles into big formations represents a "structure". Primary structure means the joining of basic particles into primary structural aggregates which are resistant to mechanically destruction. Primary structural aggregates may create bigger formations holding together by Van Der Waals forces, marked as secondary structure. This structure has low strength and easier mechanically destruction, especially by mixing of carbon black to caoutchouc matrix. The baseline particle contains the ligament of graphite layer. Accordingly the created aggregate and chain have compact, cohesive formation where are

occurred areas by concentric oriented plane layer; the outer layer have a high graphite contain than inner, there are oriented parallels to surface and have relatively few defects.

Interaction stage of caoutchouc and carbon black dependences on three factors:

- Size of interface between carbon black surface and caoutchouc, so called extensive factor. The interface between carbon black and caoutchouc equals to composition of specific surface carbon black and its concentration in mixture.
- Carbon black structure, so called geometric factor.
- Surface activity or intensive factor.

The size of particles and specific surface occurs; the softer are particles (i.e. the more is specific surface) the difficulty are mixed into a caoutchouc matrix; the viscosity of mixture increases, there accrue the energy consumption for processing, the mixtures are more heated and the safety processing time shorten. Particle size hasn't an important effect on the mixture precipitation but meaningful influence affected the mechanical properties of vulcanizates. By increasing of specific surface size (the decrease is particle size) are improving the properties detected by destructive examination: tensile strength, structure strength, wear resistance, hardness of vulcanizates increases. The modulus of vulcanizates hasn't directly dependency on particles size; the dynamical properties worsen by particle size decrease, the hysteresis increases.

Carbon black structure has more effect on prepared mixtures processing as a final vulcanizates properties. Otherwise the high structured carbon black are slower mixing into caoutchouc, but easier cause of good dispersion achievement and during mixing is created more joining caoutchouc. Viscosity of carbon black mixtures increase by growing structure and consequently the mixtures are more heated.

High structured carbon black increases the mixture anisotropy, mixtures are better extruding, they are less porous, the surface is smoother and profile edges are sharper. Similar behavior is characterized by calendering, mixtures filled high structured carbon black have smoother surface and smaller precipitation. Both causes induced due to structure influence and joining caoutchouc.

The structure of vulcanizates has a respectable effect on modulus; the influence is linked to surface activity. Strength and structural strength aren't considerably affecting by vulcanizates structure. A favorable effect is noted for wear resistance due to dispersion improvement. Hysteresis dependences on particles size and isn't markedly affected by structure.

The surface activity a factor influences besides vulcanizing process, composition of carbon black surface also electric conductivity of vulcanizates. By fewer oxygen compounds of carbon black, by softer particles and high structure the more conductive is filled vulcanizates.

When the convectional carbon black is treated high temperatures (approximately 2700 °C) there occur a big transferring of carbon atoms in the inert atmosphere. As a result is graphite carbon black with big crystalline planes on the surface. The surface energy of basic planes is low and small is also the reinforcement effect. For the smallest ordering and the highest surface energy was development so-called inverse carbon black. Compared to conventional carbon black have inverse carbon black more mutual traversing planes and edges which leads to surface energy increasing.

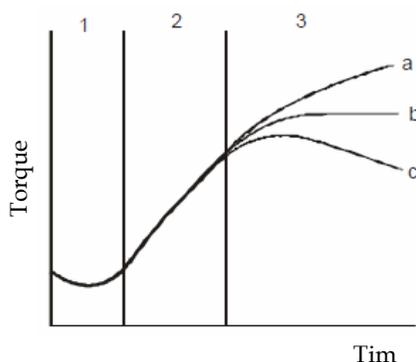
This special carbon black plays an important part by composition of treading mixtures with good adhesion and reduced rolling resistance.

Vulcanization

The next step influenced the quality of preparing mixture is vulcanizing (curing) process. This term is defined as a process when the temperature and vulcanizing system influence occur to the creation of chemical cross linked bonds among the caoutchouc chains. Throughout the vulcanization the linear chain structure is changed on 3-D during which times are markedly affected physical – mechanical properties and caoutchouc is converting from the plastic into the elastic state. The vulcanizates is characterized by its high reversible deformation by relatively low value of elasticity modulus due to creating cross linked structure. By cross linking mesh creation is limited the caoutchouc macromolecules mobility especially occurring the:

- Insolubility of cross linked polymer, just swelling vulcanizates.
- Polymer strength increase in the definite value by vulcanizing, by overrunning the optimal stage the strength decrease, but the modulus and hardness increase.
- Increasing vulcanizing degree improving the strain resistance and dynamic fatigue resistance. There is mended structural strength, i.e. resistance related with additional tearing of aborted sample.
- Low vulcanizates sensitivity on temperature changes.
- Elasticity and stiffness vulcanizates retaining in the wide temperature region.

Vulcanization course and its basic characteristics (scorch time, optimal vulcanization time, difference between maximum and minimum torsion moment, cure rate index, eventually reverse rate etc.) is most often evaluated on the basis of so called vulcanization curves measured on different types of rheometers, figure 10. There could be free sulphur content in a case of chemical changes, which decreases in vulcanization running. In case of physical – mechanical values there are strength, tensile elasticity modulus, plastic deformation, and swelling.



1- Scorch period, 2- fundamental meshing reaction, 3- structure changes created by meshing: a - marching, b - relaxation, c - reversion

Fig. 10. The schematically dependence of torque versus vulcanizing time

The induction period (scorch) characterized the time interval; there occur to very slowly reaction of vulcanizing agents with caoutchouc and other additives, during which time are created soluble caoutchouc intermediate products. This period length is important in term of vulcanizing system options for its safety mixture preparation and the next processing. Accordingly influences the processing economy and vulcanizates quality.

Fundamental meshing reaction is defined as a time interval of induction period and optimum of vulcanization. In this phase occurs to mesh creation and changes of physical – mechanical properties of caoutchouc mixtures by sequential transfer to vulcanizate.

The last area of vulcanization curve is characterized by other reactions than vulcanizing agent meshing and therefore practically occurs to no affection of the total meshing stage. This shape of vulcanizing curve dependences on used caoutchouc, vulcanizing system and vulcanizing temperature. The rate of meshing reaction is decreasing or aborting in this phase. These changes relate by the changes of cross links character. Relaxation is an area on vulcanizing curve where are no property changes in case of vulcanizate. The amount is presented by constant vulcanizate properties the heat stress for a term. Especially this property consequential from the vulcanizate thermal stability enables the achievement of optimal properties practically in all tire sections by automotive production. Reversion is the area of vulcanizing curve where occurs to the meshing density decrement and the vulcanizing properties become worsen.

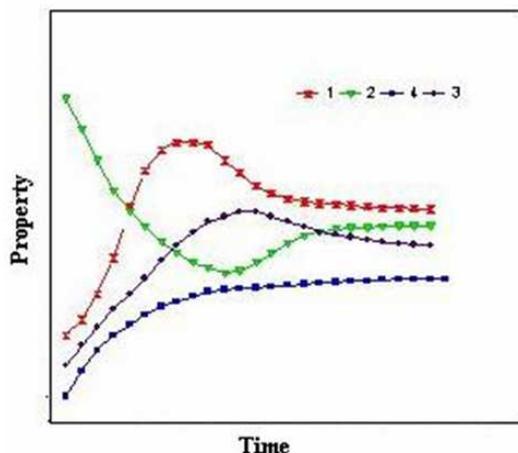
Marching is called the region area of vulcanizing curve where the meshing moderate increases; this type is vulcanization with a “walking” modulus. By vulcanizing process is used an ability to heat transformation (from metallic parts of vulcanizing press and mould, figure 11) from vulcanizing medium (steam, hot water) into tire. Consequently occur these phases in process of compression moulding and vulcanizing:

- Caoutchouc mixtures flow – the mixture must perfect flowing into the parts of compression mould in this processing phase during which time the air is removing through the air channels. The efficiency of moulding and vulcanizing process also affected on the flow rate of caoutchouc mixtures and rate of conversion to the meshing phase. Ideal processing representation in a mould characterized the faster mixture flowing into the parts of mould and follow transition into a meshing phase. By the very fast starting of meshing process is possibly risk in technical praxis where the imperfect mould filling can menace the flowing phase, whereas the cross link creation increase the viscosity and eliminate the flowing rate. Because there is very important to choose the correct rate and time of steps so can occurred a worsen visualization and total quality decline of a tire.
- The meshing of caoutchouc mixtures.
- Vulcanization finishing by achievement of the vulcanizing optimum time.



Fig. 11. Segment moulds

Some of vulcanizates properties reach optimum values even before vulcanization optimum achievement, figure 12.



1 - Tensile strength, 2 - Elongation at break, 3 - Hardness, 4 - Elasticity

Fig. 12. Change of some properties of rubbers compounds during vulcanization.

Modulus and the tensile strength at breaking are at low elongation proportional to their crosslink density ν , eventually reciprocal value of average molecular weight of rubber macromolecules segments between two cross-links M_c . Their relative connection is described by the relation:

$$\sigma = \frac{\rho}{M_c} RTA^*(\lambda - \lambda^{-2})$$

(σ is stress, λ is relative extension, R is gas constant, T is absolute temperature, A^* is the cross sectional area of the test specimen in non-deformable status).

At higher crosslink density tensile strength does not proportionally increase with the crosslink density increasing but after achievement of optimal value decreases.

Elongation at break is with the increasing of crosslink density lowered at first and then is asymptotically approached to minimum value. Vulcanizates hardness is by the vulcanization time increased like their crosslink density. The highest structural strength has soft under-vulcanized vulcanizate. After vulcanization optimum achievement this characteristic together with the time decreased. Elasticity change is similar to change of modulus. It is proportional to crosslink density and to relative elongation in all three coordinates. After vulcanization optimum achievement or at high content of cross-links between rubbers macromolecules can be with the vulcanization time decreased.

Figure 13 - the mechanism of vulcanization with sulfur, accelerators and activators') shows the variation of modulus for natural rubber (NR) and synthetic styrene butadiene rubber (SBR) during vulcanization. In both cases there is an induction period (called "scorch time") and an optimum vulcanization time, corresponding to the maximum value of the modulus. If vulcanization goes on, the modulus value decreases for NR, phenomenon which was

called reversion, while for synthetic elastomers, the modulus stays constant or gradually increases, phenomenon called overcure.

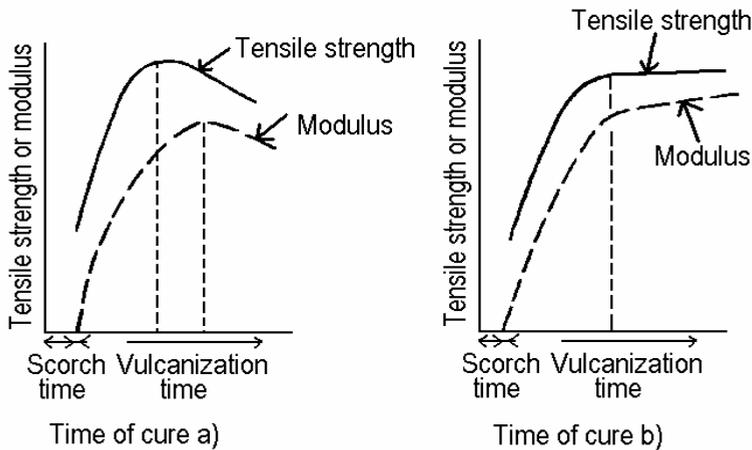


Fig. 13. Variation of tensile strength and modulus with vulcanization time: (a) NR; (b) SBR

The dependency of shear modulus G and temperature is shown in figure 14. Sulphur in position of vulcanizing agent is responsible and importantly factor for meshing of polymer chains, markedly affected also the temperature dependence of shear modulus. In case of un-vulcanized caoutchouc the shear modulus decreasing by temperature dependency, by rising of sulphur content over 0°C is constant or moderate increasing following sulphur content.

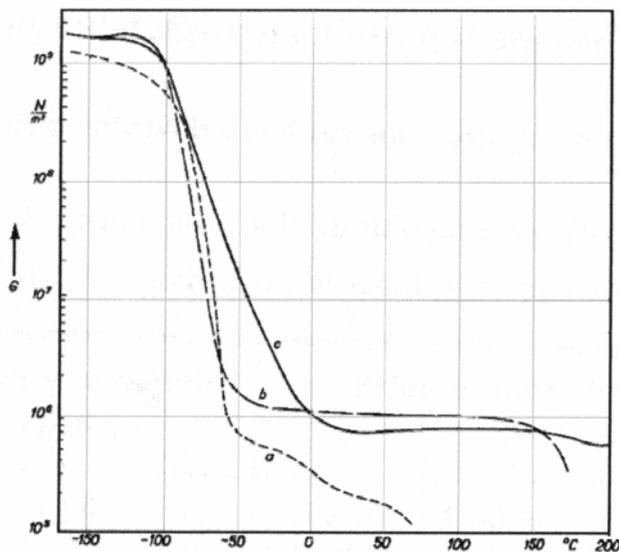


Fig. 14. Shear modulus of caoutchouc vulcanized by different stages in temperature dependence, a) un-vulcanized, b) 0,5% of sulphur, c) 5% of sulphur

The influence of more polar Acrylonitrile Butadiene Rubber (NBR) caoutchouc versus lesser-polar caoutchouc SBR is shown by real dependence the elastic part torque moment (S') versus time (t), figure 15 or elastic part of tear modulus (G'), figure 16.

In both cases is the rising of elastic part torsion moment S' following the adding the polar caoutchouc and the meshing become much faster.

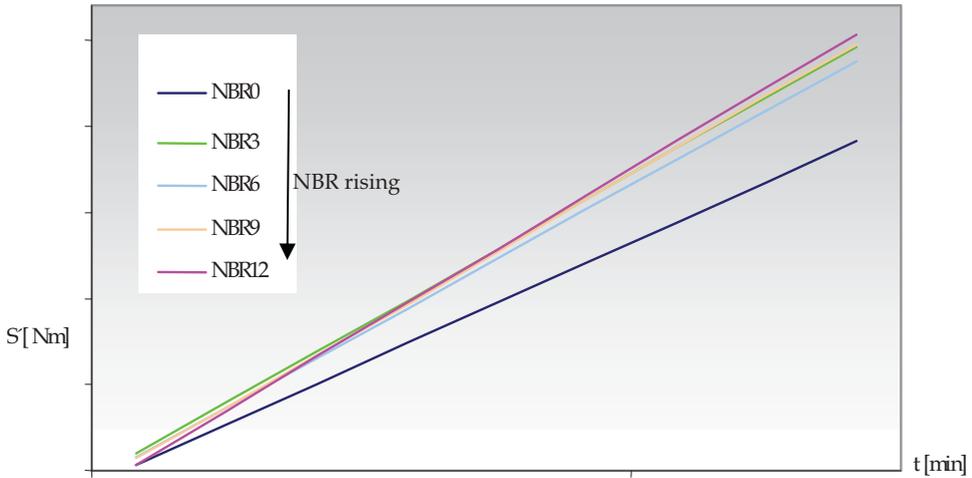


Fig. 15. The elastic part of torque moment versus time

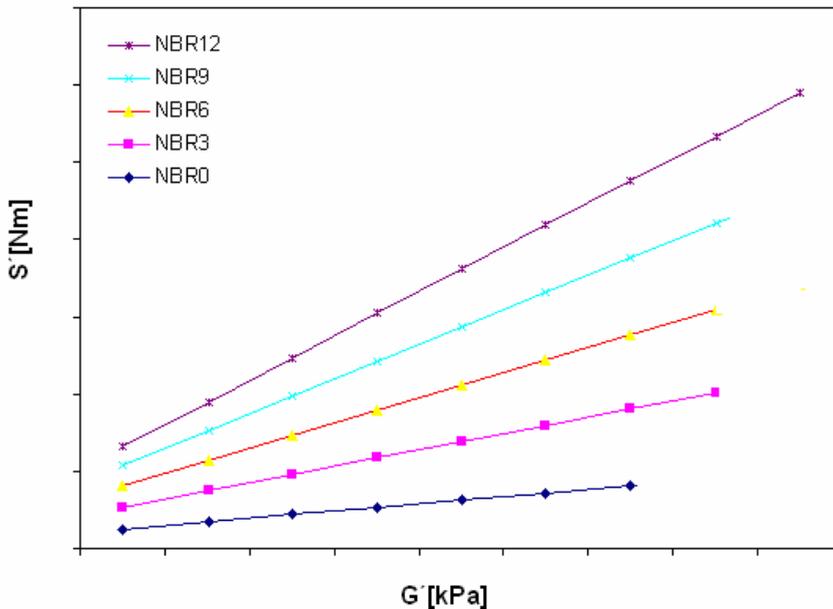


Fig. 16. The elastic part of torque moment versus real part of torsion modulus

A new progressive method in order to quality and economy mixing improving is the on-line rubber blend monitoring. By construction a following production processes of a measurement probe is possibly to perform this method, figure 17. The chamber wall acted as the second electrode.

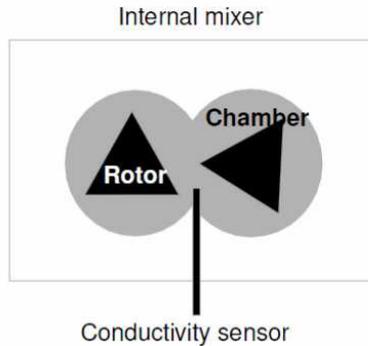


Fig. 17. The probe fixation in the mixer chamber

The sensor (probe) location is important factor. By the sensor location in the wall of chamber is occurred the problem with a periodically washing by prepared mixture (mainly when the mixing chamber isn't exactly filled). The "short circuit" following the carbon black and oil adding can occur in case of softening mixtures. At the same time the sensor doesn't provide the right information about the electrical conductivity of mixing blend. The preferable case of monitoring occurred if is the sensor located in the bottom part of mixing chamber where is provide the continuous contact between sensor and mixing blend (holds also for not exactly filled chamber).

Case of figure 18 gives the electrical parameters information's about the chemical coupling behavior into the mixing chamber; the capacity (C), impedance (Z) and resistance (R) measurements during mixing provide the relevant on-line characteristics.

As was mentioned, at first are feeding caoutchouc into a mixing chamber, the observed running is without some properties changes. By adding of fillers and oil are the properties fluctuated, the impedance decrease, the capacity increase, following the high conductance fillers. By the next mixing are the electrical parameters changed following the probability of no segregated caoutchouc - creation of agglomerates or aggregates into the chamber by zigzag character. The end of mixing process is considering by the little changes of parameters, approximately in time of 640 s - there is a probability of a good mixing. Usually are the on-line mixing periods shorter in consequence of behavior observing than if it's using classical mixture preparation following the achievement of energy consumption and quality rising.

The quality aspect is important by the question of sample preparation - if the samples would be mixed or prepared by qualitative advance the "good" influence will be noted by its useful properties.

Next are introducing the measurements of electrical parameters and atomic force microscopy as the "echo testing" of the quality preparation.

The quality of prepared samples together a filler influence was evaluated by electrical measurements method. The sample without filler content together the next three samples

filled by different chemicals (standard - no filler, barium sulphate - BaSO₄ filler, carbon nanotubes - CNT fillers, metal powder filler) were used and specifically was evaluated the homogeneity by using the characteristics of real part of permittivity versus frequency investigated on three different points, as interpreted the figures 19-22.

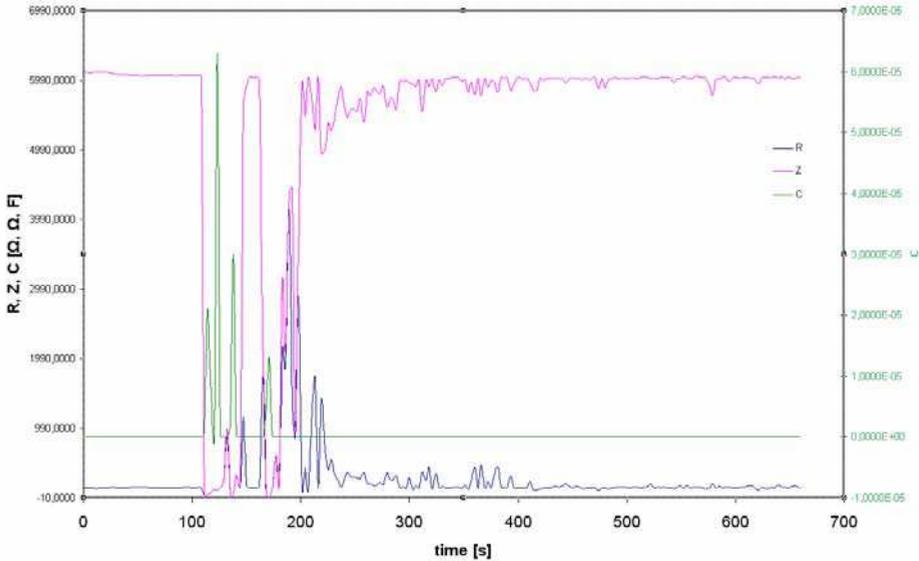


Fig. 18. On-line monitoring the chemicals mixing into the mixing chamber

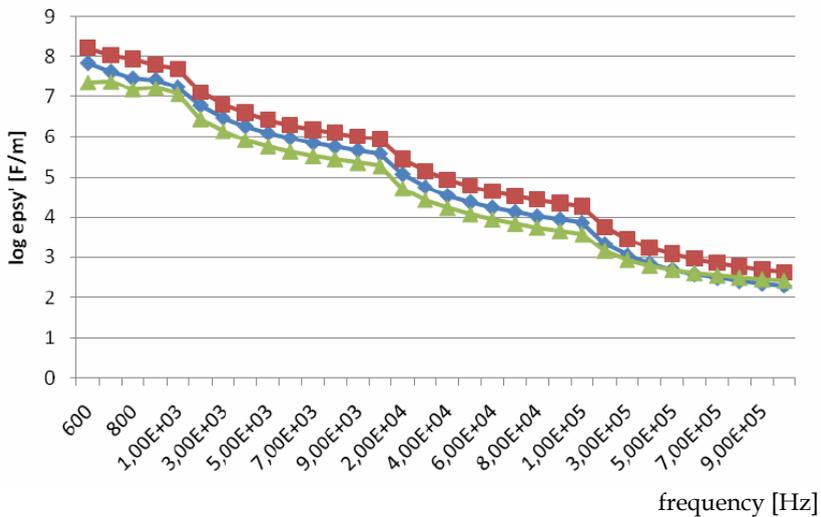


Fig. 19. Sample without filler

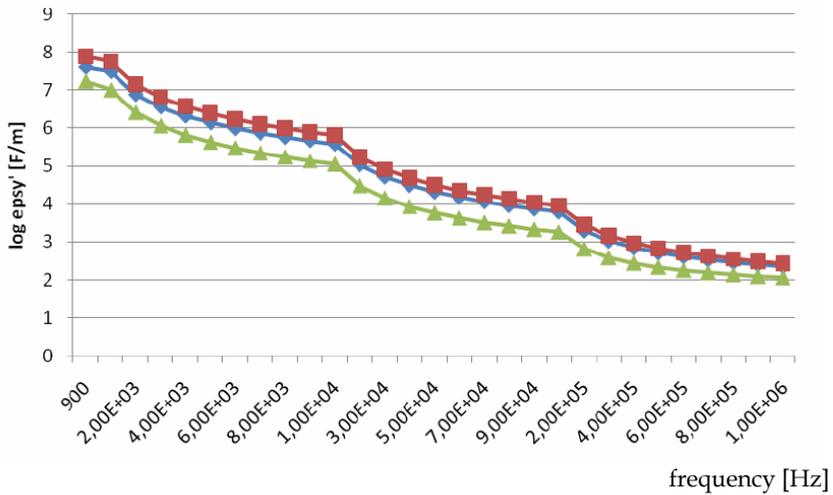
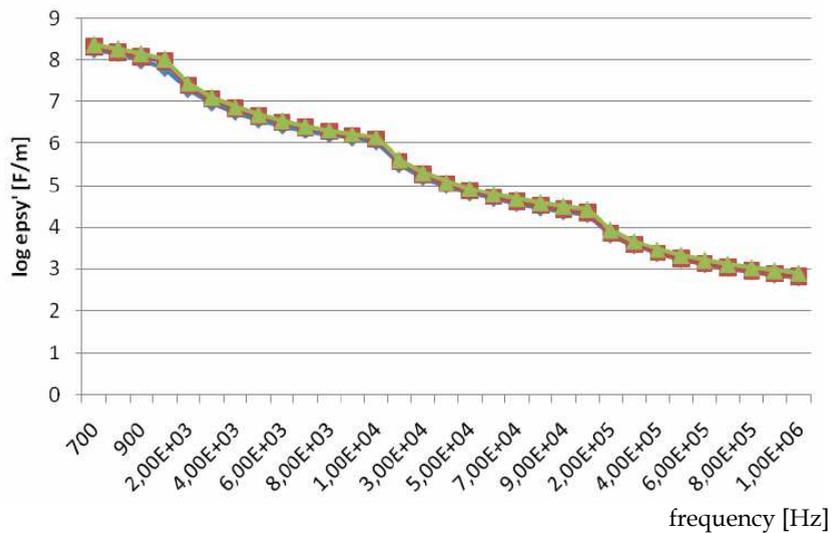
Fig. 20. Sample with BaSO_4 filler

Fig. 21. Sample with CNT filler

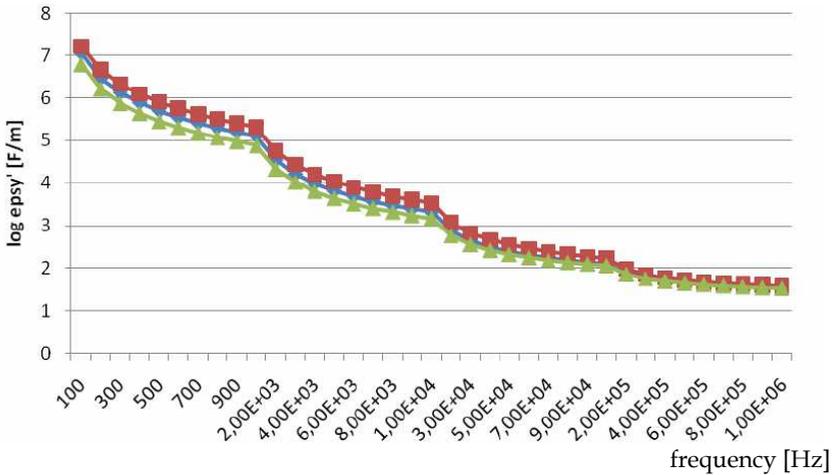


Fig. 22. Sample with metal powder filler

In connection with present results the best homogeneity has the sample with CNT and metal powder filler. There is visible the influence of mixing process for each sample compared the impedance and phase angle values during mixing time, figures 23 – 26 characterized by peaks of electrical values.

On the other hand, modern imaging methods, such as atom force microscopy (AFM), can visualize structure inhomogeneity caused by imperfection of the technological process. The next influence is visible by sample with carbon black filler.

The carbon black fines contents in this case consist of pellet fragments. In such fine materials the probability of forming bigger agglomerates increases again, because Van der Waals’ forces are influenced by the particle diameter, the distance between the particles and the number of contact points.

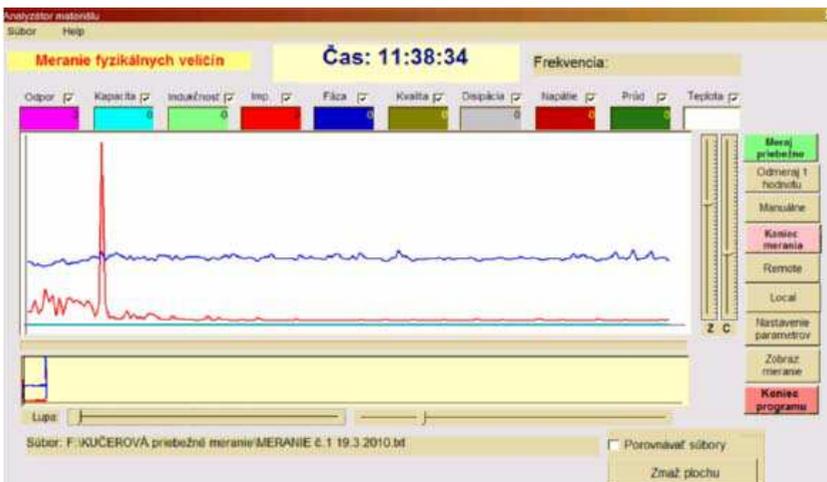


Fig. 23. The mixing behavior of caoutchouc

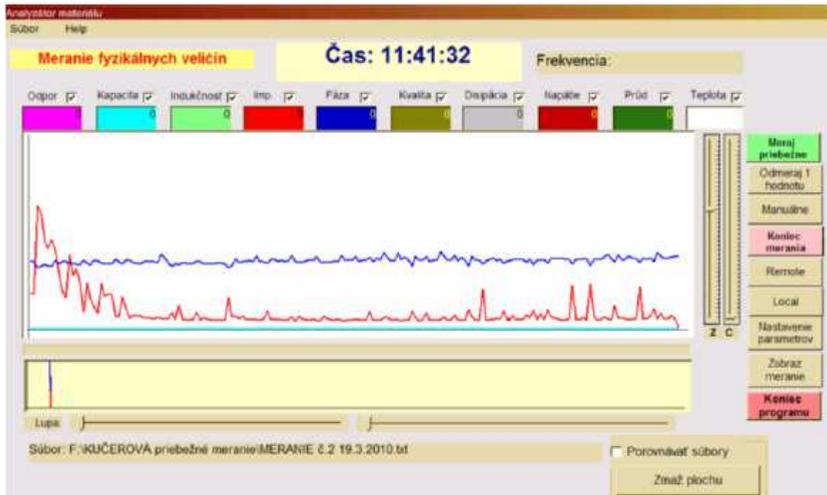


Fig. 24. The mixing behavior of caoutchouc and BaSO₄

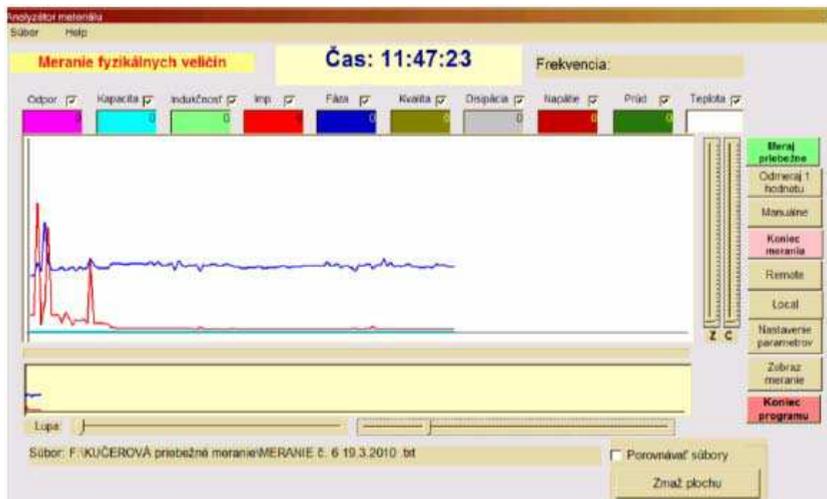


Fig. 25. The mixing behavior of caoutchouc and CNT

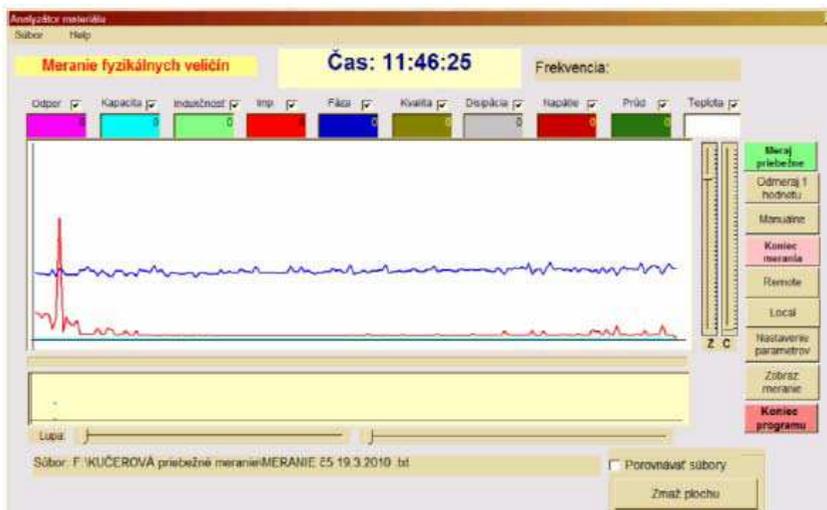


Fig. 26. The mixing behavior of caoutchouc and metal powder

In picture 27, we can see the AFM image of tested rubber sample, where three different areas are marked by arrows. The characteristic AFM curves for all three regions are in Fig. 28-30. The first rectangular breakdown (if we follow the right - left direction with the testing point), represents attraction of the tested material and point by Van der Waals forces. It is clearly seen that for all three tested regions, the values of this change are quite different, which supports the idea of sample inhomogeneity. This relative “macro” inhomogeneity (in the scale of micrometers) needs to be reflected also on electrical properties of the material, which we have presented above.

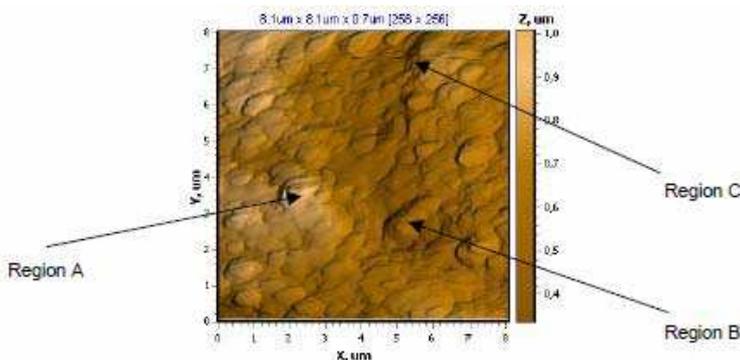


Fig. 27. AFM picture of sample with adding of carbon black fillers

On the other hand the activation energy calculated was found to be highly affected by both the type and concentration of the filler. The activation energies for the five different regions are calculated by the Arrhenius equation.

The large inhomogeneities in activation energies (E_a) of the samples with different filler composition are seen in table 2.

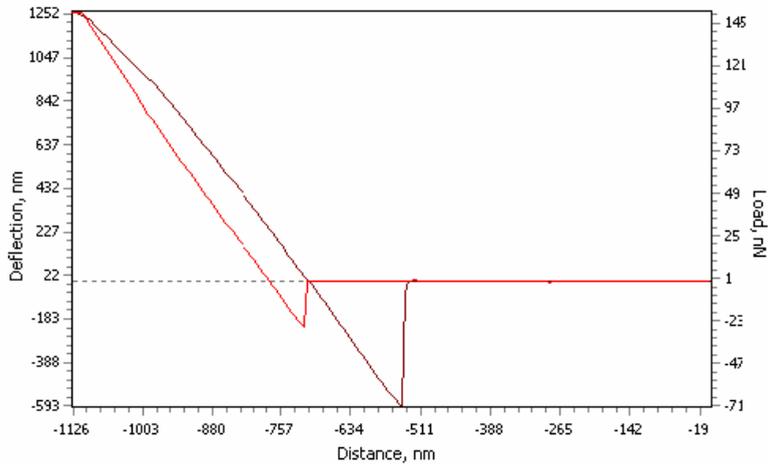


Fig. 28. Representation of Van der Waals forces for region A

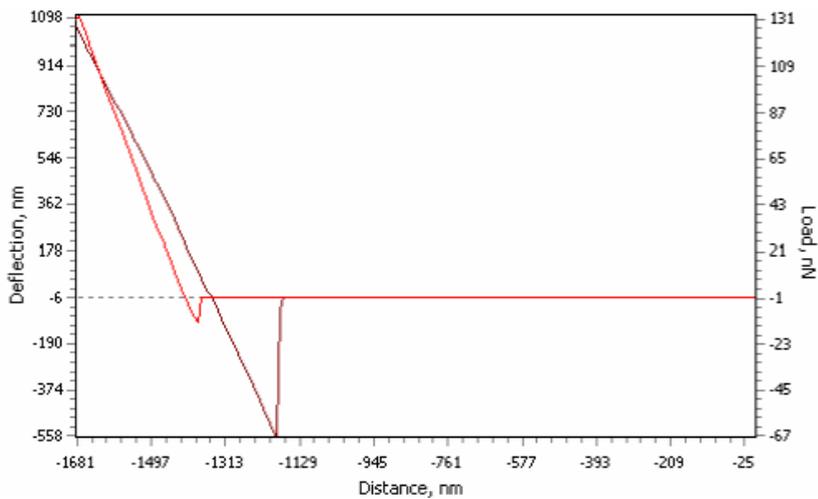


Fig. 29. Representation of Van der Waals forces for region B

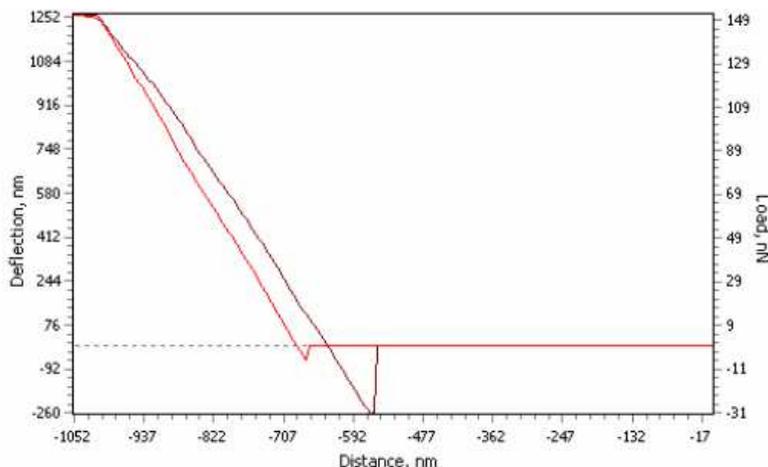


Fig. 30. Representation of Van der Waals forces for region C

Sample	Filler ratio: carbon black/SiO ₂	E _a (eV)				
		Region 1	Region 2	Region 3	Region 4	Region 5
A1	6/30	3,01E+00	5,95E+00	-	-	-
A2	6/30	1,20E+00	4,46E+00	2,82E+00	-	-
A3	6/30	1,47E+00	1,95E+00	-	-	-
B1	20,5/13,5	1,89E+00	2,43E-01	-	-	-
B2	20,5/13,5	2,17E+00	5,15E+00	1,18E+00	-	-
B3	20,5/13,5	1,84E+00	4,52E+00	-	-	-
C1	35/0	8,62E-01	2,47E+00	1,13E+00	4,26E+00	2,25E-01
C2	35/0	1,44E+00	5,76E+00	3,34E+00	-	-
C3	35/0	5,58E+00	1,80E+00	2,94E+00	-	-

Table 2. Values of the activation energy calculated from the dc conductivity measurements.

The reason for such behavior is in different mechanism of electrical conductivity which is in narrow connection with chemical composition. The other effect which influences electrical properties is homogeneity of the samples. The mismatch of electrical parameters is caused by bad dispersion of silica and carbon black respectively. For example this is demonstrated by large distribution of Van der Waals forces presented in figures 28-30 for case of carbon black fillers influence.

From presented results it can be clearly seen that electrical measurements are very sensitive tools for evaluation of chemical composition and homogeneity of sample preparation which is a crucial problem in rubber technology.

As a conclusion we can say that the ideal mixing process can be achieved good homogeneity stage without the waste caoutchouc matrix straining; when is possibly the chain reduction and following degradation of vulcanizate properties.

By observing of electrical measurements behavior this method can supply to time specification when the mixture is perfectly homogeneous and can be removed from

masticator. This exactly statement of rubber blend mixing can short the mixing time is following the energy consumption, productivity rising and the most important improving the vulcanizate properties.

At last, interesting dynamical mechanical dependency of standard mixture composition and CNT is described. The mixture composition is different by using of the triplex adding of softener owing to CNT filler mudding. The Payne effect of standard and CNT mixture is illustrated on figures 31-34 which include the influence before and after vulcanizing process as well as the loading or unloading state.

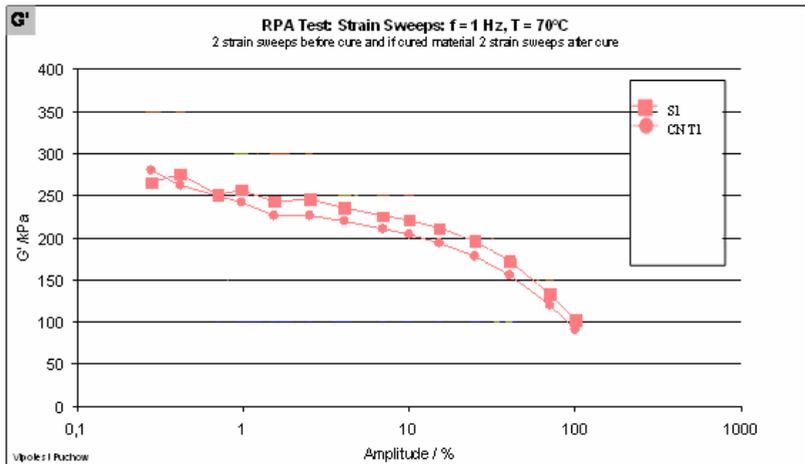


Fig. 31. Payne effect before vulcanizing in the unloading state

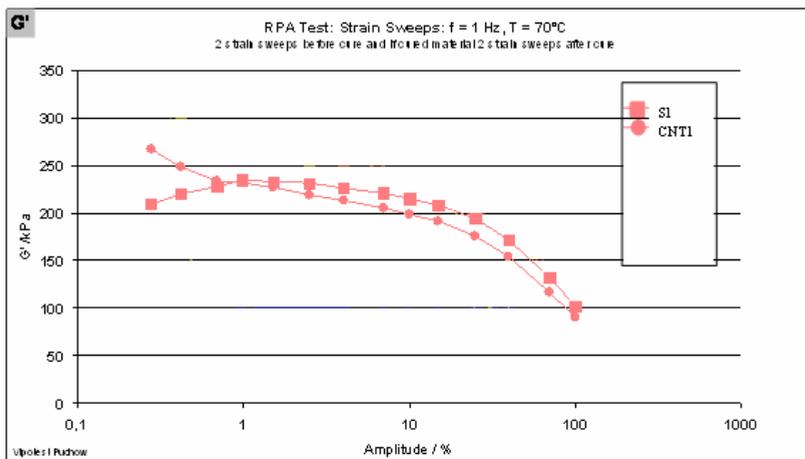


Fig. 32. Payne effect before in the loading state

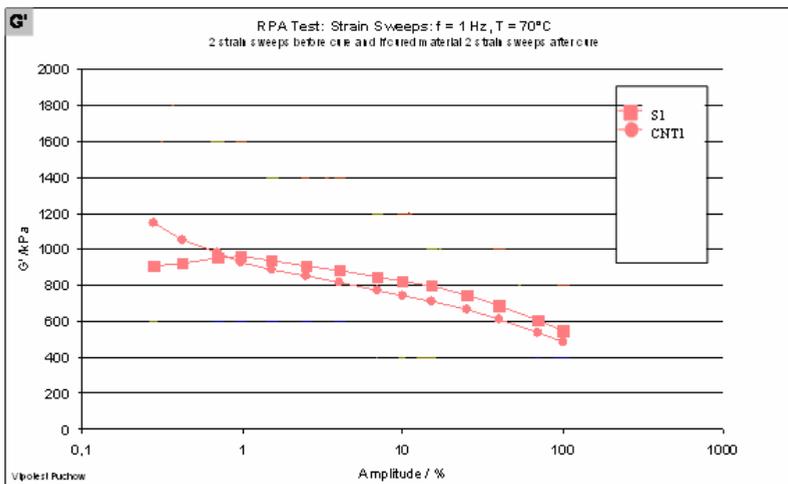


Fig. 33. Payne effect before vulcanizing in the unloading state

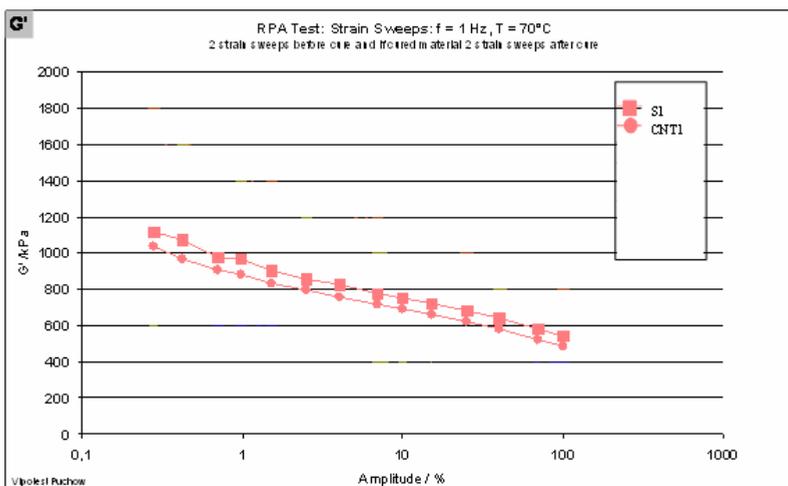


Fig. 34. Payne effect before in the loading state

Last but not least preparing mixture quality is influenced by the contamination of the entrance raw materials, which can negative affected the quality of product in the final phase. This problem relates by systematical preparation of mixing process – controlling of entrance raw materials, storage conditions consecutive manipulation and feeding into a masticator.

Polymer materials are requisite for industry at all in spite but relatively the young science. The first mention was finding by Columbus sailors the observed Americans aborigines plays with a flexible ball. This was made from dry liquid which flowing into a tree called Hevea (Latin) or “Cau-Uchu” (caoutchouc).

The primary caoutchouc was used for production of waterproof canvas and shoes, but there haven’t properly behavior – the silky and adhesive behavior during the summer, the hardened and embrittlement manner during the winter time.

To Europe was a natural caoutchouc transported in 1736, the first processing was in 1791 for sails and mailbags. Later in 1839 Charles Goodyear approached a problem with improvement of quality of caoutchouc products by its impregnation in sulphur solutions.

Thomas Hancock found that the Goodyear’s good does sulphur smell and then investigated the property changes by the caoutchouc warming in melting-down sulphur. Hancock and Goodyear found the vulcanization process, vulcanization means term of god Vulcan from a Greek mythology, process is characterized by heat influence and sulphur smelling.

The various processes of a good product and described problems by this production which we have presented above from the raw material to final product are summarized by the term of “Rubber goods process” in the figure 35.

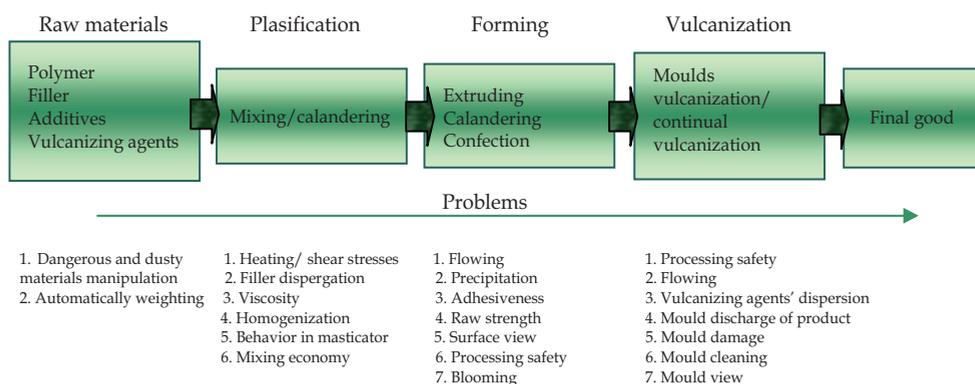


Fig. 35. The stages and processing problems occurred by rubber goods preparation

There is possibly to allege that the claims of rubber producers for a production rate together the quality of masticator are in connection into a whole process controlling increasing and are conditioned by achievement of the high quality of prepared mixture.

3. References

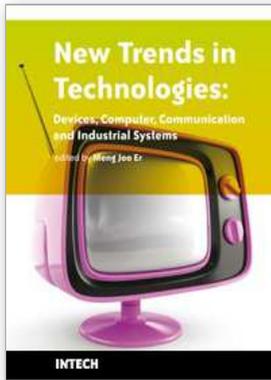
- Čokínová A. (2003). *Diploma work*, Slovak Technical University of Bratislava, /in Slovak/.
- Dierkes, W. (2006). *Economic mixing of silica-rubber compounds Interaction between the chemistry of the silica-silane reaction and the physics of mixing*, Holland, ISBN 90-365-2185-8.
- Holzmüller, W.; Altenburg, K. (1966). *Fyzika polymérov*, Praha /in Czech/.
- Hrenák T. (2009). *Bachelor work*, Alexander Dubček University, FPT Púchov, /in Slovak/.
- Jahnátek, L. et all. (2007). *Štruktúra a vlastnosti polymérov*. Materiálovotechnologická fakulta STU v Trnave, /in Slovak/.
- Jakob B. (2002). Conductivity measurement for rubber compound qualification, *Polymeric Materials*, Halle (Saale), Germany 2002.
- Jurčiová J. et all. (2008). The alternating current circuit parameters measurement as a tool for the monitoring of carbon black dispersion in a rubber blend, 7th Youth Symposium on Experimental Solid Mechanics –YSESM, Poland 2008.
- Knapec P. (2009). *Diploma work*, Tomas Bata University in Zlín, /in Slovak/.
- Košťal P. et all. (2006). The combined study of fillers dispersion in rubber blends, 5th Youth Symposium on Experimental Solid Mechanics – YSESM, Slovakia 2006.
- Kučerová J. (2006). *Dissertation thesis*, Alexander Dubček University, FPT Púchov, /in Slovak/.
- Kučerová J., Bakošová D., Mičúch M. (2006). Electric conductivity measurement of inhomogeneities of rubber blends, *18th Slovak Rubber Conference*, ISBN 80 – 969189–6–6, Púchov, May 2006.
- Kučerová L. (2010). *Diploma work*, Alexander Dubček University, FPT Púchov, /in Slovak/.
- Le H. H., Ilisch S. & Radusch H. – J. (2006). Correlation between morphology and properties of carbon black filled rubber blends, *18th Slovak Rubber Conference*, ISBN 80 – 969189–6–6, Púchov, May 2006.
- Le H. H., Ilisch S., Jakob B., Radusch H. – J. (2004). Online characterization of the effect of mixing parameters on carbon black dispersion in rubber compounds using electrical conductivity, *Rubber chemistry and technology*, vol. 77, no 1, pp. 147-160.
- Le H. H., Ilisch S., Prodanova I., RADUSCH H. – J. (2004). Russdispersion in Kautschuk – mischungen in Anwesenheit von Weichmachrölen. *Kautschuk Gummi Kunststoffe KGK*, 57. Jahrgang, Nr. 7–8.
- Liptáková T. et all. (2009). *Plastics – technical materials*, Hypertext textbook, STU Bratislava. Materials of Technical University of Tampere www.tut.fi/plastics/tyreschool Materials of Technical University of Tampere www.tut.fi/plastics/vert
- Nicolas P. Cheremisinoff. (1987). *Polymer mixing and extrusion technology*. Marcel dekker, inc./New york – Basel.
- Prekop, Š. et all. (1998). *Rubber technology I*, University in Žilina, /in Slovak/.
- Prekop, Š. et all (2003). *Rubber technology II*, GC TECH, Trenčín, /in Slovak/.
- Presentation of ATEAM
<http://www.ateam.zcu.cz/download/pryz.pdf>, /in Czech/.

Presentation of CABOT Company

<http://www.cabot-corp.com/wcm/download/en-us/sb/INTERWIRE%2020011.pdf>

Research project FPT-2/2006 – 3rd part, /in Slovak/.

Šišáková J. et al. (2010). The high density PE and its modifications, XI International conference on machine modeling and simulation – MMS 2010, Poland 2010.



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The grandest accomplishments of engineering took place in the twentieth century. The widespread development and distribution of electricity and clean water, automobiles and airplanes, radio and television, spacecraft and lasers, antibiotics and medical imaging, computers and the Internet are just some of the highlights from a century in which engineering revolutionized and improved virtually every aspect of human life. In this book, the authors provide a glimpse of new trends in technologies pertaining to devices, computers, communications and industrial systems.

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