

Buildings Materials & Structures Based on Advanced Polymer Nanostructured Matrix

Rudolf Gizelter

The GM Association, 7 HaMada St., Herzliya Pituach 46733, Israel

E-mail address: rudolf194138@mail.ru

ABSTRACT

Development of manufacture of linear diene oligomers belonging to a natural rubber class with viscous liquids consistence allowed to create a new class of conglomerated 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.

Keywords: RubCon; butadiene rubber; natural rubber, rubber industry

1. INTRODUCTION

Developments in civil engineering and industrial growth have created a continual demand for building materials with advanced 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. Figovsky 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.

Development of manufacture of linear diene oligomers belonging to 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 main binder is polybutadiene – a polymer from the liquid rubber family so that RubCon has elastic properties and it is extremely resistant to aggressive chemicals, highly repellent 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 application. 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 °C to 180 °C) with a shelf life of three months (in a closed container), and a two-component package for cold (0 °C to 25 °C) and semi-hot (70 °C to 100 °C) 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).

Table 1. Basic physical-chemical and mechanical properties of *RubCon*

INDICES	Units	Concrete Potlandcement	<i>RubCon</i>
Density	kg/m ³	2400	2100-2300
Strength at - compression - bending	MPa	20-40 35 25	80-95 25-30 12-15
Modules of elasticity	MPa10 ⁴	2-2.7	2.1-2.7
Poison's ratio	-	0.15-0.2	0.16-0.28
Thermal conductivity coefficient	W/m/°C	1.3-0.5	1.3-0.5
Wear resistance	(kg/m ²)10 ³		2-3
Specific toughness	(J/m ³)10 ³	0.5	3.5-4.5
Heat stability	°C	-	80-100
Water absorption	%	1	0.05-0.06
Coefficient of chemical resistance at 20°C (based on 280 days of exposure)			
- 20% H ₂ SO ₄			0.97-0.98
- 10% Lactic acid			0.95-0.96
- 20% Caustic wash		no stable	0.97-0.98
- 35% H ₃ PO ₄		no stable	0.96-0.98
- Water		0.61	0.99-0.995
- Salt water			1.00-1.05
Resistance to abrasion,	(kg/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

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 oligomers 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 aspects 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-NR (Russia), PBNR (Russia), Polyoil 110R (Germany) and Ricon 130R (USA). All these types belong to the group of rubbers comprising also low-molecular hydrocarbon diene-based polymers (solvent-free liquid phase of butadiene) with a large spectrum of molecular masses and microstructure. 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-structure (SKDN- NR and Polyoil 110R) and rubbers with mixed microstructure (PBNR and Ricon 130R).

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.

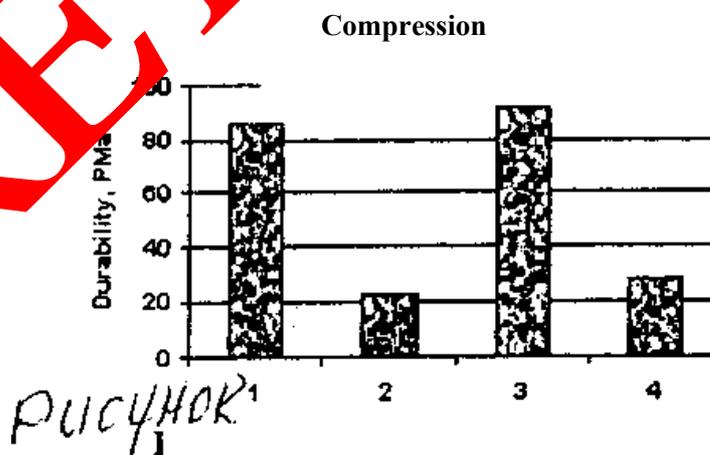


Figure 1. TValues of σ_{com} and σ_b of RubCon for various rubbers. 1- PotyoilR, 2-PBNR, 3- Ricon 130R, 4-SKDN-NR.

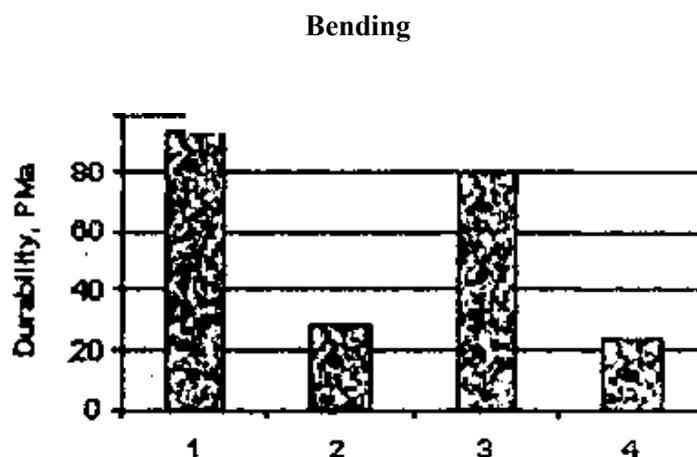


Figure 1(continue). TValues of σ_{com} and σ_b of RubCon for various rubbers: 1- Polybut, 2-PBNR, 3- Ricon 130R, 4-SKDN-NR

According to the results of the experiment (Figure 1) the maximum durability against compression and bending was found for samples on the base of liquid rubber PBNR ($\sigma_{com} = 93.0$ MPa, $\sigma_b = 28.0$ MPa) and Ricon 130R ($\sigma_{com} = 94.0$ MPa, $\sigma_b = 26.0$ MPa). Less durability was found for samples on the base of Polybut 110 R ($\sigma_{com} = 84.0$ MPa, $\sigma_b = 23.5$ MPa) and SKDN-NR ($\sigma_{com} = 81.00$ MPa, $\sigma_b = 23.5$ MPa).

Upper values of (durability of RubCon) samples on the base of PBNR and Ricon 130R in comparison with those of SKDN-NR and Polybut 110R are explained, in our opinion, by different molecular structures of polymeric chains of the used oligomers. As mentioned above, rubbers SKDN-NR and Polybut 110R contain major amount of 1,4-cis units - to 75 % of total, while in rubbers with mixed microstructure PBNR and Ricon 130R the content of 1,4-cis, 1,4-trans and 1,2 - units is approximately equal. 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 isotropy 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 oligodienes of 1,4-cis structure are more reactive and based on them Rubcon at the same other data have lower temperature and large rate of vulcanization.

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

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 PBNR 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 gaining 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 of the RubCon durability against compression and bending. The experiment used rubber PBNR 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:

$$\sigma_{\text{com}} = 46.377\eta(1 - 0.36\eta) + 60.75 \quad (1)$$

$$\sigma_{\text{b}} = 33.564\eta(1 - 4.2\eta) + 10.553 \quad (2)$$

where σ_{com} is the durability of PBNR – RubCon samples against compression, MPa; σ_{b} is that against bending; η is the rubber viscosity, Pa*s.

Based on these results, (we may conclude that the value of optimal viscosity of low-molecular polybutadiene with mixed microspheres 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.

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 (PBNR); 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 provided adequate mathematical models:

$$\sigma_{\text{com}} = 45.4\lambda(1 - 0.052\lambda) + 116.9 \quad (3)$$

$$\sigma_{\text{b}} = 18.4\lambda(1 - 0.052\lambda) - 58.2 \quad (4)$$

where λ is the content 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.

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 activation. Two accelerators were used: tetramethyl-thiuram-disulfide (thiurarn-DR) and captaxR. 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 is 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 thiurarn-D - 0.35 mass. %. The maximum durability against compression has been found at maximum content of thiurarn-D and moderate content of captax.

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

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

$$\sigma_{\text{com}} = 1120\kappa(1 - 8.9\kappa) + 65.1 \quad (5)$$

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

$$\sigma_{\text{com}} = 715\kappa(1 - 9.5\kappa) + 78.213 \quad (6)$$

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

$$\sigma_{\text{com}} = 510\kappa(1 - 8.8\kappa) + 88.25 \quad (7)$$

where κ is the mass content of captax, %.

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

$$\sigma_{\text{com}} = 4t(1 + 22.5t) + 87.075 \quad (8)$$

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

$$\sigma_{\text{com}} = 190t(t - 0.49) + 101.28 \quad (9)$$

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

$$\sigma_{\text{com}} = 240t(t - 0.35) + 101.25 \quad (10)$$

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

The general correlation equation:

$$\sigma_{\text{com}} = 173.3t(t - 0.186) - 7042\kappa(\kappa - 0.122) + 300t\kappa + 73.28 \quad (11)$$

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 thiuram-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 thiuram-D and captax, the second one -thiuram-D only. After the temperature gaining 120 °C in external regime, each 60-mm. three prism samples (40 x 40 x 160 mm) have been removed from the camera and tested against compression.

The analysis of curves 1 and 2 (Figure 2) shows that introduction 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.

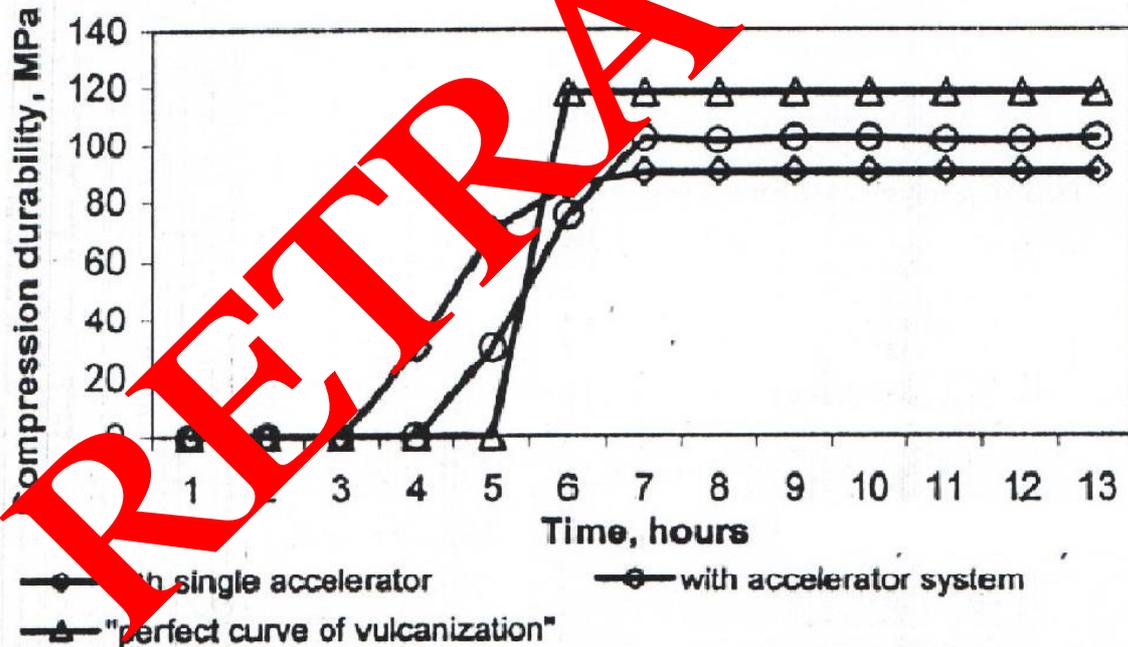


Figure 2. Kinetic curves of compression durability gain. 1 – with single accelerator, 2 – with accelerator system, 3 – “perfect curve” of vulcanization.

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 PBNR it is 7 parts of thiuram-D per 1 part of captax.

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 10 mass, % calcium-containing component (CaO) allows reduction of gas delivery and pore formation during vulcanization. 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:

$$\sigma_{\text{com}} = 0.34s(s - 100) - 0.28t(t - 17.9) - 0.14z(z - 8.36) - 782.1 - 0.08st - 0.01tz \quad (12)$$

2. Those tested against bending:

$$\sigma_{\text{com}} = 0.07s(s - 100) - 0.13t(t - 17.07) - 0.06z(z - 59.2) - 197.5 - 0.01st - 0.02sz - 0.06tz \quad (13)$$

Table 2. Optimal composition RM for RubCon - PBN®.

Type of test	Mass parts of components					
	Rubber 3	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

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.

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.

Figure 3.1. Draft of testing gadget: 1- sample of *RubCon*; 2- calibrated rods; 3- plate; 4- centering bar. Characteristic pressure – deformation relationship is shown in Figure 3.

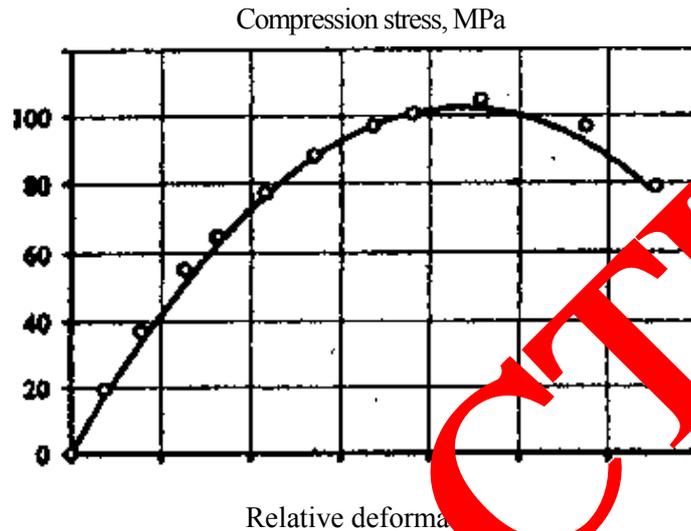


Figure 3. Relationship between relative deformation of *RubCon* and compressive stress.

Analytical form of this dependence may be submitted as:

$$\sigma = 2.6 + 241.4\varepsilon - 14\varepsilon^2$$

Let $v = \sigma/\sigma_R$; $\eta = \varepsilon/\varepsilon_R$; $k = \sigma_R/\sigma_R$. On the experimental base it is believed that dependence $v = f(k \eta)$ looks like square parabola $v = k \eta - \eta^2$, where σ , ε are the current values of compression stress and deformations correspondingly, σ_R , ε_R - coordinates of the diagram top, k - the factor depending on elastic-plastic properties of *RubCon*. Then,

$$\sigma = \sigma_R [k (\varepsilon / \varepsilon_R) - (\varepsilon / \varepsilon_R)^2] \tag{14}$$

and

$$\eta = 0.5[k \pm (k^2 - 4v)^{0.5}] \tag{15}$$

For the experiment performance the test *RubCon* samples in size 40 x 40 x 160 mm. were prepared. Tests were carried out in the special chamber, in the temperature range -80 °C ± +80° C appropriated to real operation conditions of the material. During experiments the stress-strain state of samples was determined depending on temperature of environment. In particular, the changes of the module of elasticity, ultimate strength at compression and the appropriate ultimate deformations of a material at influence of temperature were determined in comparison with the similar values obtained at test of control samples at room temperature.

Results of experiments at negative temperature range are illustrated in Figure 4. It is possible to see, that at the maximal negative temperature $-80\text{ }^{\circ}\text{C}$ the ultimate relative strain decreases on the average 14 % in comparison with control values, and ultimate strength at compression and the module of elasticity, on the contrary, are increased on 19 and 35 % correspondingly. It is necessary to note thus, that change of ultimate deformations linearly depends on temperature.

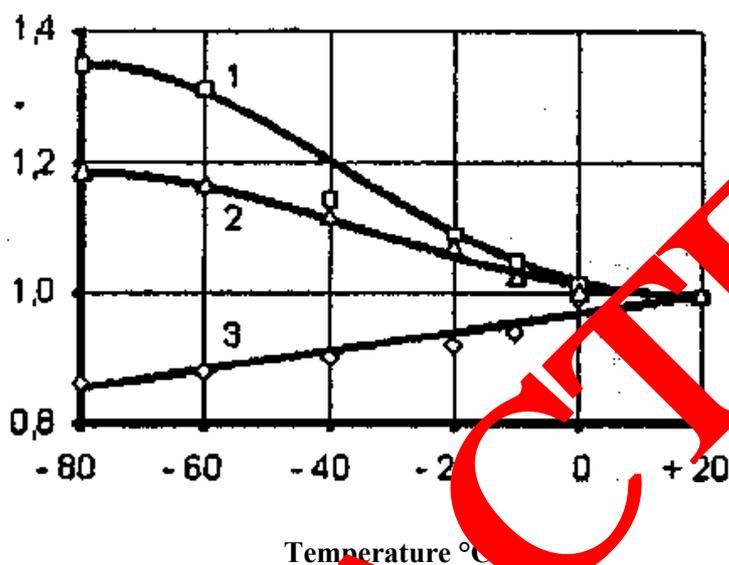


Figure 4. Influence of negative temperatures on the ratio of the module of elasticity (1), ultimate compression strength (2) and ultimate deformations at compression (3) to the similar values obtained at test of control RubCon samples at room temperature.

We have shown that microstructure of RubCon has elastic, elastic - plastic and viscous phases. The amount of elast in the composite is less in comparison with others and consequently deformability of RubCon at action a long-term and a short-term loadings in the greater degree is determined by plastic and elastic - plastic deformations.

Increase of the RubCon strength and the module of elasticity at compression and decrease of its ultimate deformations at negative temperatures can be explain by increase of a viscous phase viscosity and partial transformation of an elastic - plastic phase of a composite in elastic. The increase of an elastic phase results to embitterment of composite and by that to change of its stress-strain state.

2. CONCLUSIONS

- Experimental - theoretical investigation of central and eccentrically compressed short elements from *RubCon* (without buckling) is performed. The design procedure, which takes into account unlineary relationship between stress and strain and the valid diagram of deformation at uniaxial compression, is carried out on this base.

- The carried out researches of a new kind of polymeric concrete in a wide temperature range at action of compressive loading have shown an essential influence of the temperature environment on *RubCon* stress-strain state. Experimentally obtained temperature coefficients of strength and deformation characteristics of the material will allow to design load bearing and protecting structures in an operational temperatures rang.
- The increase of the particle size of coarse aggregate at constant reinforcement ratio results in decrease of *RubCon* compression, tensile and bending strength.
- Continuously reinforced *RubCon* has high compression, tensile and bending strength. Producing of steel fibers from tire cord is the way of tire industry wastes recycling.
- Creep deformation of rubber concretes has damping character; *RubCon* has non-linear stress - strain relationship; The mathematical model of creep deformations at long-time compressive loading agrees well with experimental results and can be put in a basis of design of *RubCon* load bearing structures;
- *RubCon* keeps high strength at complex influence of an aggressive environment and external loading. Steel fibrous *RubCon* is creep resisting material; coefficient of creep at compressive load $k_{cr} = 0.75$.
- Maritime Structures (pilings, docks and other exposed structures)
- Bridge Expansion Joints Bridge Deck Overlays
- Repairs Made to Load Bearing Supports

References

- [1] O. Figovsky, D. Beilin, *Advanced Polymer Concretes and Compounds*. CRS Press, N.Y. 2013, pages 267.
- [2] O. Figovsky, D. Beilin, A. Leykin, *Recent Patents on Corrosion Science* 3(1) (2013) 22-26.
- [3] O. Figovsky, D. Beilin, A. Leykin, *International Letters of Chemistry, Physics and Astronomy* 10(1) (2013) 107-109.
- [4] T. Borowski, *Material Letters* 62 (2008) 1382-1384
- [5] T. Borowski, *International Letters of Chemistry, Physics and Astronomy* 2 (2012) 1-6.
- [6] Borowski, T. Borowski, *International Letters of Chemistry, Physics and Astronomy* 4 (2013) 1-6.

(Received 15 February 2014; accepted 19 February 2014)