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Р. А. Гицельтер
г. Хадера, Израиль

Строительные материалы и структуры, основанные на полимерных наноструктурированных матрицах

Представлена история создания наноструктурированного материала на основе жидкого олигобутадиена, не содержащего каких-либо функциональных групп. Разработка нового строительного материала, названного «RubCon» проведена на основе исследований кинетики вулканизации при различных температурах, путем поиска оптимума методами математического планирования эксперимента.

Ключевые слова: полимерные композиции, «резиновая матрица», наноструктурированный бетон, «RubCon», физико-химические и механические свойства.

R. A. Gizelter
Hadera, Israel

Building Materials & Structures Based on Advanced Polymer Nanostructured Matrix

The article presents the history of the creation of nanostructured materials based on liquid oligobutadien that does not contain any functional groups. The development of a new structural material, called "RubCon", was based on the studies of the kinetics of curing at different temperatures by seeking the optimum methods of mathematical planning of the experiment.

Keywords: polymer composition, "rubber matrix", nanostructured concrete, "RubCon", physical, chemical and mechanical properties.

Developments in civil engineering and industrial growth have created a continual demand for building materials with new and improved performance attributes. Polymer concretes (PC) appear to offer possibilities for meeting these new requirements. By polymer concrete is meant a polymer composite with a polymer matrix and sand and rocks, like those used in Portland cement concrete, as inclusions. Service conditions often dictate specific material requirements that may be met by PC when several composite properties are considered simultaneously.

Advancements in PC materials have slowed over the past 25 years compared to the rate of advancements in the 1970s and 1980s. The knowledge base in concrete polymer materials has matured as many products have been made commercially available. There are now many polymer-based construction materials that have been shown to perform very well for their intended purposes: concrete spall repair, crack repair, concrete overlays, and precast concrete components. The cost of polymer-based systems is high relative to conventional portland cement concrete materials, and it is necessary to demonstrate the improved durability, reduced thickness/size, ability to be placed in difficult environmental conditions, and/or the fact that other non-polymer materials will not work. There are many situations for which concrete-polymer materials prove to be the most appropriate materials for the intended application.

Understanding of the nature of PC is necessary for the design of the most cost-effective PC composites and to produce materials with desired properties.

Polymer concrete is usually used in severe conditions in industrial and public buildings as well as in transportation and hydraulic structures. The main uses are repair/ strengthening, and corrosion protection of concrete structures . The main advantages of polymer concrete over ordinary concrete are improved mechanical strength, low permeability, and improved chemical resistance. The main limitation is their relatively high material cost. This is why it is important to find the optimum technical/economic compromise. To solve this problem, it is necessary to formulate a reliable predictive mathematical model of polymer concrete material properties.

One of the new kinds of the structural polymer building materials created recently is rubber concrete based on polybutadiene binder (is short for *RubCon*). The idea of use of liquid rubber as the binder for polymer concrete was the first time put forward by *Prof. O .Figovshy* and was patented in USA and Russia. Application of *RubCon* in practice of construction allows to solve a problem of corrosion, negative influence of temperature, degradation of a material at raised UV - exposure, radiation and other adverse natural and technogenic factors, to increase the between-repairs period, reliability and durability of buildings and structures especially at action of aggressive environments. It is necessary to note, that *RubCon* is more cheaper in comparison with other corrosion resistant polymer composites.

State of the art in polymer concrete: the comparative analysis of the most widespread types of polymer concretes

Developments in civil engineering and industrial growth have created a continual demand for building materials with new and improved performance attributes. By polymer concrete (PC) is meant a polymer composite with a polymer matrix and sand and rocks, like those used in Portland cement concrete, as inclusions. Service conditions often dictate specific material requirements that may be met by PC when several composite properties are considered simultaneously. Understanding of the nature of PC is necessary for the design of the most cost-effective PC composites and to produce materials with desired properties.

Concrete – polymer composites have made during the recent fifty years tremendous progress as the technical means - really engineered composites as well as the research objects. They are still very promising in application and of interest in research. PC is conglomeratic structure on the basis of synthetic resins and chemically proof fillers and aggregates without active mineral binders and water. Compositions without rubble and sand refer to mastics but without rabble refer to polymer grouts. These compositions have special application. Thus the general concept of polymer concrete composites from technical point of view involves a process by which chemicals (monomers, oligomers, prepolymers, polymers) introduced into a concrete mix and in the case of chemical activity are subjected to polymerisation and polycondensation by thermo-catalytic or other systems (Figure 1.1).

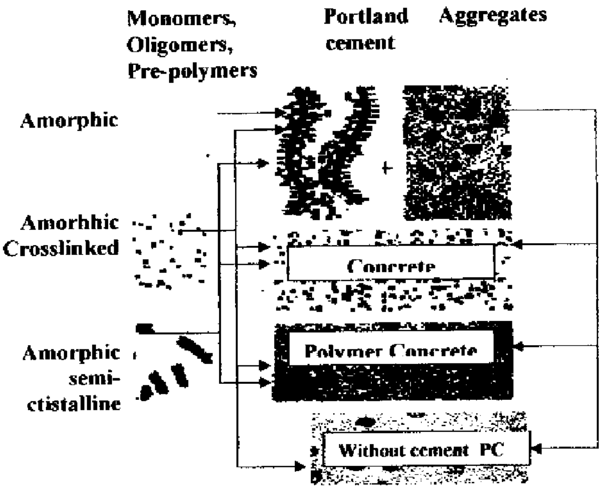

Figure 1.1. General concept of concrete-polymer composites

The properties of PC greatly depend on the formulation, but in comparison to conventional Portland cement concrete, PC generally has higher compressive, tensile, and flexural strength; greater impact and abrasion resistance; much lower permeability to water and dissolved salts; and greater resistance to weathering, freeze-thaw, and chemical attack. One of the polymer concrete advantages is the ability to damp of vibrations. That was used till now mainly in the machines foundations; now it is attempted to apply that opportunity for building structures undergoing to the dynamic loads. The excellent strength and durability properties of PC are due to the polymer binder. The polymer binder forms an impermeable matrix of the concrete and has greater chemical resistance than conventional Portland cement. PC is well-suited for the protection and repair of concrete surfaces such as bridge decks, ramps, pavements, slabs, industrial floors, secondary chemical containment areas, and canals and spillways.

By present time the opportunity of constructional and chemically resistant PC with high strength and fading creep production is completely proved.

An infinite number of different mixtures depending on the chemical nature of components, their contents and manufacturing process can be found. Some simple categorisation and definitions:

Polymer modified concrete – low dosage (<5 % by weight of Portland cement) of polymer to modify concrete; usually polymer affects mainly (if not only) the concrete mix rheological properties (before hardening).

Polymer cement concrete is a composite where either a non-reactive polymer (latex) or a reactive monomer (resin) is added to the fresh cement concrete mix.

Without cement polymer concrete (PC) is a composite having polymer binder eg. plybutadiene or epoxy-urethane.

Polymer modified concrete and polymer cement concrete have increased tensile strength and abrasion resistance, higher water and vapor tightness and resistance to frost and chemical attacks. The basic research area for the polymer-cement concretes, both containing pre-mix and post-mix additives, is determining the influence of the various modifiers on the structure and properties (time-dependent, also) of the composite. This is also connected with the effect of the concrete curing conditions. On the other hand, the presence of polymer in the cement paste can influence the process of the cement hydration , including "self-curing"of the concrete.

The synergic action of polymers and cement mortar and concrete offers great opportunities for improvement and a wide range of new and innovative applications. Society and environment require corrective actions to be taken continuously. The use of polymers should be well-considered to guarantee better performance and improved sustainability.

Polymer concrete as high-filled polymer composition can be obtained on essentially all types of synthetic binder. The monomer or resin system is the most important single factor in determining the properties of the PC. Properties of different polymers vary and produce corresponding variations in the PC. The ideal monomer or resin system is a low volatility, 100 % reactive system that can be cured at ambient temperatures to form a strong, low shrinkage polymer. Epoxy, methacrylate, and polyester resins are most commonly used. Other systems also used include epoxy-urethane, sulfur and vinyl ester. New developments with monomers and resin systems may be expected to produce further improvements in the future.

Large fractions of fillers (sand, rubble, pebble), fulfilled the role of a skeleton, influence on the basic physical-mechanical properties to a lesser degree.

The properties of PC greatly depend on the formulation, but in comparison to conventional Portland cement concrete, PC generally has higher compressive, tensile, and flexural strength; greater impact and abrasion resistance; much lower permeability to water and dissolved salts; and greater resistance to weathering, freeze-thaw, and chemical attack.

According to the resin type used, it is possible to classify polymer concretes as epoxy, polyester, acrylic, phenol-formaldehyde, etc. (Figure 1.2) The types of polymer concrete most often used in the building industry are epoxy, polyester and methacrylate concrete .The ranges of their properties are given in Table 1.1.

PC is cured by a chemical polymerization reaction that turns liquid monomer or resin into a solid polymer. Most PCs are cured at temperatures between 10 °C (50 °F) to 3S °C (95 °F); special systems are cured from -I8 °C (0 °F) to 50 °C (120 °F). Although PC is more durable and stronger than conventional Portland cement concrete, the main reasons for using PC are usually ease of use, rapid curing, very fast strength development.

Epoxy PC is a very versatile overlay material with excellent performance in bridge decks, parking garages, ramps, slabs, and industrial floors. Epoxy PC is easy to clean, can be colored and formulated for aesthetic effects, and has many architectural and decorative uses. Other uses include protection from chemicals, resistance to fungi and bacteria, control static electricity as a electrical conductive overlay, resistance to temperatures up to 260 °C (500 °F), as reflective coatings, and to increase skid resistance. Two component epoxy systems are used for epoxy PC. A wide variety of epoxy resins and curing systems are available, and the resultant properties likewise will vary widely. Most epoxy resins for civil engineering and industrial applications are made from bisphenol A and epichlorohydrin. The epoxy resins are hardened by mixing with a curing agent, usually an amine compound, which causes a crosslinking polymerization reaction with the epoxy resin. Epoxy resins have high stress-strain properties, high resistance-to acids and alkalis but they are unstable in oxidizing environments.

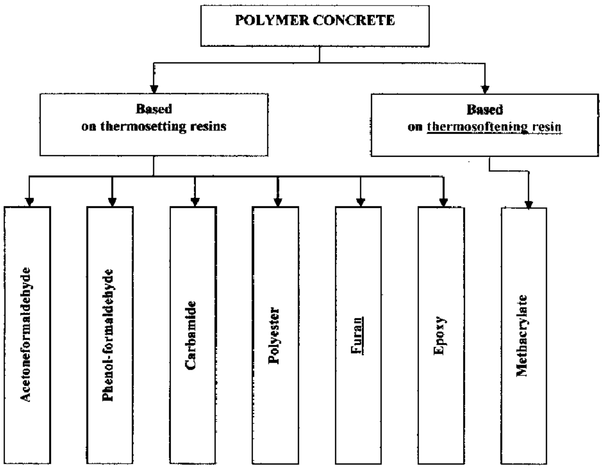

Figure 1.2. The principal types of PC

Table 1.1

Physical-mechanical properties of the most often used PC

Property	Unit	Epoxy PC	Polyester PC	Methacrylate PC
Density	$kg/m3$	1950–2400	2000–2400	2200–2400
Linear shrinkage	%	0.003–0.05	0.01–0.3	
Compressive strength.	MPa	50–150	50–150	70–90
Flexural strength	MPa	15–50	15–45	
Tensile strength	MPa	8–25	8–25	10–13
Modulus of elasticity in compression	GPa	20–40	20–40	10–15
Modulus of elasticity in tension	GPa	12–15	11–14	
Brinell hardness	MPa	250–400	160–250	
Grindability	cm	0.10–0.30	0.10–03.0	
Wear resistance	kg/m^2	0.05–0.1	0.15–0.25	
Poisson's ratio	–	0.30	0.16–0.30	0.27
Linear thermal expansion coefficient	(1/K) »W	10–35	10–30	
Heat resistance	°C	120–130	80	60
Frost resistance	Cycles	500	300	500
Specific toughness	J/cm^2	3–10	02–025	
Shrinkage at curing	%	0.005–0.9	0.08–0.1	0.15–0.2
Adhesion to steel	MPa	5–14	4–12	
Adhesion to concrete	MPa	4–6	4–5	
Water absorption	%	0.02–1	0.03–1	0.01
Labor input at manufacturing m^3	relatively	1	1	
Cost of one m^3	relatively	1	0.7	

The volume of epoxy resin output is smaller in comparison with other resins because of high cost. By this means the fields of application of epoxy resin are essentially limited, (chemically resistant industrial floors, lining, glue compositions, etc.).

Properties of epoxy systems are modified by selection of the curing agent, and by blending with other resins, monomers, and additives. Modifications are made to improve adhesion, increase flexibility and extensibility, lower the modulus of elasticity, reduce viscosity, or to produce systems that can be cured at temperatures ranging from -18 °C (0 °F) to 60 °C (140 °F) .Low viscosity epoxy resins containing solvents are not recommended as due to problems with shrinkage and with environmental regulations on volatile organic components.

Polyester PC is attractive as the materials are widely available and relatively inexpensive. Polyester PC are widely widespread material applied in sanitary techniques, lining, composite pipes and flooring.

Polyester resins are one of the kinds of thermosetting resins produced by polycondensation method. They have small viscosity; materials on the polyester resins basis display high mechanical and electrical insulation properties, high stability to acids, gasoline, oils. Polyester PCs have a greater cohesion and adhesive strength and high shrinkage.

Most polyester resins contain styrene monomer and are considered flammable. Volatile emissions should be monitored by standard air quality testing methods and should not exceed $60g/m^2$ losses. Applications should be made outdoors or in well ventilated areas. The shortcomings of the polyester binder and polyester PC are limited alkalis resistance, significant volumetric and linear shrinkage at hardening, high factor of linear expansion and lowered fire resistance.

Feature of polyester PCs is that each subsequent mixture component is entered after its careful agitation. Explosion hazard of the polyester composition is a serious obstacle on a way of its wide application. The probability of stratification and level-by-level curing of the polyester compositions is high at insufficient agitation of the mixture's components. It is worth noting that polyester resins are toxic.

Methacrylate PC has been successfully used in the US and Europe for about 30 years and has a good reputation. Much of the current attention on PC overlays is due to the early success and commercial development of Methacrylate PC. This PC is used in both thin and thick bonded overlays and patches, renderings, and bearing pads , in rehabilitation of buildings and other structures than on highways. Methacrylate PC with hard aggregates gives good wear resistance, strong, very durable, and versatile material with excellent weathering properties, and is especially good for resistance to outdoor weathering. It is suitable for resurfacing concrete, thin overlays, grouting between sections, and a variety of construction applications.

Methylmethacrylate (MMA)monomer has a very low viscosity and mixes easily with aggregates. It is also an excellent solvent, and generally does not present the clean up problems encountered with epoxy and polyester PC. The vapor pressure of MMA is similar to that of water, and may evaporate if not covered or if a evaporation reducing agent is not used. High molecular weight methacrylate monomers were developed to overcome volatility problems of MMA. These are used as sealers, crack healers, PC binders, and primer for PC overlays. Low viscosity is a main advantage of these monomer binders. Because of this, systems on their basis can contain a lot aggregates and fillers, can be painted in any colors and during 1,5 ... 2 hours after preparation can have more 30 MPa.

The brief characteristic of the new without cement polymer concrete based on polybutadiene binder (RubCon)

ДDevelopment of manufacture of linear diene oligomers belonging to a liquid rubbers class with viscous liquids consistence allowed to create a new class of conglomerate polymer composite materials-rubber concrete *(RubCon®)*. Rubber concrete is the advanced constructional material created for last years. It is polymer concrete with a unique set of physical-mechanical, chemical and technological properties which allow to obtain highly effective building structures and products on its basis.

RubCon contains no cement as a binder; its matrix is polybutadiene – a polymer from the liquid rubber family so that *RubCon* has elastic properties and it is extremely resistant to aggressive chemicals, highly repellant to water and has a remarkable compression strength. It does not exhibit the common failure mechanisms of conventional concrete such as cracking and flaking, freeze and thaw, and it resists vibrations making it an ideal pad material for pumps and compressors. Furthermore, it coats reinforcing rods making the rods impenetrable to water, hence arresting corrosion. The strength and durability of concrete is dependent upon the variation of particles and the binder used with its fabrication.

RubCon is applied in the same manner as conventional concrete, formulated first from a component mixture into a liquid and then cured for 12–48 hours for hardening. The initial binder components are formulated off-site into a mixture. The component mixture consists of a single component package for hot curing (150° to 180° C) with a shelf life of three months (in a closed container), and a two-component package for cold (20° to 25 °C) and semi-hot (70° to 100°) curing with a shelf-life of six months. The components can be easily formulated on-site in a nontoxic and completely safe manner. *RubCon* is easily applied and will adhere to metal or glass reinforcements. After two days, *RubCon* may be walked upon and after seven days, it is ready for work loads. With the use of special adhesives, *RubCon* can be applied over existing concrete flooring. RubCon's outstanding mechanical properties follow (Table 1.2)

Table 1.2

Basic physical-chemical and mechanical properties of RubCon

INDICES	Unite	Concrete on Potland cement	RubCon
Density	kg/m^3	2400	2100–2300
Strength at – compression – bending – tension	MPa	20–40 35 25	80–95 25–30 12–15
Modules of elasticity	$MPa10^4$	2–2.7	2.0–2.7
Poison's ratio		0.15–0.24	0.26–0.28
Thermal conductivity coefficient	W/m/°C	0.3–0.5	0.3–0.5
Wear resistance	$(kg/m^2)10^{-3}$		2–3
Specific toughness	$(J/m^2)10^3$	0.5	3.5–4.5
Heat stability	^UC	–	80–100
Water absorption	%	1	0.05–0.06
Coefficient of chemical resistance at 20 ^UC (based on 360 days of exposure) – 20 % H_2SO_4 – 10 % Lactic acid – 20 % Caustic potash – 35 % H_3PO_4 – Water – Salt water		 no stable no stable 0.61 	 0.97–098 0.95–0.96 0.97–0.98 0.96–0.98 0.99–0.995 1.00–1.05
Resistance to abrasion,	$(k/m^2)10^{-3}$	0.5	2–3.5
Labor input at manufacturing m^3	relatively	1	1
Cost of one m^3	relatively		0.6

Structure of RubCon selection in the polymer making part

Compositions on the base of liquid rubbers are divided, according to their degree of filling, to a number of structural sub-systems including one other as "matrix + additives": liquid rubber +hardening components → rubber matrix (RM); RM+filler → rubber binder (RB); RB + complimentary additives → rubber concrete *(RubCon)*.

A very important moment in projecting of a polymeric composition is the choice of the polymer, because its chemical composition and structure determine characteristics of the created material. That is true also for *RubCon*, the liquid phase of which consists from rubbers with various microstructure of polymeric chain. Liquid rubbers in projected compositions are able, if acted by special accelerating systems, to be vulcanized with formation of space-linked net polymers, the space net of which mainly determines the positive properties of hard base of *RubCon* composite.

As several studies show, the best combination of physical, chemical, technical etc. parameters are exhibited by RubCon based on diene olygomers without functional groups hardened in presence of sulfur-acceleration system. Composites of this kind have a number of positive properties, comprising excellent characteristics in durability, crack-resistance, water- and chemical resistance etc. For the correct selection of rubber for RM a complex of the following actors needs to be taken into account, comprising the capability of the considered polymer to satisfy the properties needed for the projected composite, its availability and technologic suitability. Following these criteria, the selection of the polymer was carried out among existing kinds of liquid rubber: SKDN-N® (Russia), PBN® (Russia), Polyoil 110® (Germany) and Ricon 130® (USA). All these types belong to the group of rubbers comprising also low-molecular hydrocarbon diene-based polymers (solvent-free liquid telomere of butadiene) with a large spectrum of molecular masses and microstructures. These are characterized by numerous non-saturated olefin bonds allowing easy linkage and chemical modifications. Moreover, each of them has determined and carefully controlled microstructure, which seriously determines the properties of liquid rubber. According to the microstructure of the polymeric group, the selected types are rubbers with 1,4-cis structure (SKDN-N® and Polyoil 110®) and rubbers with mixed microstructure (PBN® and Ricon 130®).

On purpose of selection of the liquid rubber involved into the mixture, the durability of considered kind of *Rubcon* has been studied. For this goal some prism samples 40x40x160 mm had been tested.

According to the results of the experiment (Figure. 2.1), the maximum durability against compression and bending was found for samples on the base of liquid rubber PBN® (σ_{com} = 93.0 MPa, σ_b = 28.0 MPa) and Ricon 130® (σ_{com} = 94.0 MPa, σ_b = 26.0 MPa). Less durability was found for samples on the base of Polyoil 110 ® ($|sigma_{com}$ = 84.0 MPa, σ_b = 23.5 MPa) and SKDN-N® (σ_{com} = 81.00 MPa, σ_b = 22.0 MPa).

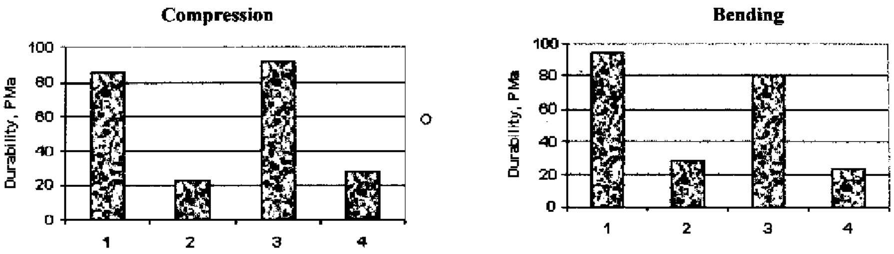

Figure 2.1. TValues of σ_{com} and σ_b of *RubCon* for various rubbers. 1- Potyoil®, 2-PBN®, 3- Ricon 130®, 4-SKDN-N®

Upper values of (durability of *RubCon* samples on the base of PBN® and Ricon 130® in comparison with those of SKDN-N® and Polyoil 110® are explained, in our opinion, by different molecular structures of polymeric chains of the used olygomers. As mentioned above, rubbers SKDN-N® and Polyoil 110® contain major amount of 1,4-cis units - to 75 % of total, while in robbers with mixed microstructure PBN® and Ricon 130® the content of 1,4-cis, 1,4-trans and 1,2 – units is comparable. Such a redistribution of the microstructure of polymeric chain is favorable for increase of the three-dimensional polymer induction formation period and degree of double bonds conversion. Moreover, rubbers with mixed microstructure have better thixotropy that allows obtain better mixing of the components when the *RubCon* mixture is prepared. These factors are favorable for processes taking place in the compositions when they are prepared and vulcanized, that determines better durability characteristics of the product. However, we have to note that olygodienes of 1,4-cis structure are more reaction_able and based on them *Rubcon* at the same other data have lower temperature and larger rate of vulcanization.

As follows from mentioned above, it found to be optimal to accept linear polybutadiene olygomers of mixed microstructure PBN® and Ricon 130 ® as the basic polymer for RM-*Rubcon*.

Optimization of rubber binder viscosity

Since viscosity is very important parameter characterizing every liquid rubber and influencing the main physical and mechanical properties of the projected composite, it frequently determines the choice of the polymer and reasonability of its use. Industry manufactures rubbers with viscosity varied in large spectrum, e.g., for polybutadiene PBN® that is interval (0.2, 7.1) Pa*s. However, there is being no data allowing estimation of viscosity of rubber useful for its employ in *RubCon* compositions. Obviously that as lower is the viscosity of rubber as lower is the viscosity of the obtained *RubCon* composition, hence there is opportunity to obtain better mixing of the components and so improve physical and mechanical properties of the composite or reduce the consumption of the polymer. On the other hand, rubber of low viscosity caused by large presence of molecules with polymerization degree from 3 to 6 cannot provide vulcanization net of high density that decreases durability of the composite in general. Although, if rubber with viscosity allowing formation of vulcanization net of high density meant excellent physical and mechanical characteristics of the composite, is used, that may cause increase of viscosity of all the composition. The last factor would cause increase of consumption of energy and efforts needed for the preparation of the mixture without gaming better properties or make the mixture loose and bad for treatment, with worse resulting properties. The series of experiments have carried out for the evaluation of the value of viscosity of rubber allowing the needed varied parameter has been viscosity, and the measured function – the RubCon durability against compression and bending. The experiment used rubber PBN® with viscosity (Pa*s.): 0.4; 0.6; 0.8; 1.0; 1.2; 1.4; 1.6; 1.8; 2.0; 2.2. The regression analysis of the obtained results allowed deduction of mathematical models adequately describing the correlation of durability of the samples against compression and bending:

$$\sigma_{com} = 46.377\eta(l - 0.36\eta) + 60.731 \quad (2.1)$$

$$\sigma_b = 33.564\eta(l - 4.2\eta) + 10.553 \tag{2.2}$$

where $|sigma_com$ is the durability of PBN® – *RubCon* samples against compression, MPa; σ_b is that against bending; η is the rubber viscosity, Pa*s.

The obtained correlation is described by parabolic curves 1and 2 (Figure 2.2) characterized by initial rising with further extreme value, then decrease of the function. Maximal values of the curves are obtained at different values of viscosity. For curve 1 of the change of durability against impression, the maximum is obtained at viscosity 1.2 Pa*s. That is probably explained by hardness of RubCon prepared from rubber with viscosity 1.6 Pa*s., in comparison with that from rubber with viscosity 1.2 Pa*s, because the density of linkage is upper for polymer with upper molecular mass related to viscosity.

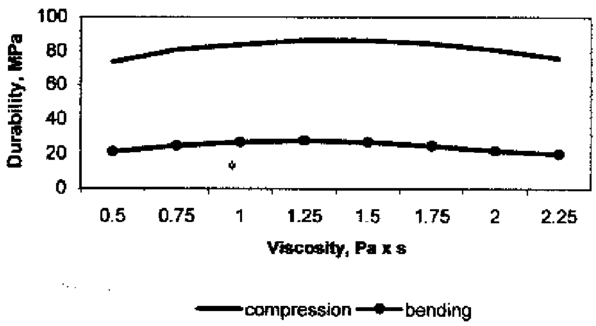

Figure 2.2. Values of σ_{com} and σ_b of RubCon for various amount of rubber viscosity

Based on these results, (me may conclude that the value of optimal viscosity of low-molecular polybutadiene with mixed microstructure, involved into the RubCon mixture, is in interval from 1.1 to 1.7 Pa x s. The further studies employed rubber with viscosity 1.5 Pa* s.

Estimation of optimal rubber content

It is obvious that the amount of low-molecular rubber in RubCon composition permanently changes with the kind, dispersion and amount of the filler, number and granular composition of filters etc. However, the evaluation of optimal content of rubber in the composition is possible on the initial stage of the composition projecting. For the solution of this problem an experiment has been carried out. Variable quantity was the amount of low-molecular rubber in the composition (PBN®); the goal functions were compression and bending strength of RubCon -The composition and technology of sample preparation have been the same that in selection of the kind of rubber. The regression analysis of obtained results (Figure 2.3) provided adequate mathematical models:

$$\sigma_{com} = 45.4\lambda(l - 0.052\lambda) + 116.9 \tag{2.3}$$

$$\sigma_b = 18.4\lambda(l - 0.052\lambda) - 58.2 \tag{2.4}$$

where λ is the content of rubber for various amount of rubber.

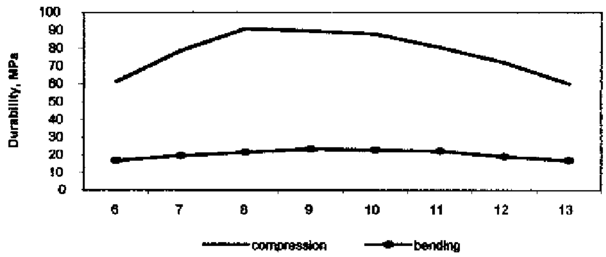

Figure 2.3. Values of σ_{com} and σ_b of *RubCon* for various amount of rubber for various amount of rubber

The analysis of obtained data allows conclusion that the optimal content of rubber in the composition is from 8.5 to 10.5 mass. %. The content of rubber less than 8.5 mass % causes discontinuance of the film structure of the polymeric matrix and pore formation, while more 10.5 mass % provides unstable inhomogeneous structure of the mixture during formation.

Choise of hardening agent for rubber matrix

Liquid polybutadienes without functional groups may be vulcanized on double bonds of the diene part of the polymeric chain in presence sulfur-accelerating, Red-Ox or peroxide system. However, the sulfur-accelerating system only is being able to provide the obtainment of maximal values of durability. Sulfur has also other advantages – low price, availability etc. The amount of involved sulfur in the system depends on desired properties of the product. For hard *RubCon* that is 47–55 mass parts per 100 mass parts of rubber.

The rising of the rate of chemical reactions between sulfur and rubber, acceleration of the vulcanization process and reduction of its temperature are gained by involving of special accelerators. The use of a few of accelerators may improve the vulcanization process because of their mutual activization. Two accelerators were used: tetramethyl-thiuram-disulfide (thiurarn-D®) and captax®. They act mutually and thus improve the vulcanization process and the resulting properties of *RubCon*.

The mentioned above suggestion has been tried in two-phase experiment, in which the variable parameters were the amounts of accelerators, and the value of *RubCon* durability as the function.

It has been found from the experience that the maximal value of *RubCon* durability is obtained at the captax content 0.05 mass. %, while thiuram-D -0.35 mass. %. The maximum durability against compression has been found at maximum content of thiuram-D and moderate content of captax.

Regression analysis of the experiment results provides the following empiric equations:

1. At the content of thiuram-D 0.15 mass. %:

$$\sigma_{com} = 1120\kappa(l - 8.9\kappa) + 65.1 \tag{2.5}$$

2. At the content of thiurarn-D 0.25 mass. %:

$$\sigma_{com} = 715\kappa(l - 9.3\kappa) + 78.213 \tag{2.6}$$

3. At the content of thiurarn-D 0.35 mass. %:

$$\sigma_{com} = 510\kappa(l - 8.8\kappa) + 88.25 \tag{2.7}$$

where k is the mass content of captax, %.

4. At the content of captax 0.03 mass. %:

$$\sigma_{com} = 4t(l + 22.5t) + 87.075 \tag{2.8}$$

5. At the content of captax 0.05 mass. %:

$$\sigma_{com} = 190t(t - 0.49) + 101.28 \tag{2.9}$$

6. At the content of captax 0.07 mass. %:

$$\sigma_{com} = 240t(t - 0.35) + 101.25 \tag{2.10}$$

where t is the mass content of thiurarn-D (%).

The general correlation equation:

$$\sigma_{com} = 173.3t(t - 0.186) - 7042\kappa(\kappa - 0.122) + 300t\kappa + 73.28 \tag{2.11}$$

The decrease of RubCon durability at the captax content is less 0.05 mass. % is caused by the violation of accelerators complex action and appearance the chemically free rubber. The content values more 0.05 % causes excess of captax and related decrease of durability. The increase of product durability, when the content of thiuiam-D closes 0.45 %, is caused by gas deliverance and pore formation in the composite volume.

The hypothesis of positive influence of captax on the durability because of kinetic factor has been checked in the described below experiment.

Series of *RubCon* samples have prepared. The content of main components (except accelerators) has been the same. The first composition used accelerators thiurarn-D + captax, the second one -thiuiam-D only. After the temperature gaining 120 °C in exothermal regime, each 60-mm. three prism samples (40x40x160 mm) have been being removed from the camera and tested against compression. The analysis of curves I and 2 (Figure 2.4) shows that involving of the second accelerator into the composition improves the kinetics of vulcanization, because of:

– increase of the induction period of vulcanization (AB) when the structure formed;

– reduction of the main period of vulcanization when the optimum gained;

– increase of the time duration when the optimum stays.

The change of parameters of vulcanization kinetics found in the experience allowed more order in the composite structure, reduction of the number of dislocations and, consequently, improvement of mechanical characteristics of *RubCon*. Let us note that the optimum content of the components in the system with additive action of accelerators for rubber of the same kind is constant; for PBN® it is 7 parts of thiurarn-D per I part of captax.

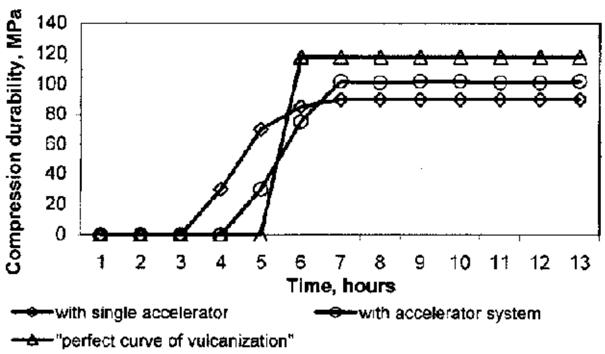

Figure 2.4. Kinetic curves of compression durability gaining.
1 – with single accelerator, 2 – with accelerator system, 3 – "perfect curve"of vulcanization

Planning of activator and calcium-containing components of the composition "rubber matrix – RubCon"

Based on analysis of references, it had been found that organic accelerators of vulcanizations are especially active in presence of several oxides and hydroxides of metals (vulcanization activators) like zinc, lead, magnesium, calcium, cadmium, bismuth and their combinations.

The most widespread activator used in technology of rubber composition treatment is zinc oxide (zinc white). In comparison with other activators it is cheaper and largely used in chemical industry as law material.

Based on the mentioned above, zinc oxide was accepted as RM-vulcanization activator, and its optimal content in the *RubCon* composition was estimated as 10–20 mass parts per 100 mass parts of rubber.

Involving of 0.5 mass, % calcium-containing component (CaO) allows reduction of gas deliverance and pore formation during vulcanization.

Optimization of the composition of the composition "rubber matrix – RubCon" in respect of its strength

The evaluation of RM optimal composition has carried out by variation of three parameters: amount of sulfur (s), amount of accelerator (t), amount of the activator (z) in RM, whereas the efficiency functions are compression and bending strength.

The amount of rubber PBN in the experiment was 100 mass parts; the content of other components: CaO (5 mass parts), filler (87.5 mass parts), sand (300 mass parts) and coarse aggregate (680 mass parts). The regression analysis of results of the experiment provided the following equations:

1. For samples tested against compression:

$$\sigma_{com} = 0.34s(s-100) - 0.28t \quad (t-23.79) - 0.14z(z-8.36) - 782.1 - 0.08st - 0.06sz - 0.01tz \qquad (2.12)$$

2. Those tested against bending:

$$\sigma_{com} = 0.07s(s-100) - 0.13t(t-17.07) - 0.06z(z-59.2) - 197.9 - 0.02st - 0.02sz - 0.06tz \qquad (2.13)$$

It has been found from the results of experience that the most influence on the change of durability is of sulfur and vulcanization activator, while that of the accelerator system is less important. The increase of sulfur content increases the durability against compression but decrease that against bending. Interactions sulfur-accelerator and sulfur-activator influence similarly.

The compositions of *RubCon* destined for operations under compression or bending charges, respectively, are given in the Table 2.1.

Table 2.1

Optimal composition RM for RubCon - PBN®

Tests	Mass parts of components					
	Rubber	Sulfur	Thiuram-D®	Captax®	Zinc oxide	Calcium oxide
Compression	100	50	4.4	0.7	15.6	6.3
Bending	100	47.5	4.3	0.5	18.8	5.6

Control tests of *RubCon* samples prepared according to the foregoing recommendations provided the following values of strength: at compression 105 MPa, at bending- 31 MPa.

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