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Development of Polymer Concrete with Polybutadiene Matrix

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Abstract

Composite materials based on polymer binders and mineral fillers are widely used as structural chemically resistant, vibration and impact proof materials for industrial construction and chemical machinery. Up to the present hetero-chain polymers, unsaturated polyesters, polyepoxy and polyuretanes are applied as binders of such concrete–polymer composites. A new type of conglomerate composites–polymer concrete based on polybutadiene belonging to the liquid rubbers (RubCon—Rubber Concrete) has been enveloped and investigated. Such a rubber is used as a binder hardened by sulphur in the presence of special admixtures. Quartz sand and fly ash may be used as fillers and fine grained granites and basalt chipping as coarse aggregate. The resulting material has high acid and alkali resistance, toughness and adhesion to metal reinforcements, low water absorption and remarkable compression strength (80–90 MPa). A series of RubCon compositions are presented and industrial production technology for chemically resistant items and structures is worked out. The experimental samples of the material were successfully applied in real plant conditions at constant action of concentrated solutions of sulphuric acid and caustic potash. © 1997 Elsevier Science Limited

INTRODUCTION

The interest in polymer concrete continues as evidenced by the activity of users and researchers. Main binders of such concrete are polyester, epoxy, furan and acrylic resins. Current and future developments in unsaturated polyesters will be strongly influenced by laws limiting styrene emissions.[1] High strength epoxy resin-based polymer concretes have the biggest cost and are used mainly as cavitation resistant materials for offshore structures, materials for monolithic floorings and for the machine-tool making industry.[2,3]

Investigations of advanced polymer concrete based on new oligomeric binders with the carbochain structure of them are very important because hydrolytically proof binders make possible the preparation of the polymer concrete with the highest acid and alkali resistance, toughness and adhesion to steel reinforcement.[3]

Composite materials on oligodiene base hardened by the standard sulphur system are successfully used in anticorrosive technology. In order to improve physical and technical properties, to decrease the compositions cost and consequently to expand an application spectrum of these composites, fillers and aggregates of organic and inorganic nature were used.[4]

COMPONENTS OF RUBCON (RUBBER CONCRETE)

Low molecular polybutadiene belonging to the class of liquid rubbers is a main binder component of the new material named by authors RubCon.[4,5] Such rubbers with consistency of viscous liquid define the possibility of its processing through the free moulding when not under high pressure.

It has been known that liquid polybutadienes are hardened through double bonds of polymer chains with sulphur, oxidizing–restorative or peroxide systems present. The curing group consists of vulcanizing agents, accelerates, vulcanization activators and special additives. The principal curing agent is an elementary sulphur. Vulcanizates, which result in sulphur application are characterized by a high strength, endurance under repeated deformation and low aging owing to polysulphur bonds.

The curing accelerators were used for the purpose of increasing the velocity of chemical reactions between sulphur and rubber and decreasing the vulcanization temperature. An acceptable curing velocity was reached using Tiuram-D and Tsimat. For more effective influence on acceleration the inorganic and organic activators are applied. We used zinc oxide as an activator. Special additives such as plastificators (for decreasing the mixture viscosity and inner stress and increasing the strength–impact loads), anti-oxidants and absorbents were introduced in matrix composition.

For the purpose of inner stress, creep and shrinkage decrease we used the fillers as finely dispersed inorganic and organic matters. Such fillers were quartz sand (specific surface S_{ss} = 100–400 m^2/kg) and fly ash (S_{ss} = 200 m^2/kg). Finally, for preparation of concrete type conglomerate composition, fine grained aggregates were added in RubCon mixture. The sands (0.14–5 mm) and different kinds of chipping and gravel with grains 5–70 mm were used as fine and coarse aggregate, respectively.

STRUCTURE AND PROPERTIES OF RUBBER COMPOSITIONS

As an investigation attempt we separated compositions based on the liquid rubber into structural subsystems series according to the matrix-inclusions' relation:

liquid rubber and all components of vulcanization group (rubber matrix);

rubber matrix and finely dispersed filler (rubber binder);

rubber binder and aggregates (RubCon)

Certain combinations of these subsystems provide a basis for production of rubber mastics and fine and coarse grained RubCon.

Rubber matrix

The compressive strength of cube samples with rib length 4 cm was selected as a criterion of optimum composition. Application of an experiment planning method (the setting up of an experiment in specified points of data space) made it possible to localize optimum with required accuracy and to reduce considerably the experiment number as compared to traditional methods of 'passive' experiment.

Optimization of the rubber matrix composition was carried out according to the Kifer–Jonson method.[6] During the test, the sulphur content optimum was localized. As illustrated in Fig. 1 the optimal content of sulphur in the rubber matrix composition is 49.6–50.8 parts per 100 parts of rubber.

Considering that in practice the vulcanization does not always proceed at high temperatures we carried out composite formulae which are used for vulcanization at lower temperatures. The acceptable vulcanization velocity was reached with Tiuram-D and Tsimat and zinc oxide as activator. The dosage of Tiuram-D is 2 parts per 100 parts of rubber at a zinc oxide content of 20 parts.

The relationship between compressive strength of composite and accelerators and activators contents was studied with the provision that the sulphur content is retained constant. The grounded quartz sand at 300 parts per 100

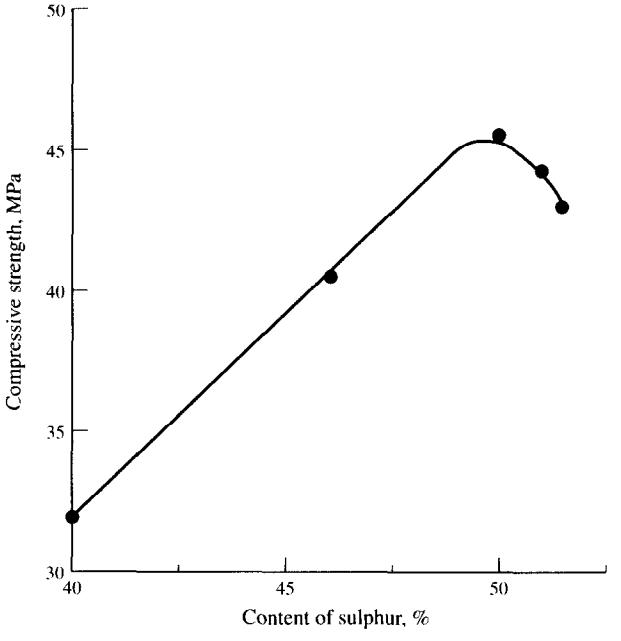

Fig. 1. Search of optimal content of sulphur in polymer matrix.

parts of rubber was added in the composition. Vulcanization proceeded at 120°C. The orthogonal plan of second order type 3^2 was realized within the framework of the experiment planning method.

After data handling the regression equation was obtained:

$$\sigma_{compr} = 35.12+4.61x_1+6.17x_2+1.83x^2_1 +1.23x^2_2-2.86x_1x_2 \quad (1)$$

where: σ_{compr}—compressive strength, x_1,x_2—content of accelerator and activator, respectively. The Fisher criterion has shown that the equation is valid with 0.95 confidence probability. Graphical representation of the response function is illustrated in Fig. 2.

Rubber binder

Filling rubber compositions belong to heterogeneous–disperse systems. Rheological variations of these systems are determined by their formulation and structure. Viscosity is a principal rheological feature and the most important technological characteristic of filling compositions. An optimal parameter of compositions and composite materials production is viscosity dependence. The number of 'connectedness' system factors may be separated: 1—viscosity at slip of particles over liquid phase interlayers, 2—dry friction at contact of articles to one another, 3—capillary attraction in the menisci formation, 4—interparticle interaction, 5—hydrodynamics under particle deformation in liquid. Manifestation of all or part of these factors predetermines the viscosity of the heterogeneous–disperse system and its rheological behavior.

The authors investigated the viscosity of rubber binder and its strength relationship according to quantity, dispersivity and kind of filler. In the latter case we used ground quartz sand with specific surface S_{ss} = 100, 200, 300 and 400 m^2/kg and fly ash with specific surface 200 m^2/kg. Rheological properties of disperse systems at specified conditions are only a function of the amount of filler. Because of this we were changing the relationship between unfilling composition and composition with different specific surfaces of fillers. The experiment results are illustrated in Fig. 3 and Table 1. Figure 3 gives the relationship between dynamic viscosity and volume of micro fillers.

Conventionally three zones may be separated on this curves.

In the first zone viscosity increases moderately with increase of fillers particle concentration. These phenomena are concerned with lack of disperse phase quantity for structuring of the system. This is known as a

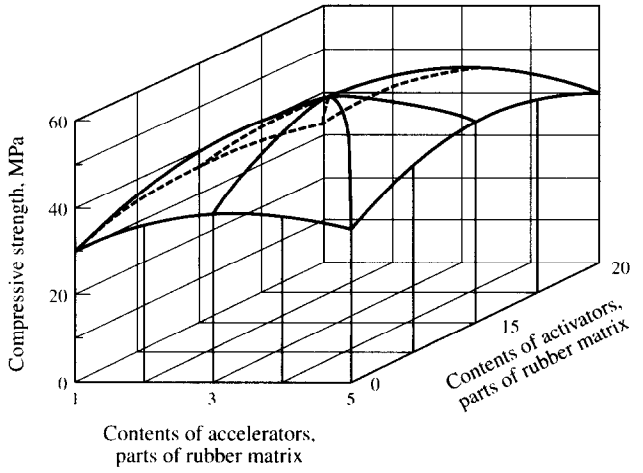

Fig. 2. Relationship between rubber matrix strength and content of accelerator and activator.

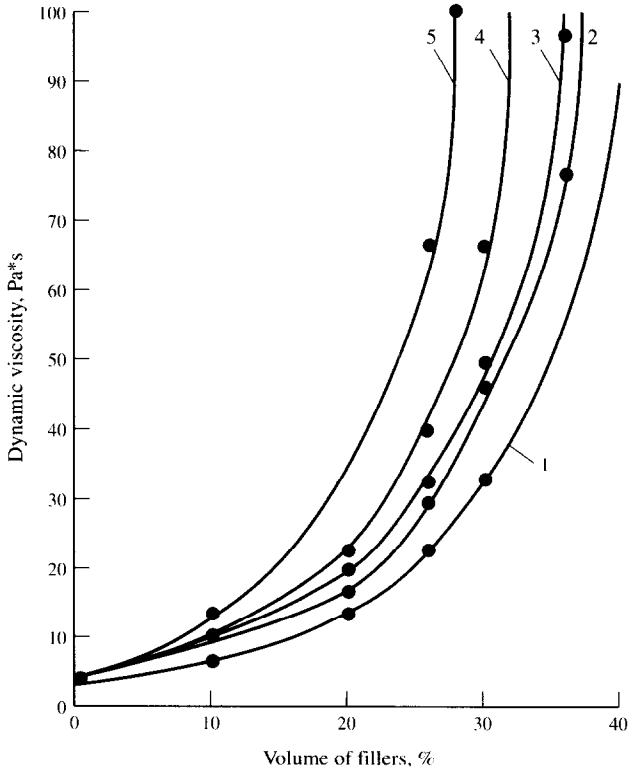

Fig. 3. Relationship between dynamic viscosity of binder and volume of fillers. 1–4: quartz sand with S_{ss} = 100, 200, 300 and 400 m^2/kg, respectively; 5: fly ash S_{ss} = 200 m^2/kg.

Table 1.

Indices	*Composition*			
	1	*2*	*3*	*4*
Density (kg/m^3)	2100–2200	2100–2200	2100–2200	2150–2300
Strength (MPa)				
at compression	70–80	75–85	80–90	70–75
at bending	18–25	20–25	25–30	18–25
at tension	12–15	12–15	13–19	12–15
Modules of elasticity (MPa $\times 10^4$)	1.2–2.5	1.2–2.5	1.9–2.7	1.2–2.5
Poison's ratio	0.20–0.26	0.26–0.28	0.26–0.28	0.26–0.28
Thermal conductivity coefficient (W/m/°C)	0.3–0.5	0.3–0.5	0.3–0.5	0.3–0.5
Heat stability (°C)	80–100	80–100	80–100	80–100
Water absorption (%)	0.05–0.06	0.05–0.06	0.05–0.06	0.05–0.06
Coefficient of chemical resistance				
–20% solution of sulphuric acid	0.97	0.98	0.975	0.97
–10% solution of lactic acid	0.95	0.965	0.96	0.95
–20% solution of caustic potash	0.96	0.975	0.98	0.96
water	0.995	0.995	0.995	0.995

'floating' structure in which filler particles are widely separated. Rheological behavior of the system in this zone is determined essentially by liquid phase viscosity.

In the second zone the viscosity is increased intensively since filler particles make a major contribution in rheological state of system. Aggregates from particles separated by thin liquid films are generated in structure. In response to the merging of primary aggregates the composite space structure is formed.

In the third zone the increase of filler causes a drastic rise of viscosity. As this takes place the system 'sensitivity' to variation of disperse phase quantity is increased. On further filler increase, a deficiency of liquid phase is detected resulting in breaks in film structure of matrix and pores.

The dependence between viscosity of filling system and quantity of quartz filler specific surface for different volume concentrations Ψ is shown in Fig. 4 by the set of straight lines with different inclinations to the abscissa.

It can be seen that with the increase of particle specific surface, the viscosity is increasing. With the rise of filler content, viscosity increases steeply.

A distinguishing characteristic of the composite materials with disperse filler is the extreme change of their strength with increase of filler volume and surface area. Optimal filler content conforms to maximal strength. In an effort to study the quantity, specific surface and filler-type influence on the rubber binder strength, we prepared and examined the series of samples $40 \times 40 \times 160$ mm.

Figures 5 and 6 give the filler strength dependence of different filler kinds volume and specific surface. As may be seen for every value of filler specific surface there is an optimal particle concentration and strength level. So, for quartz filler, maximal strength of rubber binder is achieved at specific surface 300 m^2 and filling $\cong 30\%$ (Fig. 5). It should be noted that as dispersivity increases (at constant filling) the binder strength decreases (Fig. 6). This strength decrease is due to deterioration by wetting conditions of particles and as a result the capsules

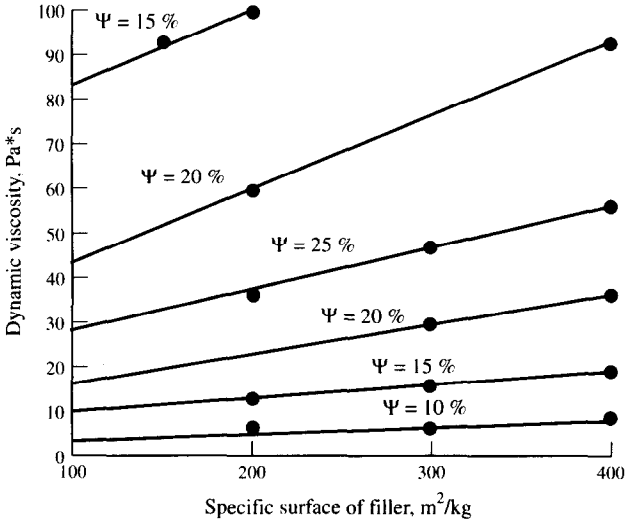

Fig. 4. The dynamic viscosity of binder dependence of filler specific surface.

from aggregating particles are formed which reduce binder strength.

Rubber concrete (RubCon)

Accomplished investigations made it possible to suggest a number of RubCon compositions for chemically resistant products and structures and to reveal the main physical and mechanical characteristics (Table 1).

We investigated the process of RubCon deformation at short term action of compressive load (T) as well. Based on obtained data, an analysis of volume deformation and change of transverse deformation coefficient was obtained. As illustrated in Figs 7(a) and (b), as the load increases, Poisson's ratio in first moment is kept constant, but sample volume is decreased. RubCon is tightened as a result of viscosity flow deformation and technology defects of structure. This process proceeds to a load point equal to 55% of the rupture load (T_R), following which the process of micro destruction and the development of micro cracks became evident. For higher loads Poisson's ratio continues to increase and volume increment is

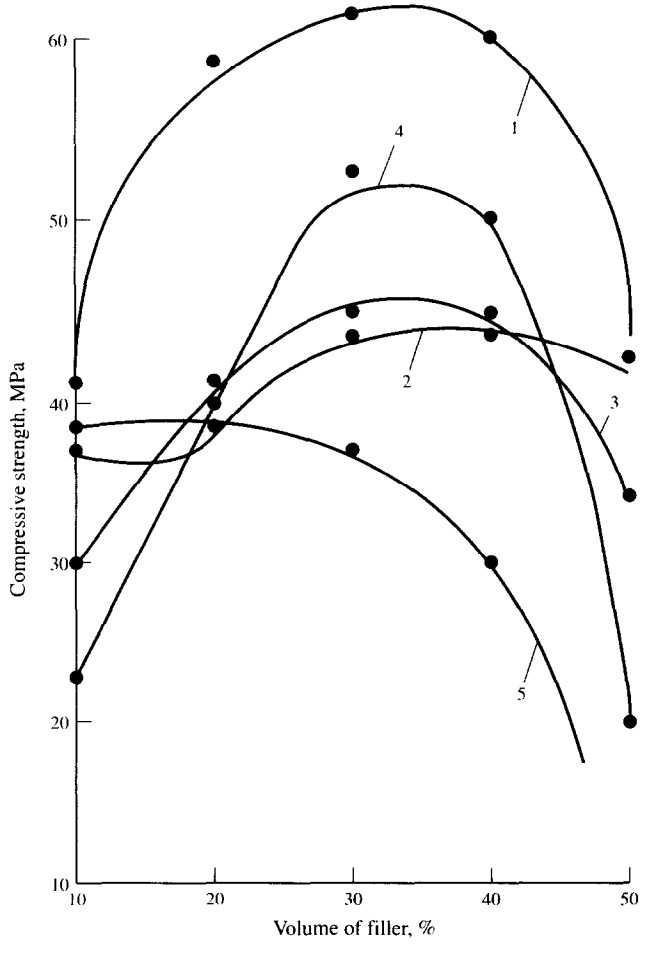

Fig. 5. Binder strength dependence of filler volumes. 1: fly ash (S_{ss} = 300 m^2/kg); 2–5: quartz sand (S_{ss} = 100, 200, 300 and 400 m^2/kg), respectively.

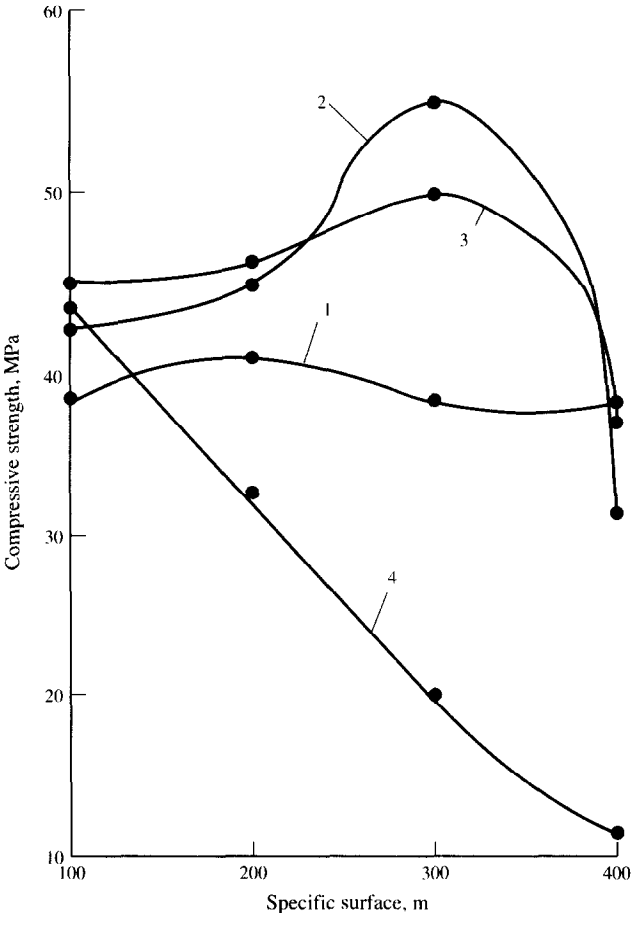

Fig. 6. Binder strength dependence of filler volumes. 1–4: 20, 30, 40 and 50% of filler, respectively.

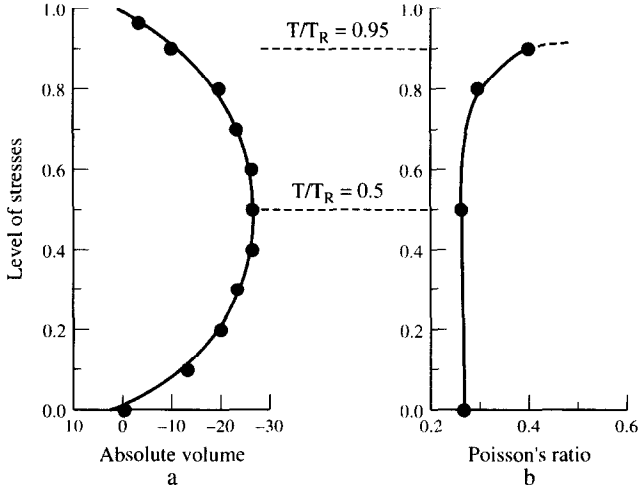

Fig. 7. The variation of sample volume (a) and Poisson's ratio (b) at compression.

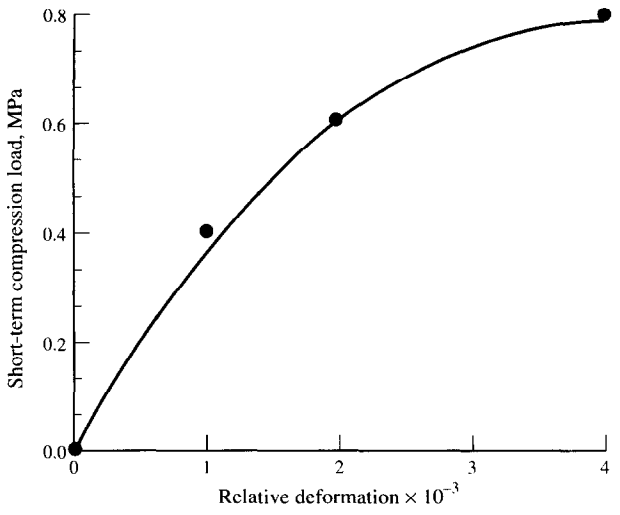

Fig. 8. Relationship between relative deformation of RubCon and compressive load.

decreased. At a load equal to 95% of the rupture load Poisson's ratio is 0.5.

The relationship between stress and strain for samples $70 \times 70 \times 280$ is illustrated in Table 1 and Fig. 8.

During the experiment we controlled a process of samples destruction. It took place in working zone along filler grains and binder structure faults. The destruction surface was a well-marked cone-shaped form which is an inherent feature of the polymer concrete. We did not detect the rupture along the boundary, consequently for RubCon the strength of adhesion connections with filler is higher than the latter strength and cohesion strength of polymer binder.

In the investigation framework we studied creep of RubCon as well. Samples $70 \times 70 \times 260$ mm were loaded with the help of a special lever system and ball supports. As a result the samples were subjected to axial compression. During the test we analyzed the dependence of RubCon stress–strain state on the value and time of compressive load action. The samples series were tested under constant compression and equal to 35, 45, 55, 65, 75 and 85% of mean ultimate strength, which was received from short time tests.

Analysis of creep test results revealed that at compression load action (35, 45 and 55% of T_R) creep deformation is stopped after 30 days and is not changed for a year. Creep of samples under 65 and 75% of ultimate load was terminated for 2 months. Rupture of samples at 85% of T_R was detected after 20 days.

Chemical resistance is a main criterion for application of structural materials used in aggressive media. Assessment of the vulnerability of polymer concrete based on the polybutadiene matrix chemical durability was tested.

The criterion of chemical resistance of RubCon was a compressive strength test after immersion in chemical solutions. Samples $(40 \times 40 \times 160)$ were immersed in aggressive media and thereafter tested at compressive load after 30, 90, 180 and 270 days. In addition we examined six control samples which were stored in normal conditions. For chemical resistance study of RubCon we used 20% solutions of sulphuric acid, 10% solution of lactic acid and 20% solution of caustic potash and water.

The coefficient of chemical resistance K_{CR} is:

$$K_{CR} = \frac{\sigma\tau}{\sigma v} \tag{2}$$

where σ_τ, σ_v compressive strength of samples exposed in aggressive media and normal condition for a time τ days, respectively. The variation of sample mass ΔM after associated exposition terms is:

$$\Delta M = \frac{M_\tau - M_v}{M_\tau} \tag{3}$$

where M_τ, M_v—sample mass after and before exposition in medium for a time τ days. The relationships between compressive strength, coefficient of chemical resistance and variation of samples mass on the one hand and exposition time on the other hand are presented in Fig. 9 and Table 1.

One can see that the maximal resistance of RubCon is observed in water medium. Within the span of investigation the strength drop of RubCon was not noticed, water absorption is 0.05 mass%. That small change is due to high water-repellent properties of RubCon samples. Their surface practically will not be wetted by water. Aggressive media action is manifest more intensively in the course of the first three months. As this takes place, about half of the strength decrease was noticed on the first exposition month. A strength reduction and variation of sample masses for a time 170 days in sulphuric and lactic acids and caustic potash

were (%): 2.9 and 0.2, 3.5 and 0.26, 2.4 and 0.16, respectively. After 270 days exposition the color and appearance of samples have not changed and the surface layer has not softened apparently. This means that RubCon on the low molecular liquid rubber base is characterized by high chemical resistance and low sorption to different aggressive media.

Based on the tests it was determined that strength change of RubCon with time under the action of aggressive media is governed by:

$$R_{\tau i} = R_v e^{-\lambda\tau} \tag{4}$$

where $R_{\tau i}$—strength of material for time τ, R_v—initial strength of material, λ—coefficient of wear. The latter is the relative velocity of associated durability parameter change. Then, the coefficient of chemical resistance:

$$K_{CR} = \frac{R_d}{R_v} = e^{-\lambda\tau} \tag{5}$$

After taking the logarithm for time moment τ one obtains:

$$\ln K_{CR} = -\lambda\tau \tag{6}$$

If for some set (τ, R_v, R_τ) the values of K_{CR} are known, the optimal value of coefficient λ will correspond to a minimum according to the following expression:

$$\sum_i^n (\ln K_{CR} + \lambda\tau^2) \Rightarrow \min \tag{7}$$

where n—number of tested samples. Then

$$\lambda = \frac{\sum_i^n \tau_i \ln K_{CR}}{\sum_i^n \tau^2} \tag{8}$$

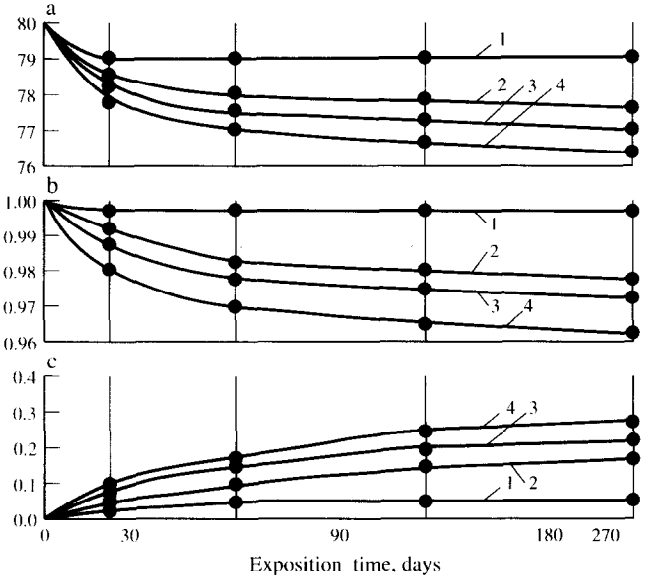

Fig. 9. The RubCon characteristics dependence of exposition time on aggressive media. 1—water; 2—solution of sulphuric acid; 3—solution of caustic potash; 4—solution of lactic acid; a—compressive strength (% from ultimate load); b—coefficient of chemical resistance; c—variation of mass%.

Experimental and calculated results are given in Table 2. From this table it follows that RubCon is a high-reliability material and in particular may be used as floor covering in conditions of aggressive media action. RubCon floor plates and wall lining plates were tested industrially in synthetic rubber plant (shop of acids pumping). After 3 years operating in conditions of permanent action of sulphuric acid and caustic potash solutions, we did not detect surface changes. Control plates from the same

Table 2.

Medium	*Coefficient of wear after 1 month*	*Coefficient of chemical resistance*		
		12 months Experimental	*Calculated*	*10 years Predicted*
20% solution of sulphuric acid	3.13×10^{-3}	0.971	0.965	0.687
10% solution of lactic acid	4.97×10^{-3}	0.963	0.956	0.551
20% solution of caustic potash	3.90×10^{-3}	0.976	0.972	0.626

composition show higher resistance after 720 days exposition ($K_{CR} = 0.05 - 0.97$).

CONCLUSION

A new type of polymer concrete with polybutadiene matrix (RubCon) was developed and studied on the experimental base. Optimal component composition of RubCon was determined by experimental planning methods. A variety of important physical and mechanical properties in part stress–strain state at short- and long-term loading was studied. Particular emphasis has been placed on material behavior in aggressive media. Investigations demonstrated that RubCon is characterized by higher chemical resistance and low sorption to difference corrosive media.

The combination of high stress–strain, water and chemical resistance indices make it possible to recommend RubCon for application in products and structures operating in aggressive media, e.g. floors of industrial buildings, lining structures, pickling, galvanic and electrolysis baths, etc.

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