Chapter 19

DEVELOPMENT OF GREEN ENGINEERED CEMENTITIOUS COMPOSITES

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ABSTRACT

In this article, a new green composite is developed. The green composite presented in this paper, consisted of renewable raw materials such as soil, cement and natural fibres. Natural fibres used at an appropriate length and amount can develop sufficient bond with the soil-cement to enhance the overall toughness of the green composite.

1. INTRODUCTION

Manufacturing high performance engineering materials from renewable resources is one ambitious goal currently being pursued by researchers across the world the ecological benefits of renewable raw materials are clear: they save valuable resources, are environmentally sound and do not cause health problems[1-5].

Natural fibres are getting attention as a reinforcing agent in both thermoplastic and thermoset matrices. These composites possess good mechanical properties Such as relatively high strength and stiffness of natural fibres combined which makes it a covetable substitute for synthetic fibres that are potentially toxic [6-10]. Their low-density values allow producing composites that combine good mechanical properties with a low specific mass [11]. With regard to the environmental aspects it would be very interesting if natural fibres could be used instead of glass fibres as reinforcement in some structural applications. Natural fibres have many advantages compared to glass fibres, for example they have low density, they are recyclable and biodegradable [12, 13-18].

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Two major areas of enquiry exist in the field of fibre-matrix adhesion in composite materials. One is the fundamental role that fibre-matrix adhesion plays on composite mechanical properties. The other is what is the best method used to measure fibre-matrix adhesion in composite materials[5, 20-24].. In order to analyze the mechanical behaviour of adhesively bonded joints, several studies have been conducted.

It appears that the most promising method for joining fiber-reinforced composite structures is adhesive bonding. The use of right coupling agent is expected to improve the fiber-matrix adhesion [25]. It is interesting to see that increasing tensile strength with increasing fibre content is only valid for the systems with the coupling agent. . For the systems without coupling agent, the fibre acts as an included filler in the resin matrix, which actually weakens the composite because of poor interfacial adhesion [26].

The mechanical properties of a composite material depend primarily on the strength and modulus of the fibers [27]. An effective use of fibre strength is dependent on both the interfacial adhesion properties and the critical fibre length.

We must consider that the major part of the cellulose consists of a micro-crystalline structure with high order of crystalline regions. Generally, higher cellulose content leads to higher stiffness, in turn the cellulose content have a major influence on the mechanical properties of the resultant composites. Because of the structural features, the high level of moisture absorption and poor wettability of the natural fibre material results in insufficient adhesion between fibres and polymer matrices leading to debonding during use and aging so that the quantity of the fiber in the composite must be optimum [26,28-29].

As aforementioned, the measured average fibre length in the short-fibre composite plate is far below the critical fibre length for all the systems in this study. This allows us to use a modified rule of mixture taking account of interfacial properties for the strength of natural fibre/ polymer composites, σ_c , as a function of volume fraction:

$$\sigma c = [\eta L f \tau /(d\text{-}\sigma m)]Vf + \sigma m \tag{1}$$

where η is the fibre orientation factor σm and Vf are tensile strength of matrix and volume fraction of fibre, respectively [30].

Young's modulus reflects the capability of both fibre and matrix material to transfer the elastic deformation in the case of small strains without interface fracture. The Young's modulus of the composite is determined by the equation :

$$Ec = \beta \, (\acute{E}mV \, m + EfVf) + (1\text{-} \beta) \, EfEm \, /(\, EmV f + EfV \, m) \tag{2}$$

where β is a factor of efficient stress transfer between fibre and matrix. E is the Young's modulus; c, m, f, refer to the composite, matrix and fibre respectively. For all systems, Ec values increase almost linearly with increasing fibre content.

Micromechanical models that incorporate the properties of the composite and matrix material may be employed to determine the elastic properties of the composite.

2. Experimental Program and Results

Soil stabilization is a process to improve certain properties of a soil to make it serve adequately an intended engineering purpose. The improving of the ground properties with various methods is a common case of geotechnical engineering. The aim of the soil stabilization is to decrease the consolidation and permeability capacity and to increase bearing and shear resistance capacity [32].

Natural fibres used at an appropriate length and amount can develop sufficient bond with the soil-cement to enhance the overall toughness of the composite. The slope of stress/strain curve (below yield point) denotes material's stiffness; steeper the curve, the stiffer material, gradient is known as modulus of elasticity or Young's modulus.

The soil used in this experimental program is a common mason sand with a grain size distribution such that 100%, 94%, 56%, 22%, 9%, and 5%, of the material passes the No. 10, No. 20, No. 40, No. 60, No. 120, and No. 200 sieves, respectively. The coefficient of uniformity, C_u and the coefficient of curvature, Cc, for this soil are 2.65 and 1.02, respectively.

Gradation and soil classification of samples is given in figure 1 in terms of particle size distribution and soil classification.
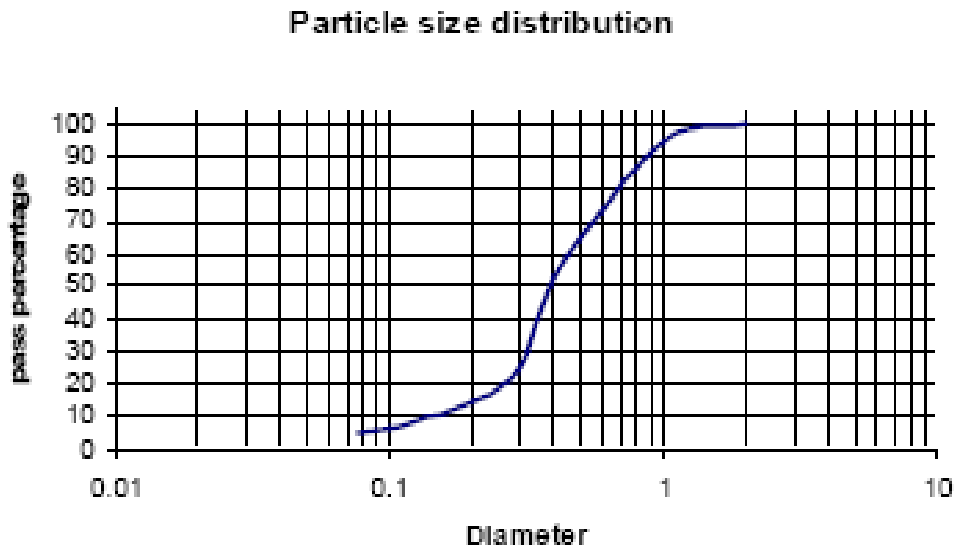

Figure 1. Particle size distribution.

The cement used is ordinary Portland cement. The physical and chemical properties of the cement are given in table 1.

Jute yarn of 1100 tex yarn fineness was obtained from local firms. Jute yarn was dried in an oven at 100 °C for 4 h, then it was tested for moisture absorption by exposing the yarn to 50% and 95% RH atmosphere (in desiccators), at 23° C.

Table 1. Physical and chemical properties of the cement

Physical properties	Cement
Fineness	3.12
Chemical composition	
Silica (SiO2)	20.44%
Alumina (Al2O3)	5.5%
Calcium oxide (CaO)	64.86%
Potash (K2O)	22.31%
Magnesia (MgO)	1.59%
Loss on ignition	1.51%
PH	12.06
3CaO. SiO2	66.48%
2CaO. SiO2	10.12%
4CaO. Al2O3. Fe2O3	9.43%
Free lime	1.65%
3CaO. Al2O3	8.06%

Brazilian tests were performed to obtain the tensile strength of specimens, based on ASTM C496 for indirect tensile test. The size and curing time of both tensile and compressive samples were similar. The load to failure was recorded and the tensile strength was computed as follows:

$$\sigma_t = \frac{2P}{\pi l d}$$

(3)

Where:

σ_t = Indirect tensile strength

P = Applied maximum load

l and d = length and diameter of the specimen, respectively

The experiments were conducted with cement content varying jute percentage (figures 2 and 3).
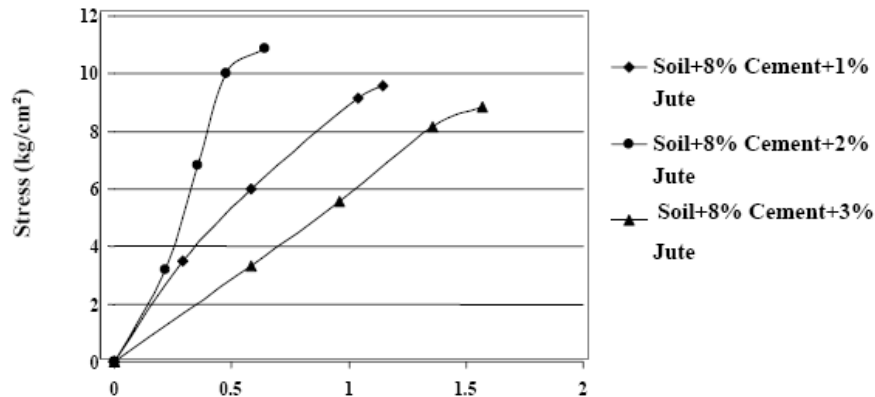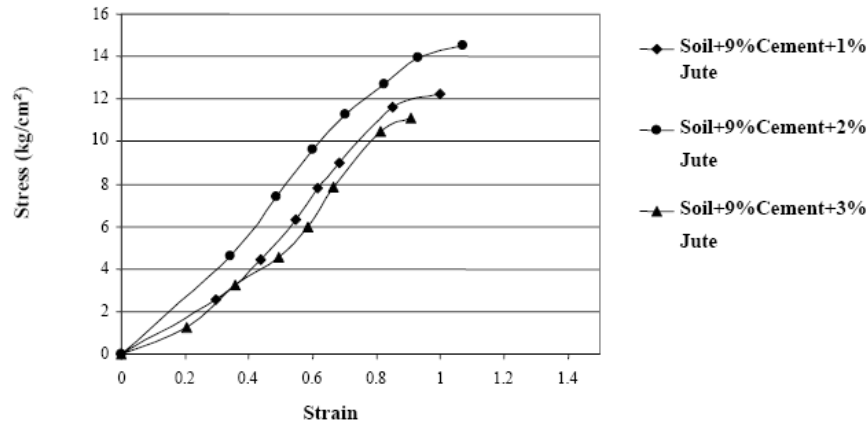
Figure 2. Stress-strain green composite.

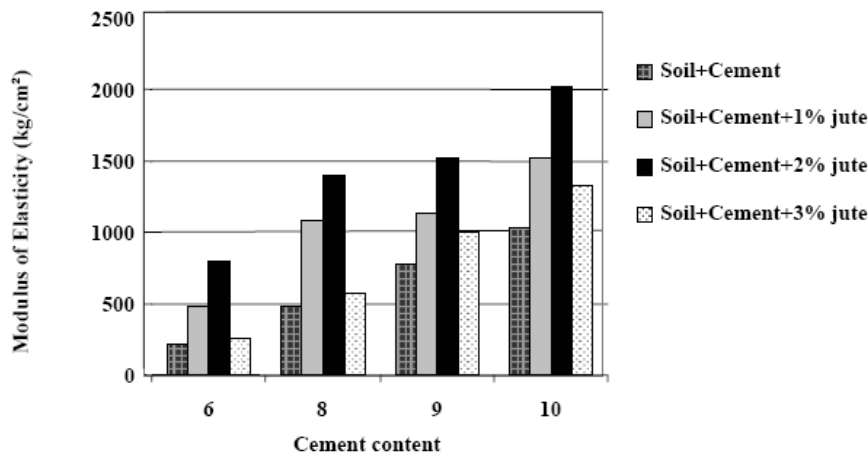Figure 3. Stress-strain of green composite.

Figure 4. Comparison between modulus of elasticity of reinforced and non-reinforced green composites.

Figure 4 shows comparison of modulus of elasticity between different mixture conditions.

Experimental results show that an increase in the percentage of cement content results in an increase in the modulus of elasticity. Also, adding Fibres by one constant percent of cement results in an increase in the modulus of elasticity and toughness. Figure 4 shows that the maximum modulus of elasticity obtains from mixtures by 2% fibres content and it drops after the improvement of fibres from 2 %.(but it still is higher than similar rates in cases without fibres.)

Indirect tensile strength tests were conducted on stabilized soil specimens containing 8,9,10 percentage of cement, non-reinforced and reinforced with 1, 2, 3 percentage of Jute.
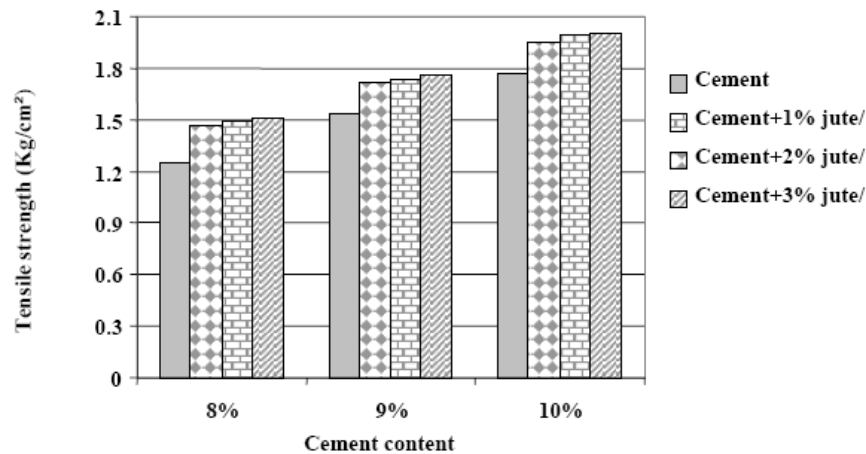
Figure 5. Tensile strength of green composite.

Two important parameters can be considered and discussed, when Jute used as reinforcing fibres in cement stabilized sand samples. First of all, an increase in the tensile strength of specimens can be observed when specimens are reinforced with Jute. Secondly; increase of cement content for a constant Jute percentage increases the tensile strength of mixture.

The results of this experimental investigation in general indicate the importance of modulus of elasticity in evaluation of composite stiffness and interfacial bond between natural fibre and matrix.

3. OVERVIEW

The elastic properties of short fiber reinforced plastics can be experimentally determined or derived from a variety of mathematical models. The advantage of a comprehensive mathematical model is it reduces costly and time-consuming experiments. Furthermore, a mathematical model may be used to find the best combination of constituent materials to satisfy material design considerations. Lastly, a physical (as opposed to empirical) model can yield insight into the fundamental mechanisms of reinforcement. [33]

The purpose of the micro mechanical models is to predict the properties of a composite based on the properties of each constituent material [48]. Properties such as the elastic modulus Ec, Poisson's ratio (ν) and the relative volume fractions (V) of both fiber and matrix are the fundamental quantities that are used to predict the properties of the composite. In some cases, fiber aspect ratio and fiber orientation are also included [33].

The variation of the amount of fibers in a natural fiber composite can be successfully chosen to correlate with the mechanical properties of composite. The amount of fibers is one of the most important characteristics of any composite material since their mechanical properties are strongly dependent on it [34].

The volume fraction of fibers is commonly used to estimate certain mechanical properties of the composite material. Besides, the type of fibers distribution (aligned or random) and

their mechanical properties as well as properties of resin should be available. The volume fraction of a composite is obtained by the following formula:

$$Vf = \rho m Wf / (\rho m Wf + \rho f Wm) \tag{4}$$

Where *Wf* is the fiber weight fraction, *Wm* the matrix weight fraction, *ρf* the density of the fibers and *ρm* the density of the matrix [26,48-49].

The mechanical properties of a composite material depend primarily on the strength and modulus of the fibers, the strength and the chemical stability of the matrix and the effectiveness of the bonding between matrix and fibers in transferring stress across the interface. Generally, the utilization of natural fibers as reinforcing materials in thermoplastics requires strong adhesion between the fiber and the matrix. Cellulose has a strong hydrophilic character due to three hydroxyl groups per monomeric unit, but biopolymers are generally hydrophobic [27]. A large number of research interests were dedicated to theoretical and numerical models with varying degrees of success.

It is necessary to perform comparison of the methods in order to determine the best approach. In this paper the following models are applied to green composites:

1. Rule of mixture (ROM) [35]
2. Inverse rule of mixture (IROM) [36]
3. Cox's model [37]
4. Halpin-Tsai equation [38-39]
5. Our proposed model

3.1. Rule of Mixture (ROM)

The simplest available model that can be used to predict the elastic properties of a composite material is the rule of mixtures (ROM). To calculate the elastic modulus of the composite material in the one-direction E_1, it is assumed that both the matrix and fiber experience the same strain. This strain is a result of a uniform stress being applied over a uniform cross sectional area. The ROM equation for the apparent Young's modulus in the fiber direction is:

$$E_1 = E_f V_f + E_m V_m \tag{5}$$

Where E_f, E_m, V_f and V_m are the moduli and volume fractions of the fiber and matrix materials respectively. This model works extremely well for aligned continuous fiber composites where the basic assumption of equal strain in the two components is correct [33, 40-47].

The modified representation of the ROM which was adopted to estimate the modulus of elasticity of a composite material with long randomly distributed fibers is as follows [48-49]:

$$E_1 = \eta E_f V_f + E_m V_m \qquad \text{Or} \qquad E_1 = \eta E_f V_f + E_m \left(1 - V_f\right) \tag{6}$$

It takes into account the weakening of the composite due to fibers orientation and fiber length factors through introduced additional coefficient, $\eta < 1$. Some attempts by other researchers have been done in order to estimate η. For example, in [50] it is suggested to apply $\eta = 0.2$ for a composite reinforced with randomly oriented natural fibers [34].

3.2. Inverse Rule of Mixture

The elastic modulus of the composite in the two-direction (E_2) is determined by assuming that the applied transverse stress is equal in both the fiber and the matrix (Reuss's assumption) [51]. As result, E_2 is determined by an inverse rule of mixtures equation that is given as:

$$E_2 = \frac{1}{\dfrac{V_f}{E_f} + \dfrac{V_m}{E_m}} \qquad \text{Or} \qquad E_2 = \frac{1}{\dfrac{V_f}{E_f} + \dfrac{1-V_f}{E_m}} \tag{7}$$

3.3. Modified Rule of Mixture

The Cox shear lag theory adds to the ROM the shear lag analysis, which includes a fiber length and a stress concentration rate at the fiber's ends. The model is described by equation (2), in which the coefficient η is written as follows:

$$\eta = 1 - \frac{\tanh\left(\dfrac{\beta l}{2}\right)}{\left(\dfrac{\beta l}{2}\right)} \tag{8}$$

where l is the length of fibers and β is the coefficient of stress concentration rate at the ends of the fibers, which can be described by the following equation. 9:

$$\beta = \frac{l}{r}\sqrt{\frac{E_m}{E_f(1+v)\ln\sqrt{\dfrac{\pi}{4V_f}}}} \tag{9}$$

where v is Poisson's ratio of fibers and r is the fiber radius.

3.4. Semi-Empirical Equations

The semi-empirical equations developed by Halpin and Tsai are widely used for predicting the elastic properties of SFRT. The following form of the Halpin and Tsai equation is used to predict the tensile modulus of SFRT [33]:

$$E_1 = E_m \left(\frac{1 + \xi \eta V_f}{1 - \eta V_f} \right) \tag{10}$$

In equation (6) the parameter η is given as:

$$\eta = \frac{\left(E_f / E_m\right) - 1}{\left(E_f / E_m\right) + \xi} \tag{11}$$

Where ζ in equations (6) and (7) is a shape fitting parameter to fit the Halpin–Tsai equation to the experimental data. The significance of the parameter ζ is that it takes into consideration the packing arrangement and the geometry of the reinforcing fibers [33, 48-49]

A variety of empirical equations for ζ are available in the literature, and they depend on the shape of the particle and on the modulus that is being predicted [39]. If the tensile modulus in the principle fibre direction is desired, and the fibers are rectangular or circular in shape, then ζ is given by the following equation [39]:

$$\xi = 2\left(\frac{L}{T}\right) \text{ Or } \qquad \xi = 2\left(\frac{L}{D}\right) \tag{12}$$

where L refers to the length of a fibre in the one-direction and T or D is the thickness or diameter of the fibre in the three-direction. In equation (8), as $L \rightarrow 0$, $\zeta \rightarrow 0$ and the Halpin–Tsai equation reduces to the IROM equation. In contrast when $L \rightarrow \infty$, $\zeta \rightarrow \infty$ and the Halpin–Tsai equation reduces to the ROM equation [33, 48] .

3.5. A Model for Green Composites

A new theoretical model of the modulus estimation for natural fiber composite is necessary, since the existing models (at least those found in literature) can not predict the Young modulus of composites with natural fibers in a reasonable error. A new model should be able to estimate reliably of the modulus of composite with different fiber volume fraction and with different elastic properties of fibers (with constant volume fraction) as well. On the other hand, the development of a new theoretical model from scratch is not reasonable, while combination of the existing models can be used as the basis for a new model.

During the benchmarking of the existing theoretical models it was found that Halpin model and IROM model give the modulus estimation quite close to the experimentally obtained data (figure 6).
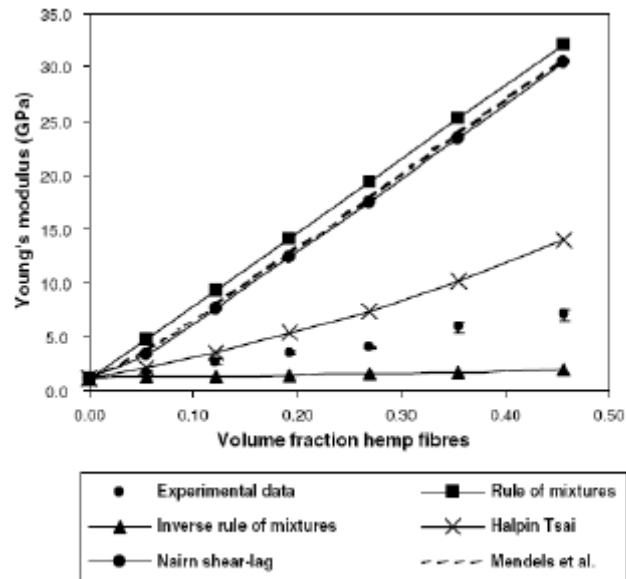
Determination of composite modulus containing hemp fibres.
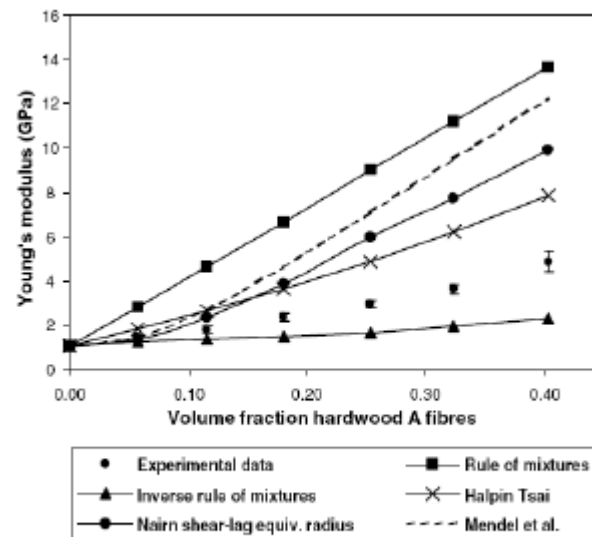
Determination of composite modulus containing hardwood A fibres.

Figure 6. Agreement of IROM and Halpin models with experimental data (graphs from Ref. [1]).

Therefore, the equations of these models can be used as a reference for the development of a new model. In composites with randomly distributed fibers there are fibers which are parallel, series and under an angle orientated to the chosen main direction. Unfortunately ROM model does not take into account the influence of fibers which have orientation perpendicular to the chosen main direction, because in its equation the series part is absent. So the equation of this model has a linear behavior with respect to V_f fiber volume variable

which does not give enough flexibility to adjust the model's behavior to interpolate the non-linear trend of experimentally obtained data. But because of great ability of ROM model in main direction, it can be used in conjunction with two other models; say Halpin and IROM.

A try like this approach has been done in Ref [34], combining ROM and IROM models, with two new weight coefficients α and β:

$$E_c = \alpha\left[V_f E_F + \left(1 - V_f\right)E_m\right] + \beta\left(\frac{1}{V_f/E_f + \left(1 - V_f\right)/E_m}\right)$$ (13)

But a non scientific method has been used to find α and β coefficients.

In this paper, least squares methods with "r" and "s" criteria will be used to find the unique coefficients with the best convergence. The data for PP/Jute composite reinforced with randomly oriented fibers with different fiber volume fraction will be used, with $E_f = 41000 MPa$ and $E_m = 800 MPa$ [34].

Following models will be studied and compared:

• Model 1: IROM and modified ROM model (figure 7).
• Model 2: modified ROM and Halpin (figure 8).

**Table 2. Green composite reinforced with randomly oriented
fibers with different fiber volume fraction**

V_f	E_c, MPa
0	800
0.06	1300
0.12	1650
0.18	1800
0.24	2000
0.29	2100
0.34	2200
0.45	2250

Model 1

$$E_1 = a\left(\eta E_f V_f + E_m\left(1 - V_f\right)\right) + b\left(\frac{1}{\dfrac{V_f}{E_f} + \dfrac{1 - V_f}{E_m}}\right)$$ (14)

In this model three weight coefficients, namely a, b and η should be found in order to fit the data of table 2 with best convergence.

With applying standard error and correlation coefficient criteria, a, b and η constants are calculated as follows:

a =5.665136
b = - 4.5332004
η =0.05943155
Standard Error: 83.6682820
Correlation Coefficient: 0.9899705
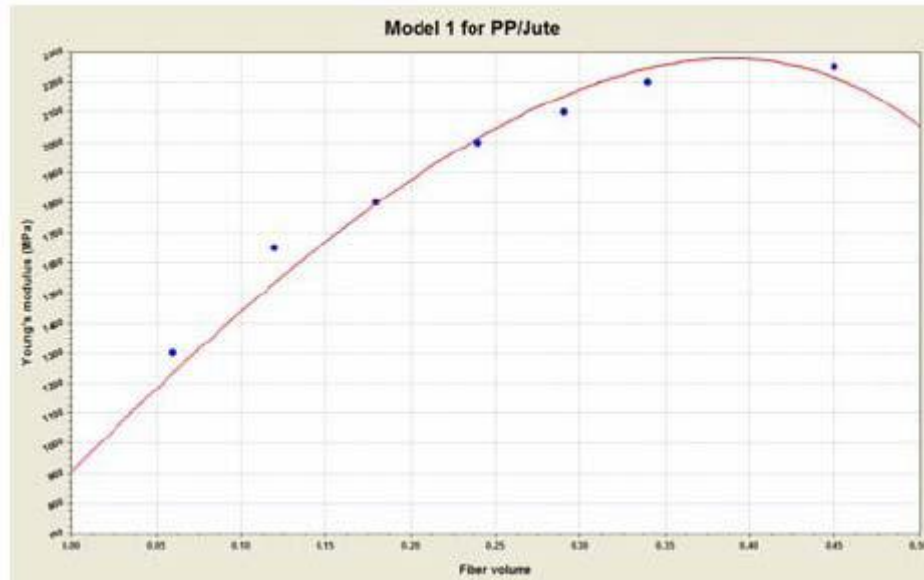
Figure 7. Data fit for IROM and modified ROM model.

Model 2

$$E_1 = a\left(E_m \left(\frac{1 + \xi V_f\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+\xi}\right)}{1 - V_f\left(\frac{(E_f/E_m)-1}{(E_f/E_m)+\xi}\right)} \right) \right) + b\left(\eta E_f V_f + E_m\left(1 - V_f\right)\right) \tag{15}$$

In this model four weight coefficients, namely a, b, ζ and η should be found in order to fit the data of table 2 with best convergence.

With applying standard error and correlation coefficient criteria, a, b, ζ and η constants are calculated as follows:

η =0.65704045
ζ = - 4.9221785
a =0.82190093
b =0.31977636
Standard Error: 97.3997226
Correlation Coefficient: 0.9891221
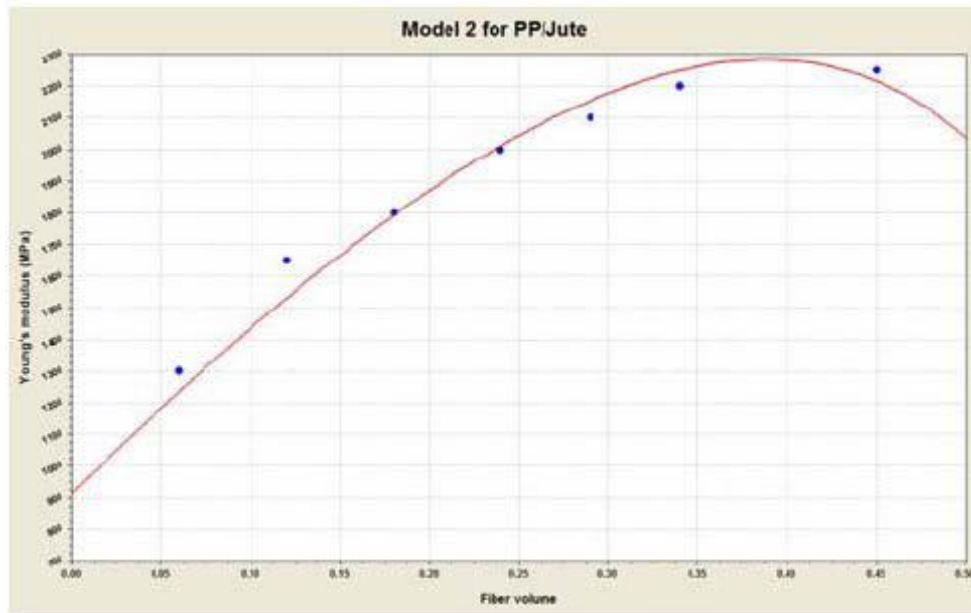
Figure 8. Data fit for modified ROM and Halpin.

4. MATHEMATICAL MODELS

When applying these approaches to choose a good model for fitting available data, some interesting properties of them has been considered and some pure mathematical models has been tested. Best series of models was sigmoidal family of models. Processes producing sigmoidal or "S-shaped" growth curves are common in a wide variety of applications such as biology, engineering, agriculture, and economics. These curves start at a fixed point and increase their growth rate monotonically to reach an inflection point. After this, the growth rate approaches a final value asymptotically. This family is actually a subset of the Growth Family, but is separated because of its distinctive behavior:

Gompertz model: $E = ae^{\left(-e^{\left(b-cV_f\right)}\right)}$ (16)

MMF model: $E = \dfrac{ab + cV_f^d}{b + V_f^d}$ (17)

Logistic model: $E = \dfrac{a}{1 + e^{\left(b - cV_f\right)}}$ (18)

Richards model: $E = \dfrac{a}{1 + e^{\left(b - cV_f\right)^{\frac{1}{d}}}}$ (19)
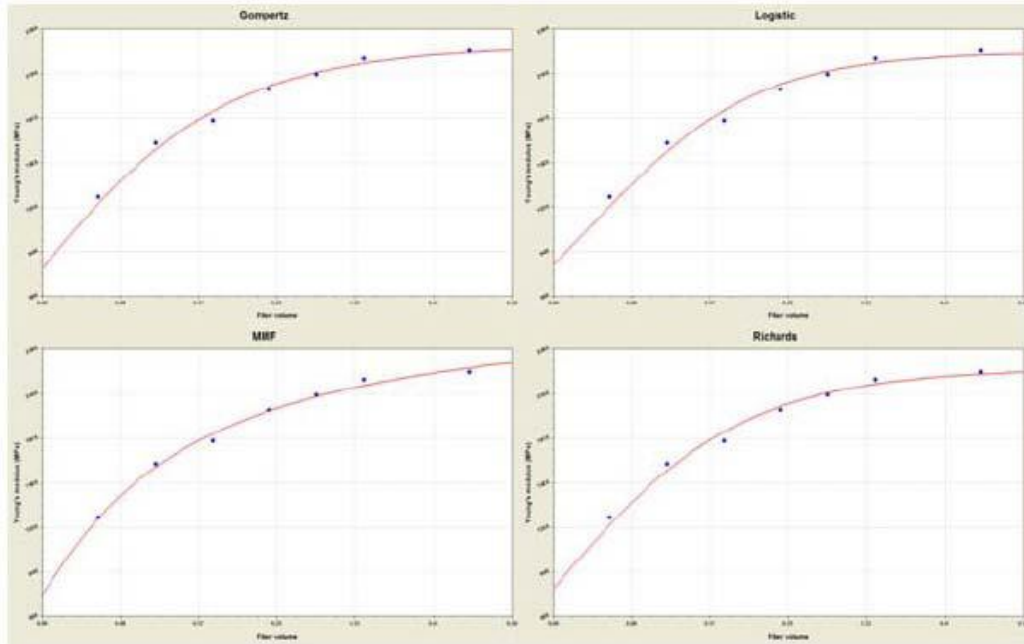
Figure 9. Data fit and comparison of models.
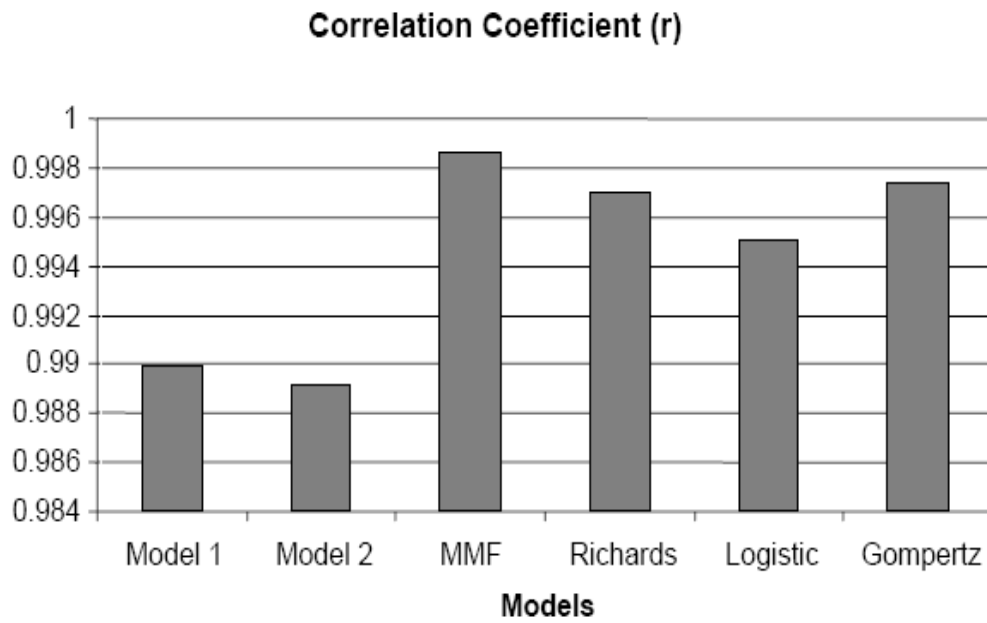
Figure 10. Models correlation coefficients.
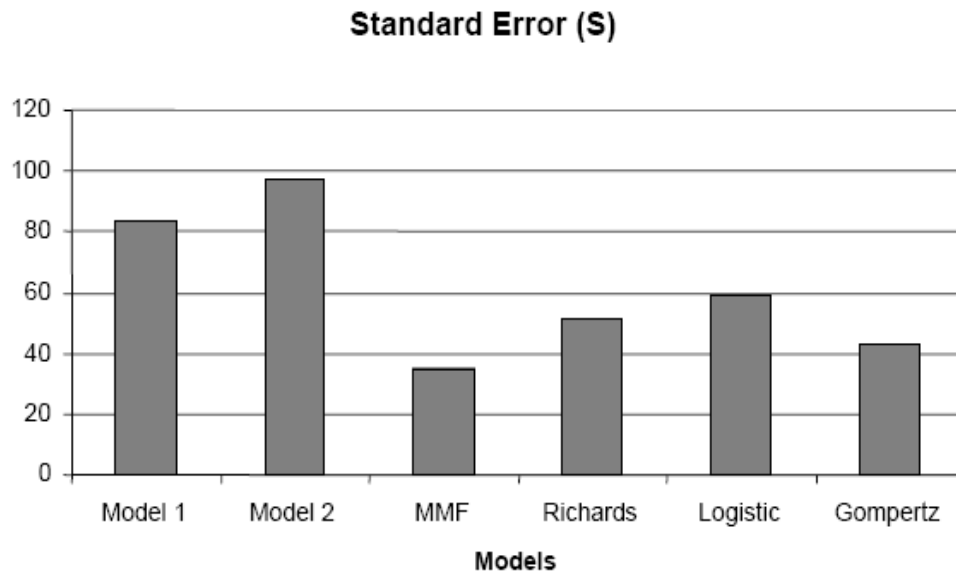
Standard Error (S)

Figure 11. Models standard errors.

5. DISCUSSION OF RESULTS

The results of this study in general indicated that:

- The alternative base course composite has desirable strength and mechanical characteristics to be considered as a good quality stabilized pavement material.
- The higher the percentage of cement added, the higher the increment in strength and stiffness of treated soil.
- the compressive strength of the mixture increases with the increase of Jute/pp content until it reaches to its optimum value and then the additional fibre more than optimum value has decreasing effect on compressive strength.
- The maximum modulus of elasticity was obtained from mixtures by 2% Jute.
- Reinforcing cement stabilized materials with Jute/pp improved the durability of soil-cement mixtures.
- Reinforcing cement stabilized materials with Jute improved indirect tensile strength of soil-cement mixtures.
- Although our numerical investigation yields results that conform to the expected trends we explained, more research and modifications are necessary to be able to use it confidently. After the period spent studying this particular topic, we believe there is much potential for success in developing a more accurate model. It would be a time-consuming task, but foundations are laid and the benefits are truly worthwhile.

6. CONCLUSION

In this paper a method for predicting the elastic modulus in green composites interfaces was developed. Through theoretical examinations a new model developed to estimate reliably of the modulus of elasticity in green composite interfaces with different fiber volume fraction and elastic properties. This approach allows a simple model for systems without resorting to complicated constitutive equations. The approach presented here, leads to theoretical predictions which can reasonably be explained from the physical point of view. Clearly, the final verification can only reached by systematic experimental investigations which, at present, are being carried out.

7. APPENDIX

Two criteria were adopted to evaluate the goodness of fit of each model, the Correlation Coefficient (r) and the Standard Error (S).

The standard error of the estimate is defined as follows:

$$S = \sqrt{\frac{\sum_{i=i}^{n_{po\,int\,s}} (E_{\exp,i} - E_{\mathrm{pred},i})^2}{n_{po\,int\,s} - n_{param}}} \tag{20}$$

Where $E_{\exp,i}$ is the measured value at point i, and $E_{\mathrm{pred},i}$ is the predicted value at that point, and n_{param} is the number of parameters in the particular model (so that the denominator is the number of degrees of freedom).

To explain the meaning of correlation coefficient, we must define some terms used as follow:

$$S_t = \sum_{i=1}^{n_{po\,int\,s}} (\bar{y} - E_{\exp,i})^2 \tag{21}$$

where, the average of the data points ($\bar{y}$) is simply given by

$$\bar{y} = \frac{1}{n_{po\,int\,s}} \sum_{i=1}^{n_{po\,int\,s}} E_{\exp,i} \tag{22}$$

The quantity S_t considers the spread around a constant line (the mean) as opposed to the spread around the regression model. This is the uncertainty of the dependent variable prior to regression. We also define the deviation from the fitting curve as

$$S_r = \sum_{i=1}^{n_{points}} (E_{\exp,i} - E_{pred,i})^2 \tag{23}$$

Note the similarity of this expression to the standard error of the estimate given above; this quantity likewise measures the spread of the points around the fitting function. In view of the above, the improvement (or error reduction) due to describing the data in terms of a regression model can be quantified by subtracting the two quantities. Because the magnitude of the quantity is dependent on the scale of the data, this difference is normalized to yield

$$r = \sqrt{\frac{S_t - S_r}{S_t}} \tag{24}$$

where, r is defined as the correlation coefficient. As the regression model better describes the data, the correlation coefficient will approach unity. For a perfect fit, the standard error of the estimate will approach S=0 and the correlation coefficient will approach r=1. [52]

The standard error and correlation coefficient values of all models are given in figures 10 and 11.

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Chapter 20

PHYSICAL MODIFICATION AND NEW METHODS IN TECHNOLOGY OF POLYMER COMPOSITES, REINFORCED BY FIBERS

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ABSTRACT

In this work, we report main directions of study, produced by authors in Technological Institute of SSTU. Purposes of these researches are:

- realization economizing technologies of polymer composite materials (PCM),
- improvement technological properties of half-finished products,
- regulation characteristics of PCM by the help of different physical influences.

It is done minimum of theoretical bases of observing phenomena in this paper, main attention is given to practical results. Some new physical influences may be used as supplemental stages in traditional technology.

Main positive effect consists in new property appearance or in increasing of strength characteristics of new materials on several tens percents in comparison with materials, produced by traditional technology. Comparatively high durability of improved reinforced by fibers materials permits to use these materials as in the manufacture of consumer goods as in more responsible application.

ABBREVIATIONS AND CONDITIONAL MARKS

APFR – aniline-phenol-formaldehyde resin;
bustilate – emulsion of butadienestyrene rubber;
Capron – polycaproamide fibers (nylon-6);

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CF – carbon fibers;
CLP – components layer putting;
CMC – carboxymethyl cellulose;
CMF – constant magnetic field;
CSP – components separate putting;
DAF – cellulose diacetate fibers;
E_b – modulus of elasticity under static bending;
ER – epoxy resin;
f, Hz – frequency of vibration;
Fenilon – aromatic polyamide fibers;
H_B – solidity;
MF – magnetic field;
MT – magnetic treatment;
Nitron – polyacrylonitrile fibers;
PC – polymer composite;
PCF – polycondensational filling;
PCM – polymer composite material;
PEPA – polyethylenpolyamine;
PF – polymerization filling;
PN-15 –(non-limited) unsaturated polyester resin;
PVA – polyvinylacetate;
T_{stab} – thermostability;
TAF – cellulose triacetate fibers;
TEA – triethanolamine;
TETRA – triethylenetriamine;
VF – viscose fibers;
VT – vibratory treatment;
W – daily water absorption;
α, kJ/m^2 – impact strength;
λ, W/ m K – coefficient of heat conduction;
ρ, kg/m^3 – density;
σ_b, MPa – stress causing failure under static bending;
σ_{eff}, C/m^2 – surface concentration of electric charge;
σ_t, MPa – tensile strength.

INTRODUCTION

In the traditional way of wares production from materials, reinforced by fibers (PC) on the basis of cross-linked polymers (figure 1), thread from bobbin 1 goes to the bath 2, where resin solution is saturating fibers. Thread, saturated by binding, runs to reception mechanism 4 over warming-up pipe 3, which is necessary for removal the solvent and for initial binder hardening appearance. Different versions of produced half-finished products conversion exist. It is possible to produce wares by means of continuous fibers reception by mechanism 4 with

following thermal treating. If it is necessary, we cut saturated half-finished product and then process it, for example, by straight pressing.
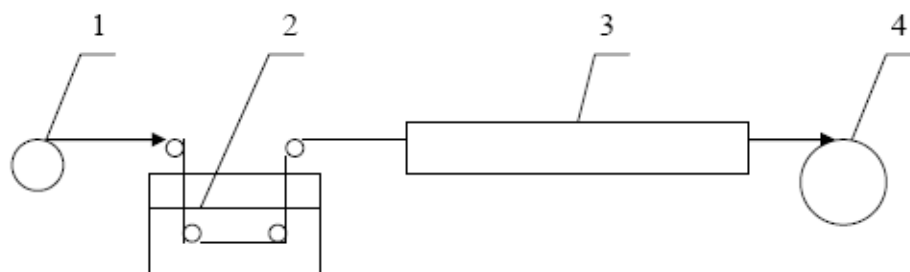

Figure 1. Scheme of traditional method of wares production of PC, reinforced by fibers: 1 – bobbin with thread; 1 – saturating bath; 3 – warming up pipe; 4 – reception mechanism.

1. POLYCONDENSATION FILLING AND NEW POLYESTERS

Polycondensational filling (PCF) – is logical continuation of polymerization filling (PF) [1] . General line of PCF and PF is realization of polymer synthesis in presence of filler. Differences of these methods: synthesis of polymer has mechanism of polymerization for PF and mechanism of polycondensatoin for PCF respectively.

In general PCF scheme is similar to scheme of traditional method. Distinction is: in the bath 2 thread is saturated by mixture of monomers, not by mixture of resin and hardener, for example in PCF of epoxy resin thread may be saturated by solution of 1,2-epoxy-3-chlorpropane and diphenylolpropane.

Synthesis of resin realizes in the warming-up pipe 3. The point of gel-formation must be obtained (degree of conversion 60-70%) in pipe 3. Unification of resin synthesis stage and stage of filler saturating shortens the common amount of technological process stages. This is dignity of PCF method. Difficulty of hardener penetration to the synthesized resin is deficiency of PCF method (table 1), that may aggravate PC characteristics in comparison with material, produced by traditional method. New technological methods and new methods of physical modification are given further.

**Table 1. Characteristics of materials, reinforced by short fibers
and produced by polycondensational filling of epoxy resin**

Filler	Method of PC production	σ_b, MPa	σ_t, MPa	α, kJ/m^2	ρ, kg/m^3	W,%
Capron	Traditional	9	4	46	1060	26
Capron	PCF	15	4	41	980	23
VF	PCF	19	14	8	1100	16
VF	PCF+MT+CLP	8	28	40	950	31

The way of new copolymer of APFR and ER production by PCF method is suggested [2].

PCF method is connected with production of new polyesters. For example, polyester, produced from organic base – glycerine (it has 3 functional groups, f=3)- and organic acid, differing from well-known polyesters by contents of organic base (with f $\geq$ 2) as supplement – threeethanolamine (TEA) or polyethylenepolyamine (PEPA), and as organic acid it is taken adipine acid (AA) (f=2) either tartar acid (TA) (f=2) or lemon acid (LA) (f=3). In method of this polyester production synthesis and hardening run simultaneously at the same reactive volume [3].

Glycerine, TEA and PEPA contain functional groups of base type. These groups react chemically with acid groups of AA, TA, LA. Maximum degree of initial components conversion into cross-linked polymer achieves, if quantities of acid and base groups are equal, that is at stoichiometric proportion between initial components or at proportions near this proportion.

Produced materials don't contain dangerous volatile matters. Resin synthesis runs at the same time with its hardening. New materials are more cheap in consequence of production, packing, storage and transportation expending absence for semi-product – oligoresin.

New polyester in PCM is suggested. It is produced by soak of fiber filler by non-saturated polyester resin and by new hardening system with following pressing, differing from well-known matters (substances) by application of kapron, nitron or VF as fiber filler and by application of 60-80% mass. solution of RF-342A in acetone as hardening system for resin PE-15 [4]. Also it is possible to apply following mixture as hardening system, % mass.:

Aniline-phenol-formaldehyde resin RP-342A	9,3 – 9,8
Carboximetyle-cellulose (CMC)	26,5 – 30,8
Acetone	3,1 - 3,3
Water	56,8 - 60,5

It is necessary at firstly to saturate fiber filler by non-limited polyester resin PE-15, secondly – by hardening system. Produced material contain, % mass.:

Resin PE-15	40 - 61
Hardening system	12 - 42
Fiber filler	18 – 33.

In this material toxic and expensive hardeners (organic peroxides) are absent. New materials have following characteristics:

ρ = 1160 - 1510 kg/m^3, σ_b = 67 - 151 MPa, α = 112 - 208 kJ/m^2.

2. METHODS OF INCREASE PERMISSIBLE STORAGE OF PREPREGS

The problem of increasing permissible storage of prepregs, when we use binder, for which application of hardener is necessary, is solved successfully by selection hardening

system now. Two methods of deciding this problem by technological way mainly, when we use hardeners, which may work at the normal temperature, are suggested in this paper:

1. In the method of components separate putting (CSP) some elements of filler is saturated by binder with plenty (surplus) of resin function groups and thus type 1 prepreg is produced, other elements of filler is saturated by binder with surplus of hardener function groups [5] comparatively to stoichiometric proportion of resin and hardener, type 2 prepreg is produced by this way. Prepregs of both types may be preserved separately about two months in the normal conditions. Prepreg, which is produced by traditional method and contains epoxy resin and one among examined hardeners, for example, PEPA, must be treated several hours past production of it. Prepregs of both types in ware formation conditions are mixed and resin in the type 1 prepreg is hardened by plenty of hardener of the type 2 prepreg. Diffusion difficulties increase in this method, it enables to produce porous materials. Such materials may be used, for example, as heat insulation materials (table 2) with more high toughness, than usual heat insulating materials. Low coefficient of heat conduction is index of high heat insulation properties of material, water absorption is in proportion of porosity.
2. In the method of components layer putting (CLP) every element of filler, that is to say, every thread of filler is soaked (saturated) by resin at first, then by hardening system (figure 2). The lay of resin is hardened in the result of hardener molecules diffusion from external (second) lay in the conditions of ware formation [6]. CLP increases permissible storage of prepregs to two weeks and more and improves all the PC durability characteristics comparatively with materials, produced by traditional method (table 3) [6, 7,8].

Main parameters (concentrations of solutions, composition of hardening system, linear speed of thread, temperature of between-baths thermal treatment in warming-up pipe 3) essential influence on the properties of produced PC. Hardening system cans contain protective polymer (bustylate, CMC or PVA). Different types of CLP depend on combination of those parameters.
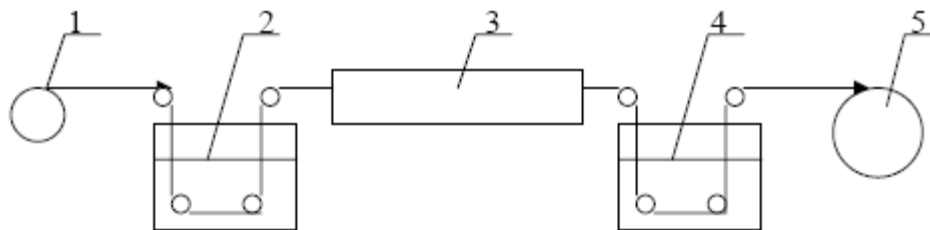

Figure 2. Scheme of method of components layer putting (CLP): 1 – bobbin of thread; 2 – bath of solution of resin; 3 – warming-up pipe; 4 – bath for hardening system; 5 – reception mechanism.

**Table 2. Characteristics of materials on the basis of
epoxy resin, filled by short fibers**

Method of PC production	Hardener	λ, W/ m K	σ_b, MPa	σ_t, Mpa	α, kJ/m^2	ρ, kg/m^3	W,%
Traditional	TETRA	0,096	81	28	80	1120	36
CSP	TETRA	0,057	5	3	10	1050	68
CSP	TEA	0,032	8	2	8	1000	61
Coniferous wood	-	0,07-0,16	72-79	108-115	-	450-550	-

**Table 3. Characteristics of materials on the basis of
epoxy resin, filled by continuous threads**

Method of PC production	Filler, reference	σ_b, MPa	$\Delta\sigma_b$, %	α, kJ/m^2	$\Delta\alpha$, %	ρ, kg/m^3	W,%
Traditional	Capron, [7]	31	-	53	-	930	3,7
CLP	Capron, [7]	64	+106	55	+4	1080	4,0
Traditional	Nitron, [7]	39	-	68	-	1030	4,8
CLP	Nitron, [7]	42	+8	74	+9	1150	5,5
Traditional	VF, [8]	45	-	144	-	1200	3,4
CLP	VF, [8]	71	+68	152	+6	1100	2,8

3. MAGNETIC TREATMENT

Magnetic treatment (MT) and other non traditional influences may be employed as the additional stage of traditional technology [9, 10, 11, 12] or as the stage of new technology [8]. In result of interaction between external magnetic field (MF) and magnetic moments of resin's molecules or of segments of macromolecules probability of definite orientation of binding particles increases [13], that leads to formation of anisotropy structure of polymer in the process of hardening. This is able to have positive influence on the PC durability (table 4). External MF increases adhesion between binder and filler, that influences positively on all durability characteristics of PC. Necessary type of MT depends on temperature and duration of treating, on its place in the technological process, on characteristics of MF (orientation, polarity, stress). We used constant and homogeneous MF only.

MT of MN-type is more economical and more effective in accordance with following reasons:

- it is necessary plus short times of MT (about several seconds, but not about several hours);
- it is necessary large values of working volume for placing of all product wholly, since only one thread, saturated by binder, is subjected by MT;
- segments of binder in saturating solution are more agile, than in hardened product.

Table 4. Influence of MT on the toughness of PC, reinforced by long threads (MN – magnetic treatment of thread, saturated by binder; NM – hardening in CMF; ⊥ and ‖ - orientation of thread perpendicular or parallel to external CMF; Δ σ $_b$, Δα – change of value σ $_b$, α relatively meaning for PC, produced by traditional method)

Example	Method of PC production, type of MT	Resin	Filler	σ $_b$, Mpa	Δσ $_b$, %	α, kJ/m^2	Δα,%	Reference
1	Tradi-tional	APFR	fenilon	107	-	17	-	8
2	MT, ⊥MN	APFR	fenilon	110	+3	39	+129	8
3	MT, NM‖	APFR	fenilon	204	+91	25	+47	8
4	MT, NM⊥	APFR	fenilon	169	+58	40	+135	8
5	Tradi-tional	ER-20	capron	94	-	157	-	10
6	MT, ⊥MN	ER-20	capron	221	+135	283	+80	10
7	Tradi-tional	ER-16	CF	187	-	82	-	10
8	MT, ⊥MN	ER-16	CF	364	+95	189	+130	10
9	Tradi-tional	ER-16	DAF	90	-	308	-	10
10	MT, NM⊥	ER-16	DAF*	151	+68	377	+22	10
11	Tradi-tional	ER-16	TAF	73	-	165	-	10
12	MT, NM⊥	ER-16	TAF*	148	+103	235	+42	10
13	Tradi-tional	ER-100	CF	170	-	89	-	9
14	MT, ⊥MN	ER-100	CF	188	+11	120	+35	9
15	Tradi-tional	ER-100	CF	532	-	104	-	9
16	MT, ⊥MN	ER-100	CF	591	+11	120	+15	9

* - structure of fibers decays in the process of hardening in CMF, PC is homogeneous mixture of two polymers: polymer of binder plus polymer of filler.

Orientation of threads ‖ leads to increasing of concentration of cross-linked chains, orientation of threads ⊥ leads to decreasing of concentration of cross-linked chains, that is why ‖ orientation increases value of σ_b mainly ($\Delta \sigma_b = +91\%$), but ⊥ orientation increases value of α mainly ($\Delta \alpha = +135\%$) comparatively with traditional method of production (table 4, examples 3,4). In general MTs strengthen materials in limits from 3 to 135 %.

It is possible to combine magnetic treatment and formation of product by pressing in single device [14]. For this effect prepreg is placed in interpole volume, the effort of pressing is provided by mutual attraction of poles of electromagnet in this device.

4. VIBRATORY TREATMENT

Used vibratory treatment (VT) consists in following: filler, saturated by solution of binder, is subjected in addition to vibratory treatment through solution of binder by vibration in optimum interval of frequencies [15]. Such treatment may be used in traditional method or in any new method, for example in CLP method. As rule vibration leads to increasing of toughness characteristics of PCM (table 5). Vibratory treatment improves penetration of binder to thread, material becomes more homogeneous, but thread loses compactness simultaneously herewith.

Table 5. Influence of vibration on the toughness of PCs, filled by different threads ($\Delta\sigma_b$, $\Delta\alpha$ – relative changes in consequence of VT or new method)

Binder	Method	f, Hz	σ_b, MPa	$\Delta\sigma_b$, %	α, kJ/m^2	$\Delta\alpha$,%
Capron	Traditional	0	96	-	31	-
Capron	Traditional	66	110	+14	50	+61
Capron	CLP	0	133	+38	54	+74
Capron	CLP	66	135	+2	83	+54
Nitron	Traditional	0	23	-	93	-
Nitron	Traditional	66	42	+83	95	+2
Nitron	CLP	0	51	+128	110	+18
Nitron	CLP	66	50	-	114	+4
VF	Traditional	0	105	-	56	-
VF	Traditional	66	110	+5	50	-
VF	CLP	0	137	+30	63	+12
VF	CLP	66	145	+6	66	+5

5. ELECTRIC POLARIZATION OF CROSS-LINKED POLYMERS

Electric polarization of polymers may be considered as reception of physical modification of PCM. Materials, saving stable electric charge during long time (weeks, months), are named by electrets. In our time electrets are produced from thermoplastics by drive of warmed thermoplastic between two tapes of different metals mainly with following cooling of material. Such materials save stable electric charge during several weeks. In new method [16] electrets are produced by hardening of thermosetting (filled or not filled) systems

between two tapes of different metals. New method provides following advantages by comparison with known electrets (table 6):

- more long conservation period of value of surface concentration σ_{eff} of electric charge in consequence of location and isolation of charged particles into elements of cross-linked structure of polymer;
- more high thermostability is stipulated by temperature of hardening of suggested systems;
- more high toughness characteristics are stipulated by application of reinforcing fibers.

Table 6. Comparison of characteristics of new and known electrets

Physical, mechanical characteristics	New electrets	Known electrets on basis of thermoplastics
τ_e, days	200	7 - 30
σ_{eff}, C/ m^2	$10^{-6} - 10^{-7}$	10^{-5}
σ_b, MPa	150	20
α, kJ/m^2	50	2 - 150
T_{stab}, K	453	403
E_b, MPa	2000	900
H_B, MPa	120	14 – 58
ρ, kg/m^3	1500	930

CONCLUSIONS

1. Technically simple and effective methods of physical modification are offered, these methods permit to increase toughness characteristics of PC, reinforced by fibers:

Method	Increase of σ_b, %	Increase of α, %
CLP	8 –128	4-9
MT	3-135	12-135
VT	6 – 83	5 - 61

2. Method of components separate putting and method of components layer putting increase permissible storage of prepregs, containing the hardener of hot hardening, to several months (instead of several hours in traditional method).
3. Offered syntheses of new resins and formation of cross-linked polymers are proceeding simultaneously in production of new polyesters.
4. New cross-linked polymer electrets differ by magnified conservation period of value of surface concentration of electric charges.

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Chapter 21

TECHNOLOGICAL AND ECOLOGICAL ASPECTS OF THE PRACTICAL APPLICATION OF QUATERNARY AMMONIUM SALTS IN RUSSIA IN PRODUCTION OF SYNTHETIC EMULSION RUBBERS

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Coagulation of the rubber emulsion is one of the main stages during production of synthetic emulsion rubbers. The routine quite efficient way of emulsion rubbers extraction from latexes is the application of inorganic salts (first of all, NaCl) under acidification of coagulating system with mineral acid [1]. It is known that for coagulation of 1 ton of the industrial emulsion of different rubbers (butadiene-styrene, butadiene-nitrile, polybutadiene ones or some others) it is necessary to use from 250 to 1500 kg of NaCl. Mineral salts in the process of wastewater treatment at the waste disposal plants are not decomposed and entrapped but are drained to the natural wells. This results in pollution of the environment, soil and drinking water salinization . For example, if production capacity of emulsion butadiene-styrene rubbers is of 100000 tons per year waste discharge of salts in the form of aqueous solution attains 30000 tons per year just for the extraction workshops. Thus, the annual waste discharge from the extraction workshops at emulsion rubbers production to the natural wells is of hundreds thousand tons of NaCl and other salts making an irreversible ecological damage.

The most efficient way for the perfection of technology of rubbers extraction from latexes is the elaboration of principally new coagulating agents providing a decrease of salt components consumption or their complete elimination from the technological process. Such coagulating agents can be water-soluble ammonium salts, particularly, quaternary ammonium salts (QAS).

However, only in Russia a full-scale investigation work has been made concerning:

- the study of physico-chemical processes of latexes coagulation for industrial rubbers production with the use of cationic polyelectrolytes;

- the study of rubbers properties, their mixtures and vulcanizers;
- applied investigations on the study of a possible application of cationic polyelectrolytes in industry.

Previously, flocculation mechanisms of polystyrene latexes [2-4] and some rubbers [4-7] with the use of QAS were investigated. However, the works aimed at solution of the chemical and technological problems of the industrial production of synthetic emulsion rubbers were made later in Russia.

This article presents the results of investigations of the authors concerned with the application of different QAS's as coagulating and flocculating agents of industrial latexes used in the production of synthetic rubbers. The works that are directly aimed at the elaboration of new approaches to the technology of extraction of synthetic rubbers from butadiene-styrene latexes are considered in most details.

According to the abbreviations accepted in Russia emulsion rubbers are denoted as follows

- SKS-30 – butadiene-styrene rubber (styrene content is 30 %);
- SKMS-25 – butadiene-(α-methyl) styrene rubber (styrene content is 25 %);
- EPB – emulsion polybutadiene;
- SKN-26 SM – butadiene-nitrile rubber (acrylonitrile content is 26 %);
- Letters A, R, K, P, M, O, C after the numbers denote: A - means the rubber of low-temperature polymerization, R - means regulated, K – colophony emulsifier, P – waxed emulsifier, M – oil-filled, O – oxide-filled, C – carbon-filled (technical carbon), respectively.

LOW-MOLECULAR AMMONIUM SALTS

In [8] a reduction of coagulating activity of ammonium halogenides was observed in a series of $NH_4F > NH_4Cl > NH_4Br > NH_4J$ for the discharge intensity of these salts equal to 20, 25, 50 and 100 kg/ton of rubber (pH = 2.5-3.0; temperature of 60°C). Efficiency of SKS-30 ARK and ARKPN rubber extraction from latexes in the presence of NH_4Cl in a dependence on different parameters was studied in details in [9]. The estimation of the rubber properties as well as compounded rubbers and vulcanizing agents on their basis demonstrated that these properties do not change in fact under the change of the usually applied coagulating agent NaCl by NH_4Cl (see table 1).

By the example of SKS-30 ARKP and SKS-30 ARK latexes it was shown [10,11] that with the use of Me_4NCl, Et_4NCl, Et_4NBr and n-Bu_4NI a complete coagulation of latex can be achieved for consumption standards of 60 ÷ 150 kg/ton of a rubber. These values are by 2-5 times less than consumption standard for the industrial coagulating agent – NaCl.

As a whole, a coagulating ability of all the low-molecular salts was not very high.

**Table 1. Properties of SKS-30 ARKPN rubbers extracted with
the use of NaCl and NH₄Cl as well as rubber compounds and rubber resins**

Quality performance	Coagulating agents	
	NaCl	Ammonium chloride
Mooney viscosity	45	46
Conditional toughness under stretching, Mpa	25,0/26,9	27,5/26,9
Relative extension under fracture, %	690/670	675/650
Relative residual deformation after fracture, %	16/18	14/16
Rebound elasticity, %	42/40	41/39
Content of antioxidant (Agidol-2), %	1,0/1,0	1,2/1,0
Mass fraction of organic acids, %	4,92	6,06
Mass fraction of saponaceous organic acids, %	0,16	0,05
Loss of mass under drying, %	0,17	0,12
Mass fraction of the bound styrene, %	22,5	22,5

MIXTURES OF THE ROUTINE COAGULATING AGENTS WITH POLY-N,N-DIMETHYL- N,N-DIALLYLAMMONIUM CHLORIDE

By the example of SKS-30 ARKP (ARK, AKO, ARKM) and butadiene-(α-methyl) styrene latexes SKMS-30 ARKP (ARK, ARKM) of industrial rubbers [12-15] it was shown that addition of PDMDAACl to the routine coagulating agents (NaCl, leather glue, protein hydrolyzate) allowed:

- to provide long-term preservation of protein coagulating agents in aqueous solutions at 20-22°C without their decomposition and appearance of unpleasant smells;
- a part of any of coagulating agents in a composition of 2- or 3-component mixture was considerably less than under their individual usage; that allowed to reduce consumption of a leather glue by 1.5-2.0 times;
- application of NaCl- PDMDAACl mixtures allowed to reduce NaCl consumption by 5-10 times up to the values of 20-50 kg/ton of rubber;
- complete coagulation was attained in a wider range of pH values pH = 2.5-4.5 making it possible to reduce consumption of H₂SO₄ from 15-18 to 8-12 kg/ton of rubber;
- consumption rate of PDMDAACl was of 0.4-1.2 kg/ton of rubber;
- extracted rubbers satisfied all-Union State Standard (GOST) and technical specifications (TU) requirements for the corresponding grade marks of rubbers;
- properties of vulcanizates did not yield to the properties of check samples.

All of the oil-filled rubbers and their vulcanizates satisfied the requirements of the Russian national standards for the corresponding grade marks of rubbers [13]. The role of PDMDAACl was a decisive one in the experiments and if the dosage of PDMDAACl was more than 2 kg/ton of rubber the possibility of a complete elimination of NaCl application was demonstrated in this case.

POLY-N,N-DIMETHYL- N,N-DIALLYLAMMONIUM CHLORIDE

Since according to [12-15] an individual PDMDAACl is an efficient flocculating agent for the industrial emulsions of rubbers a large amount of investigations was performed concerning the influence of different parameters (latex and coagulating agent concentrations, polyelectrolyte consumption and its molecular mass, temperature of the process) on the process of extraction and on the properties of different rubber grade marks – SKS and SKMS. The rubbers extracted with the use of NaCl were used as reference samples [16-20].

Mass of the extracted coagulum was shown to increase with an increase of PDMDAACl amount added into the latex [17, 18]. Flocculation completeness was achieved for the consumption rate of PDMDAACl ≈ 4 kg/ton of rubber and rate of application for $H_2SO_4 \approx 15$ kg/ton of rubber. Here the application rate of cationic polyelectrolyte required for attaining of a complete SKS-30 ARK latex coagulation depends on temperature: optimal coagulation temperature was 60°C. Application of higher temperatures did not result in a considerable increase of a coagulum yield. For the temperatures of 20 and 80°C flocculation curves did not in fact depend on the value of PDMDAACl molecular mass (172000, 62000 and 16000). Concentration of the initial aqueous solution of cationic polyelectrolyte did not have any considerable effect on its consumption rate necessary for a complete extraction of a rubber from latex.

The extracted rubbers very slightly differed from the check rubber samples by their chemical composition and satisfied the requirements of Russian standards. The main quality coefficients of vulcanizates on the basis of the experimental and check samples were equivalent (see table 2). However, rubber compounds on the basis of SKS-20 ARK rubber extracted with the use of PDMDAACl were vulcanized more rapidly. According to [17-19] the role of vulcanization activators could belong to polymer QAS remained in a rubber after its flocculation and/or products of its interaction with the components of emulsion system.

Under investigation of flocculation of the emulsive polybutadiene (EPB) [21] it was found that the consumption rate value for PDMDAACl was 8.0 kg/ton of rubber. At 60-80°C the rate value was reduced up to 5.0 kg/ton of rubber. The change of concentration of the operation PDMDAACl solution from 2.0 to 45.0% did not have effect on its consumption rate value. For H_2SO_4 consumption rate value 11-15 kg/ton of rubber a complete latex flocculation takes place. But the amount of coagulum was regularly reduced from 96-98% to 94-96% under decrease of H_2SO_4 consumption rate value from 10 to 9 kg/ton of rubber. As a whole, the process of flocculation is less sensitive to the dosage of H_2SO_4 than under the use of NaCl as a coagulating agent. Rubbers, rubber compounds and vulcanizates of EPB extracted with the use of PDMDAACl and NaCl were equivalent by the main quality parameters. Just as in case of butadiene-styrene rubbers EPB rubber compounds were vulcanized a little bit more rapidly (table 3) [21].

Similar regularities were found for latex flocculation process of butadiene-nitrile rubber SKN-26 SM with the use of PDMDAACl [22] as well as for its two fractions with mean-viscous molecular masses of $11.5 \cdot 10^4$, $2.3 \cdot 10^4$, $17.4 \cdot 10^4$, respectively.

Table 2. Properties of SKS-30 ARK rubbers extracted with the use of PDMDAACl and NaCl as well as rubber compounds and vulcanizates based on these rubbers

Quality performance	Flocculating agent	
	PDMDAACl	NaCl
Mass content, %		
free organic acids	6,3-6,8	5,8
bound organic acids	absent	0,15
antioxidant VTS-150	1,3	1,3
ashes	0,12	0,18
bound styrene	22,5	22,5
Mooney viscosity	54	52
Loss of mass at 105 °C, %	0,13	0,19
Duration of vulcanization, min	60	80
Elastic recovery, mm	3,0	3,0
Strain under 300% extension , MPa	9,4	8,3
Toughness under extension, MPA	27,8	28,8
Relative extension under fracture, %	580	630
Relative residual deformation after fracture, %	14	10
Rebound elasticity, %	40	42

Table 3. Properties of rubbers extracted with the use of NaCl and flocculating agent PDMDAACl as well as rubber compounds and vulcanizates based on oil-filled EPB

Quality performance	Flocculating agent	
	PDMDAACl	NaCl
Mass content, %		
free organic acids	6,0	5,6
bound organic acids	absent	0,10
antioxidant VTS-150	0,25	0,25
ashes	0,12	0,18
oils of PN-6K	15	15,0
Loss of mass at 105 °C, %	0,15	0,20
Mooney viscosity	40	40
Strain under 300% extension , Mpa	12,0	10,3
Toughness under extension, MPA	17,7	18,6
Relative extension under fracture, %	430	480
Relative residual deformation after fracture, %	6	10
Plasticity	0,37	0,37

# PDMDAACL COPOLYMER WITH SULPHUR DIOXIDE

Flocculation activity of alternative low-molecular copolymer of N,N-dimethyl- N,N-diallylammonium chloride with sulphur oxide (PDMDAACl-OS) was studied for the industrial latex samples of SKS-30 ARK and EPB [23]. Completeness of the flocculation for SKS-30 ARK latex was attained at the flocculating agent supply rate of 18-20 kg/ton of a rubber, while for EPB latex – 14-15 kg/ton of rubber. Introduction of the increased amount of

sulphuric acid as the acidifying agent under the optimal discharge rate of PDMDAACl-OS did not have a considerable effect on the amount of the obtained coagulum. However, the influence of H_2SO_4 dosage was more significant under reduced discharge rate of the flocculating agent. For example, discharge rate of PDMDAACl-OS was almost twice reduced up to 9.0 kg/ton of rubber for the discharge rate of sulphuric acid equal to 8.0 kg/ton of rubber. Rubber compounds on the basis of SKS-30 ARK rubber resin extracted from the latex with the flocculating agent of PDMDAACl-OS were vulcanized more rapidly than the check sample due to the presence of the flocculating agent or the products of its interaction with the components of emulsion system. Physico-mechanical quality indexes of vulcanizates on the basis of SKS-30 ARK rubber correspond to the requirements of Russian standards.

Similar regularities were observed under flocculation of EPB latex. For the discharge rate of PDMDAACl-OS 10.8 kg/ton of a rubber completeness of the flocculation for EPB latex attained under the discharge rate of H_2SO_4 6.0 kg/ton of a rubber. Thus, the use of PDMDAACl-OS as a flocculating agent would require its high-precision dosage.

POLY-(N,N-DIMETHYL-2-OXYPROPYLENEAMMONIUM) CHLORIDE

Dependence of the flocculation process for SKS-30 ARK latex on the concentration of dispersed phase in the presence of poly-(N,N-dimethyl-2-oxypropyleneammonium) chloride (PDMOPACl) was investigated in [24]. The formula of this salt is:

$$
\begin{array}{c}
CH_3 \\
| \\
[-\ ^+N-CH_2-CH-CH_2-]_n \\
|\ Cl^-\quad | \\
CH_3\quad OH
\end{array}
$$
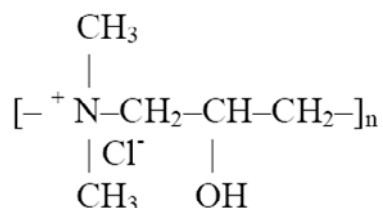
A maximum (optimal point) of flocculation was found just as in case of latexes extracted with the use of PDMDAACl. According to [24] this maximum was related with two factors (neutralization and bridge ones) that can influence on the flocculation mechanism. The value of the concentration of dispersed phase in the range of values 50, 100, 150 g/l was insignificant in the discharge rate value of the flocculating agent.

The change of temperature did not have a considerable effect on the process of rubber extraction from latex. Nevertheless, a slight increase of mass of the forming coagulum was observed with the increase of temperature from 20 to 80°C at the initial stage of the extraction process (for low discharge rate of PDMOPACl). Decrease of PDMOPACl discharge rate from 4 to 3 kg/ton of rubber allowed to attain a complete flocculation of SKS-30 ARK latex only in the case of the process performance at high temperatures of 80-95°C and discharge rate of acidifying agent up to 30 kg/ton of rubber. If the discharge rate of PDMOPACl was reduced up to 2 kg/ton of rubber, complete extraction of the rubber was not achieved even at these temperatures.

Discharge rate of acidifying agent demonstrated a greater influence on the flocculation process than the temperature and concentration of dispersed phase in the investigated

intervals of the process conditions. For example, under discharge rate of PDMOPACl ~ 4 kg/ton of rubber mass of the formed coagulum was regularly increased with an increase of amount of the introduced H_2SO_4. Coagulum mass attained ~ 100% for the discharge rate of sulphuric acid 15 kg/ton of rubber that proved to be the optimal technological parameters of the process.

Rubber compounds and vulcanizates did not surrender the check sample (table 4) [24].

Table 4. Properties of rubber compounds and vulcanizates on the basis of SKS-30 ARK rubber extracted with the use of NaCl and PDMOPACl flocculating agents and rubber resins

Quality performance	NaCl	PDMOPACl
Mooney viscosity	53	42,5
Carrer placticity, arb. un	0,30	0,28
Recovery, mm	1,86	1,84
Optimum of vulcanization at 143 °C, min	80	60
Conditional strain under 300% stretching, Mpa	8,4	14,0
Conditional toughness under stretching, Mpa	27,0	27,6
Relative extension under fracture, %	600	540
Relative residual deformation, %	16	15
Rebound elasticity, % at 20 °C at 100 °C	37 50	32 46
Shore hardness, arb. un.	59	65
Shopper-Schlobach abrasion, 10^{-3} cm^3/m	1,80	1,31
Resistance to the growth of cuts up to 12 mm with a puncture, thousands of cycles	39200	115200
Conditional toughness under stretching after ageing (100°C, 72 h)	18,0	20,0
Relative extension after ageing (100°C, 72 h)	242	257

IMPLEMENTATION OF THE NEW TECHNOLOGY IN THE INDUSTRY OF RUSSIA

Performed investigations demonstrated a high efficiency of the application of QAS's as flocculating agents. According to a set of properties the most perspective one proved to be PDMDAACl. As a result of the complete elaboration of the technological conditions for the process of rubber extraction from latex in the laboratory it was demonstrated:

- PDMDAACl is a high-efficient flocculating agent for rubber latexes;
- optimal technological parameters of the flocculating process for latex have been elaborated;
- application of cationic polyelectrolyte PDMDAACl does not have a negative effect on the properties of the obtained rubbers, rubber compounds and vulcanizates on the basis of these compounds.

During 1992-94 period of time realization of the obtained laboratory results was performed at the synthetic rubber plant, namely:

- operating modes of the industrial flocculation for SKS-30 latex were completely elaborated;
- more than 372 tons of SKS-30 rubber was produced;
- application of PDMDAACl did not require considerable changes in the technology of rubber extraction from latexes as well as no any capital investments were needed;
- factory treatment works operated in normal mode;
- the produced rubber satisfied Russian standards.

Thus, in case of transition to a new technology of all the manufacturers of emulsion rubbers of only SKS marks in Russia (production volume is about 240 thousands of tons) the annual ecological damage can be reduced due to:

- the absence of the discharge of 100000-135000 tons/year of sodium chloride;
- decrease of the amount of industrial waste discharge by 8-10% (240000 m^3 per year).

As a result of the performed investigations the fundamental of a new ecologically reasonable industrial technology of latex flocculation for the emulsion rubbers were elaborated for the first time in the world with the use of cationic polyelectrolyte poly-N,N-dimethyl- N,N-diallylammonium chloride. This technology was realized in industry in Russia.

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