

Physical and Chemical Interaction Mechanisms in Silicone Rubbers

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Synopsis

Silicone rubbers were prepared with graded concentrations of two different fillers—conventional silica capable of both physical and chemical interactions with the methyl vinyl siloxane polymer and magnetic ferrite powder capable of physical interaction only. The mechanical properties of the experimental rubbers (containing both these fillers at the same time) gave characteristic plots of property isolines in the two filler concentration coordinates. To obtain theoretical counterparts of these plots, physical considerations were used to define the polymer–filler contact surface area in real polymer–filler systems and to derive probable variants of its filler concentration dependence. A mathematical model of the polymer–filler interaction was developed and was explored by computing a series of model diagrams. Comparison of the experimental and computed plots indicated that, even with a chemically active filler present, physical interaction mechanisms are dominant; their contribution in determining the mechanical properties of filled silicone rubbers appears to exceed 93%.

INTRODUCTION

In the broader sense, the interaction between polymer and filler can be regarded as encompassing all the processes which are taking place at the interfaces present in the polymer–filler system. The presence of an interaction is demonstrated by the improvement in the mechanical properties of the filled vulcanizate over those of an unfilled, vulcanized elastomer.

Reinforcement of silicone elastomers is usually achieved by adding fillers based on silicon oxide which, owing to its chemical character and high purity, can best satisfy the requirements of the radical vulcanization employed, involving either peroxides or radiation. Opinions prevail that the polymer–filler interaction in this system is complicated to an unusual degree by the fact that an identical element, silicon, is the fundamental building block of both the polymer and the filler; thus the overall interaction incorporates both physical and chemical effects, reflected to a varying degree in different properties of the system. The problem of identifying the contributions of the physical and chemical interaction components and distinguishing between them has attracted considerable interest over the years,^{1–5} but little conclusive evidence can be found except for specific systems such as that described by Berrod et al.,⁶ where hydrogen bonding was demonstrated to be the only interaction component.

The problem would be greatly simplified if it were possible to duplicate the granulometry and structure of conventional fume silica fillers, which are active chemically, by some inert or chemically different material in order to stop those interaction mechanisms which involve chemical processes. While this is impossible, the application of inert fillers of known properties can still be rewarding,

inasmuch as the effects of silica and the inert filler can be compared with each other, i.e., in rubber filled with both these materials simultaneously, thus reducing the number of interfering variables in the system.

This consideration underlied the scope of experimental activities devoted to laboratory preparation and testing of silicone rubber blends and vulcanizates which contained the following two fillers:

1. fume silica regarded as capable of both physical and chemical interactions with the polymer;
2. powder ferrite which can only interact physically.

With a view to distinguishing between the physical and chemical components of the interaction, a theoretical analysis was made of the conditions at the interfaces present in a real system to provide the background from which a mathematical model of the interaction can be developed. The model compares the theoretical and the experimental properties of the three-component system polymer-filler A-filler B.

EXPERIMENTAL

All specimens were prepared using a Czechoslovak commercial polymethylvinylsiloxane elastomer Lukopren G 1000 of viscosity-average molecular weight 504,000 and of specific weight $975 \text{ kg}\cdot\text{m}^{-3}$; it contained 0.17 mol % of MeViSiO groups and less than 3 mol % of monomer. The fume silica used as filler was Aerosil 130 by Degussa, of $2,100 \text{ kg}\cdot\text{m}^{-3}$ specific weight and $130 \pm 30 \text{ m}^2\cdot\text{g}^{-1}$ specific surface area (BET), and the inert filler was magnetically hard barium ferrite, Czechoslovak commercial grade D 330, of $5,100 \text{ kg}\cdot\text{m}^{-3}$ specific weight and $4.28 \text{ m}^2\cdot\text{g}^{-1}$ specific surface area (BET).

Reference samples containing a single filler, either silica or ferrite, were provided by preparing nine compounds filled with Aerosil 130 (at filler concentrations within the range of 0.2–18.8 vol %) and 10 compounds filled with D 330 ferrite (4.4–58 vol %).

The system involving two fillers was represented by 25 compounds containing 4.4–18.8 vol % Aerosil 130 plus 4.4–18.8 vol % ferrite D 330; the concentrations were so selected as to obtain samples having five different ferrite levels at five constant silica levels.

The fillers were incorporated into the silicone rubber on a laboratory two-roll mill at room temperature for the time necessary to obtain fully homogeneous materials. The compounds prepared were shelf-aged for 7 days, remilled, and catalyzed by an agent called P 24 (a 30% dispersion of 2,4-dichlorodibenzoyl peroxide in methyl silicone oil, product of Wacker Chemie GmbH) added to the amount of 1.5 phr. The catalyzed compounds were fed into various test piece molds and cured under pressure for 20 min at 125°C in an electrically heated press. The test pieces obtained were subsequently reheated for 4 h at 150°C plus 16 h at 200°C in a circulating air oven to complete the cure.

The behavior of the compounds during shelf-aging was studied by penetrometric plasticity measurements and by calculating the so-called total crepe hardening.⁷

The vulcanizates were tested as per valid Czechoslovak standards for their tensile properties, i.e., the module M_{100} , strength, and elongation,⁸ hardness,⁹ and compression set.¹⁰ The method of equilibrium swelling in toluene was

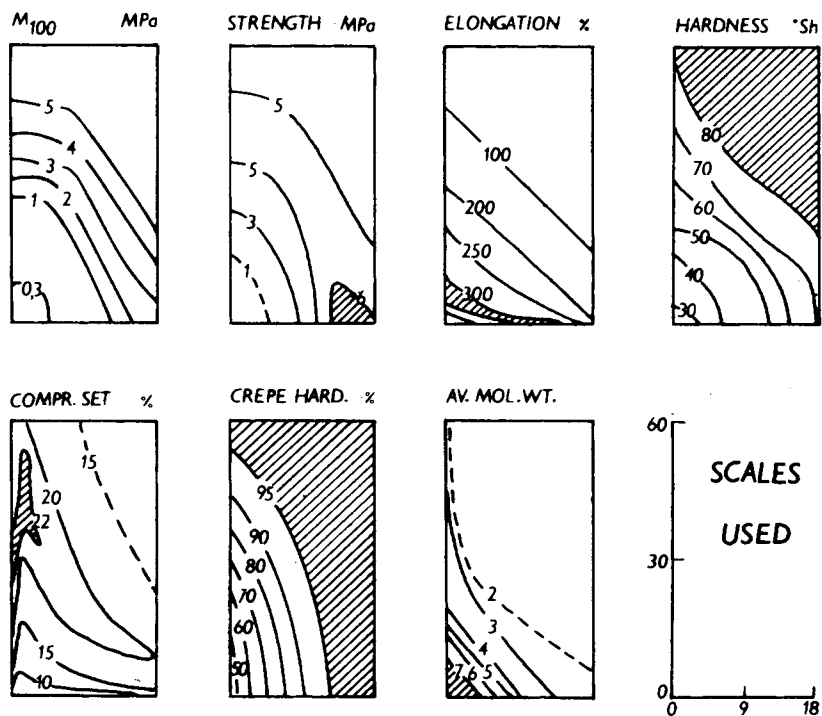


Fig. 1. Properties of experimental rubbers containing two fillers as function of filler concentration: (x-axis) vol % Aerosil 130; (y-axis) vol % ferrite D 330.

employed to establish their physical crosslinking density¹¹ and to calculate the mean molecular weight of the crosslinked chains.

EXPERIMENTAL RESULTS

The experimentally established vulcanizate properties are shown in Figure 1, where the x -axis of each diagram window gives the concentration of Aerosil 130 (from 0 to 18 vol %) while the y -axis gives the concentration of the ferrite filler D 330 (from 0 to 60 vol %). Linear concentration scales were employed. The values of the individual properties are expressed by isolines. Hatched areas denote maxima of the properties.

The general shape and course of the isolines is nearly the same for all the properties tested; the tensile strength diagram features a "tongue" of maximum strength issuing from the absolute peak at the Aerosil axis and protruding into the field where both fillers are present. In the elongation diagram there is even a continuous zone of maximum elongation, formed in fact by an interconnection of two such tongues protruding into the diagram field from the two absolute peaks corresponding to each pure component filler. Hardness of the rubbers keeps increasing with rising concentrations of the fillers over the entire range tested, whereas the mean molecular weight of the crosslinked chains keeps decreasing.

Clearly, the interaction which took place between polymer and filler (or fillers) is not a mere sum of the contributions by each of the fillers, as can be demon-

strated by comparing the values for the system with the filler A or with the filler B, on the one hand, and the three-component system on the other hand. As was expected, the resultant vulcanizate properties are affected differently by each filler.

This is why the subsequent paragraphs are aimed at clarifying the significance and role of some of the factors which influence the polymer–filler interaction.

FACTORS INFLUENCING THE POLYMER–FILLER INTERACTION

Maximum Filler Loading

Maximum theoretical loading is determined by filler geometry. In the case of noncompressible, unidispersion spherical filler of particle diameter $d \ll 1$, a unit cube having the volume 1.0 will hold a filler volume of 0.7405 so that the maximum theoretical loading is 74% by volume.¹²

However, this filler is too much of an abstraction to even remotely simulate the actual conditions in a real polymer–filler system; one of the reasons is that the filler–filler contact surface area remains zero with noncompressible spheres at all filler contents.

A model filler approaching more closely the real fillers is the filler represented by polyhedral particles, viz., by equal tetradecahedrons such as are obtained by “chopping off” all the corners of a cube. Such particles are roughly spherical in shape as their surface is never farther from a circumscribed sphere than $0.146d$, but, at variance with true spheres, they enable us to assess the effect of the filler–filler surface area. The maximum tetradecahedron filler loading is 75% by volume.

For a real, polydispersion filler containing multifaceted and irregular particles next to spherical particles, it is reasonable to assume that the maximum attainable volumetric loading is higher, e.g., 80 vol %, since it will better fill space when close-packed than a unidispersion filler.

The Contact Surface

The components present in a polymer–filler system, i.e., liquid polymer L, solid filler S, and gas-filled cavities or pores G, contact each other giving rise to the following contact surfaces:

polymer–filler, K_{LS}

filler–filler, K_{SS}

filler–cavity, K_{SG}

polymer–cavity, K_{LG}

The total solid surface area introduced by filler, P_S , gives rise to K_{SS} , K_{LS} , and K_{SG} contacts, so that

$$P_S = K_{SS} + K_{LS} + K_{SG}$$

The aforementioned theoretical (unidispersion) spherical filler having the

specific surface area $M \text{ m}^2\text{-g}^{-1}$ and the density $\rho_S \text{ g}\cdot\text{m}^{-3}$, if close-packed in a container of unit volume, will give the contact surface areas $K_{SG} = 0.74\cdot\rho_S\cdot M$ and $K_{SS} = 0$. After a polymer of the density ρ_L is poured into the container which already is "full" of filler, the contact surface areas will become $K_{SG} = 0$ and $K_{LS} = 0.74\cdot\rho_S\cdot M$, whereas K_{SS} remains zero.

All filler particles will be wetted by the polymer in the presence of excess polymer. If the quantity of polymer added is insufficient (i.e., at 74 vol % of the spherical filler but less than 26 vol % of polymer), not all the filler will be wetted but rather just a part of it, roughly proportional to the volumetric fraction,

$$L/(L + G)$$

The other unidispersion model filler mentioned, consisting of equal tetradehedrons and having the same specific surface area M and density ρ_S , if close-packed in a container of unit volume, produces a contact surface area $K = K_{SG} + K_{SS} = 0.75\cdot\rho_S\cdot M$, of which $K_{SG} = 0.366\cdot K$ and $K_{SS} = 0.634\cdot K$.

On adding polymer, the contact surfaces will become $K_{SG} = 0$, $K_{LS} = 0.366\cdot K$; K_{SS} remains unchanged.

In the case of a real polydispersion filler, again having the same values of ρ_S and M , the total filler surface area P_S will grow linearly with increasing filler concentration C_S up to maximum loading. However, not even at low concentrations of the real filler can we expect all the filler particles to be wetted with polymer; wetting will be particularly limited in the case of fillers which have a tendency to cluster. The total surface area P_S introduced by the filler produces no K_{SG} up to the point of maximum loading, but K_{SS} grows to considerable values as the filler concentration C_S increases; the growth in K_{SS} is effected at the expense of K_{LS} .

Hence, at maximum loading the contact surface area K_{SS} is zero for the unidispersion spherical filler, $0.63\cdot P_S$ for the tetradehedrons, and nearly 100% P_S for real polydispersion fillers.

The Concentration Dependence of Contact Area

Data are available showing a strong dependence of properties on the filler structure.¹³ However, the actual dependence of the contact surface area K_{LS} of a real polydispersion filler on concentration is not known. Intuition suggests that the contribution of K_{LS} decreases slowly at first and then more rapidly as the filler concentration C_S increases, and will approach zero just at the point of maximum loading, i.e., at $C_S \doteq 80$ vol %. Assuming that K_{SG} is nearly zero throughout the range of C_S from 0% to 80%, the contribution of K_{LS} produced in the presence of a total filler surface area equal to P_S can be defined as

$$\eta = K_{LS}/P_S = K_{LS}/(K_{LS} + K_{SS})$$

The quantity η defines the fraction of total filler surface area available for polymer-filler contacts.

The situation alluded to above, i.e., with a progressively decreasing value of the "availability" η , can be suitably approximated by the availability function

$$\eta = 1 - 0.005 \exp(0.066\cdot C_S) \quad (1)$$

where C_S is the filler concentration (vol %).

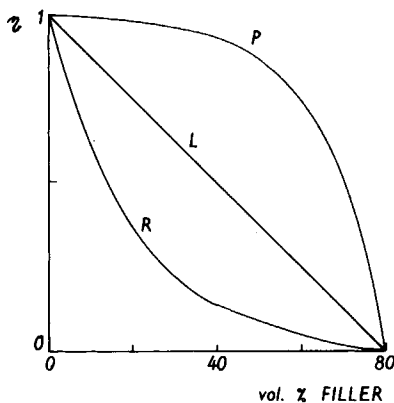


Fig. 2. Filler surface availability η for polymer–filler contacts as function of filler concentration: (P) progressively decreasing; (R) regressively decreasing; (L) linearly decreasing.

Another availability function, characterized by regression rather than by progression as concentration increases, may also be considered:

$$\eta = \exp(-0.05 \cdot C_S) \quad (2)$$

Both these functions approach zero at the point of maximum loading.

The true function $\eta = f(C_S)$ may also be linear, equally distant from the two extremes defined by eqs. (1) and (2):

$$\eta = 1 - 0.01225 \cdot C_S \quad (3)$$

These three probable variants of the concentration dependence of the availability function η are depicted in Figure 2. Figure 3 gives a comparison of the concentration dependencies of the contact surface area K_{LS} for the unidispersion spherical filler (top) and for a real polydispersion filler (bottom). The function describing a real filler differs from that for the theoretical filler chiefly by its rounded peak and by its range of absolute K_{LS} values. Both these characteristics depend on the function η chosen. The three curves of the relationship $K_{LS} = f(C_S)$, shown for the real filler, differ from each other exactly in the parameters of the availability function $\eta = f(C_S)$. The curve denoted “P” was computed using eq. (1). The availability of P_S for K_{LS} contacts runs a decreasing course with a progression as concentration increases; the curve denoted “R”, computed using eq. (2), decreases with regression; the third curve, denoted “L”, corresponds to a linear decrease in availability. In fact, the curve “P” stands for low structure fillers and the curve “R” represents high structure fillers.

These curves, which indicate the filler concentration dependence of the polymer–filler contact area, are a prerequisite to any mathematical modelling of the polymer–filler interaction in real silicone rubbers containing fillers.

THE MODEL OF POLYMER–FILLER INTERACTION

In the mathematical model proposed herein, the interaction between polymer and filler is understood as a generalized process incorporating the effects of all the physical and chemical forces acting upon the polymer–filler interface, and as an absence of this generalized process at the filler–filler interface.

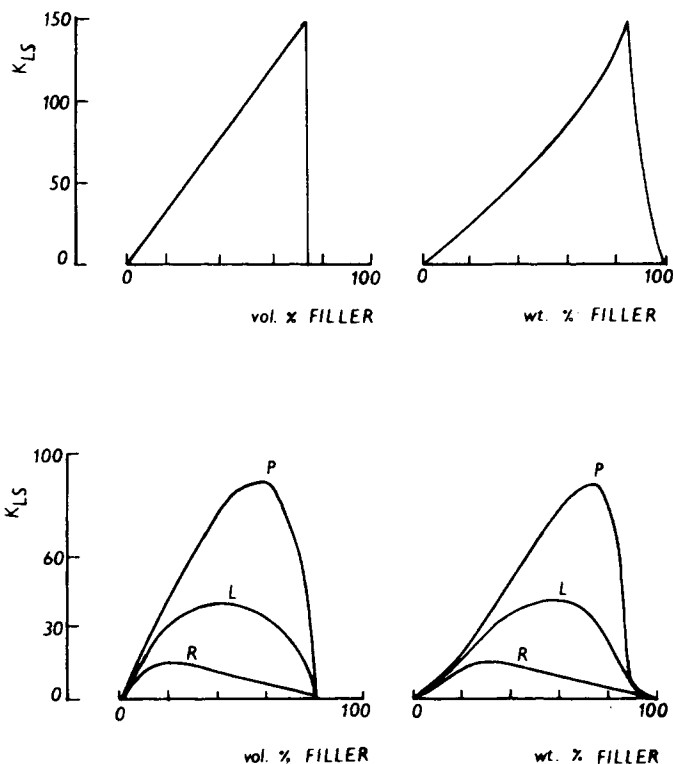


Fig. 3. The contact surface area K_{LS} as function of filler concentration for undispersion spherical filler (top) and for real polydispersion filler (bottom).

The following quantities must be defined: C_A = volumetric concentration of filler A; C_B = volumetric concentration of filler B; ΣC_S = overall filler loading; $\Sigma C_S = C_A + C_B$; M_A = specific surface area of filler A ($m^2 \cdot g^{-1}$); M_B = specific surface area of filler B ($m^2 \cdot g^{-1}$); ρ_A = specific weight of filler A ($g \cdot cm^{-3}$); ρ_B = specific weight of filler B ($g \cdot cm^{-3}$); K_A = contact surface area (K_{LS}) introduced by filler A; K_B = contact surface area (K_{LS}) introduced by filler B, $K_B = C_B \cdot M_B \cdot \rho_B$; R = specific surface ratio of the two fillers (volumetric), $R = M_B \cdot \rho_B / (M_A \cdot \rho_A)$.

Further it holds that

$$I = I_c + I_f = 1 = 100\%$$

where I is the over-all interaction, I_c is chemical interaction, and I_f is physical interaction. An auxiliary quantity 'q' defined as

$$q = I_c / I_f$$

is used giving the ratio of chemical to physical interaction; these values are not known. The remaining quantities required by the model are φ = an interaction range factor (different for individual rubber properties) and $\varphi' = \varphi / (M_A \cdot \rho_A)$ = an auxiliary constant.

Having defined the concepts, quantities, and relationships, we may approach the formulation proper of the interaction model equation intended to describe the behavior of compounds and rubbers filled with filler A, filler B, or both,

bearing in mind that filler A is capable of both physical and chemical interactions with the polymer, whereas filler B can only interact physically.

For every given composition of rubber compound or vulcanizate determined by the values of C_A and C_B , the generalized interaction process (i.e., the sum of all the interaction forces at play) has as its product the resultant value of a generalized property, henceforward denoted as the interaction product Π .

The availability η of the introduced contact surface area P_S for K_{LS} -type contacts is given by either eqs. (1) or (2). At given overall loading ΣC_S , it assumes the value η_A for the filler A and η_B for the filler B. The values η_A and η_B need not be the same at identical values of ΣC_S .

On the assumption that the interaction product Π is a function of the total contact surface area K_{LS} , i.e.,

$$\Pi = f(K_{LS}, \varphi)$$

the above considerations lead to a *contact model* and the interaction model equation is of the form

$$\Pi = \varphi' \cdot [K_A \cdot (I_c + I_f) \cdot \eta_A + K_B \cdot I_f \cdot \eta_B]$$

An alternative assumption, viz., that the interaction product Π is directly a function of filler concentration, would lead to a *concentration model*.

Model Exploration and Its Objective

Practical implementation of the model was approached in such a way that, in a situation where neither the absolute contributions of the two component interactions I_c and I_f nor their ratio are known, an advantage was wrought out from the fact that filler B can merely interact physically.

The interaction model equation is an equation with four unknowns: φ , I_f , η_A , and η_B . Hence, the objective of modeling is to arbitrarily assign the functions η_A and η_B and to keep solving the model equation for various values of the physical interaction I_f until the correct solution is found by comparing the computed model diagrams of the generalized property Π with the experimental diagrams of the individual properties of real compounds and vulcanizates containing two fillers, i.e., with the experimental diagrams for the three-component system studied.

The model was explored using a Texas Instruments TI-59 calculator with PC 100 C Printer. Series of Π -diagrams were computed having the coordinates C_A (x -axis, concentration range 0–18 vol %) and C_B (y -axis, concentration range 0–60 vol %).

To obtain a synoptical representation of the distribution of the integer values of Π printed out over the entire field of each diagram, envelope curves were drawn to separate adjoining different integers; these isolines represent the resultant model interaction diagram.

Model Diagrams for $\eta_A = \eta_B$

The first series of diagrams of the interaction product Π (Fig. 4) has been computed assuming that both filler A and filler B exhibit the same concentration dependence of the quantity η ; thus $\eta = \eta_A = \eta_B$.

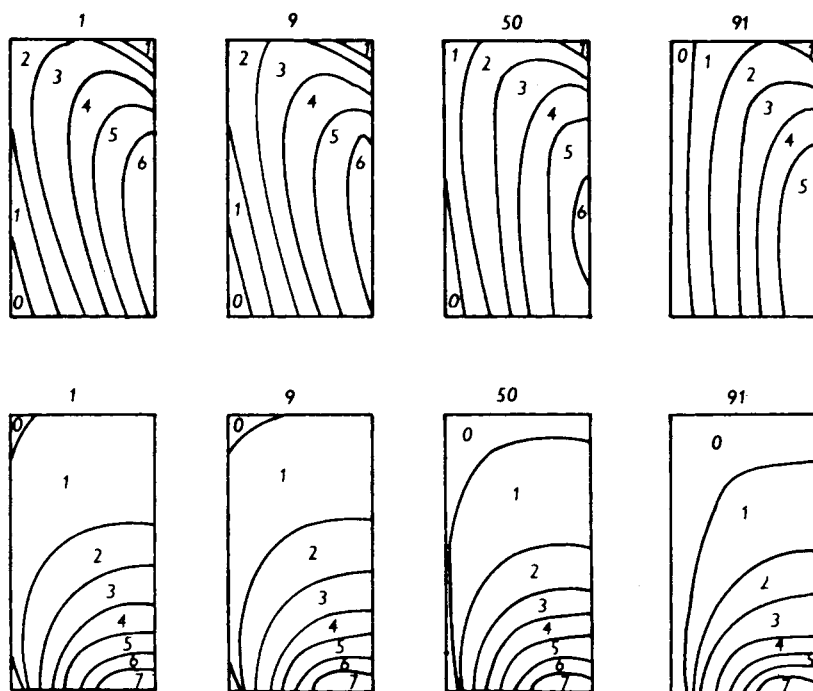


Fig. 4. Model diagrams as per the contact model ($R = 0.16$), assuming that η decreases with progression (top) and with regression (bottom) as filler concentration increases. The chemical interaction share I_c is indicated in percent atop each diagram window. The four I_c values shown correspond to q -ratios of 0.01, 0.1, 1.0, and 10.0, respectively.

The series obtained for progressively decreasing η [eq. (1)] shows that the isolines of Π corresponding to dominant shares of the physical interaction, $q = 0.01 \div 0.1$, differ only slightly from those corresponding to domination of the chemical interaction, $q = 10 \div 100$.

Comparison with the experimental diagrams of the polymer–Aerosil–ferrite system (Fig. 1) demonstrates a total lack of fit; this kind of contact model is unsatisfactory.

If the regressively decreasing η function is used instead [eq. (2)], the Π -isolines are displaced, but even here there is no agreement between the computed and the experimental plots.

An analysis of this series of model diagrams revealed that the maxima of the interaction product Π can never be shifted to “correct” positions, and the isolines can never conform with the experimental isolines as long as one and the same concentration function of η is assumed for both the fillers.

Model Diagrams for $\eta_A \neq \eta_B$

The aforementioned lack of conformity between theory and experiment has prompted us to explore yet two other modified models based on the assumption that the function η (1) decreases regressively for Aerosil and progressively for ferrite or (2) decreases progressively for Aerosil and regressively for ferrite. The model diagrams as per assumption (1) are shown in Figures 5 and 6. The

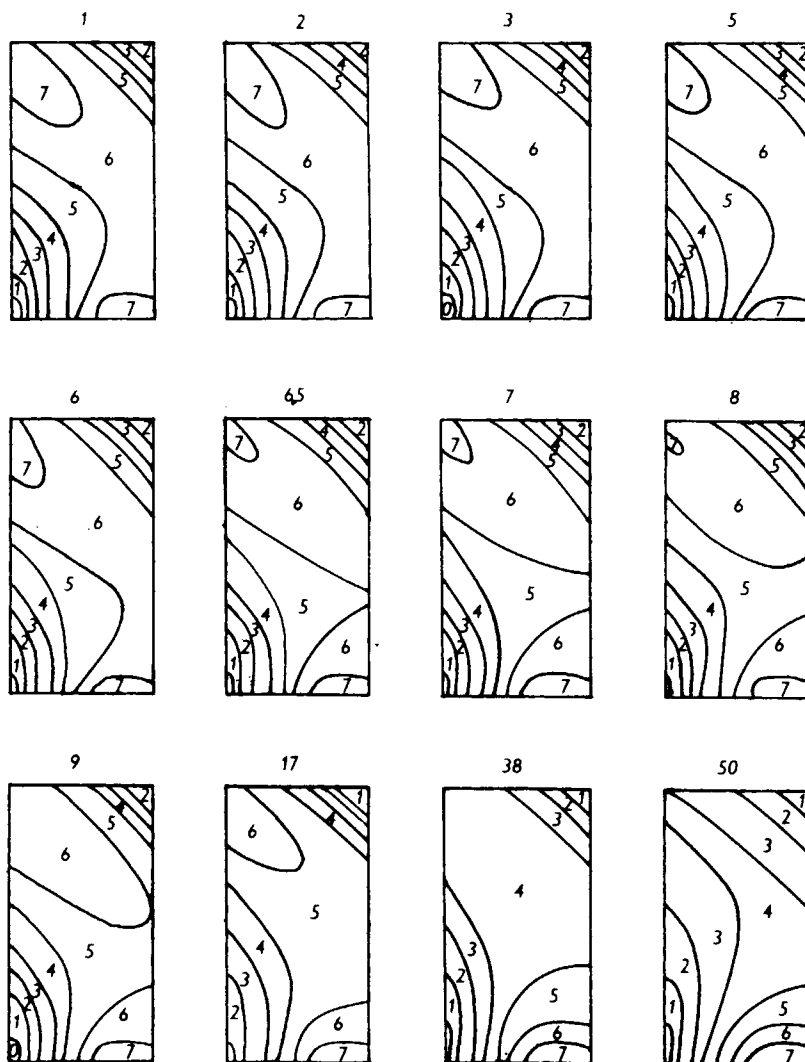


Fig. 5. Model diagrams with physical interaction dominating. Contact model ($R = 0.16$), η_A decreasing regressively, η_B decreasing progressively with increasing filler concentration. The chemical interaction share I_c is indicated atop the diagrams.

Π -isolines are identified by digits, integer values of Π , inserted between them.

A study of the series of diagrams (Fig. 5) concludes that at chemical interaction values I_c not exceeding 6% there is a reasonable agreement between model and experimental strength. The values assigned in computing the diagrams (Figs. 5 and 6) were $\varphi = 1$ and $R = 0.16$; the function η_A was given by eq. (2) and the function η_B by eq. (1). A relative agreement as to shape and values between model and experiment was reached, with the values φ , η_A , and η_B given above, only just at $I_f = 99 \div 94\%$. This is how even the remaining fourth unknown of the interaction model equation, i.e., I_f or q , was established to a sufficient accuracy.

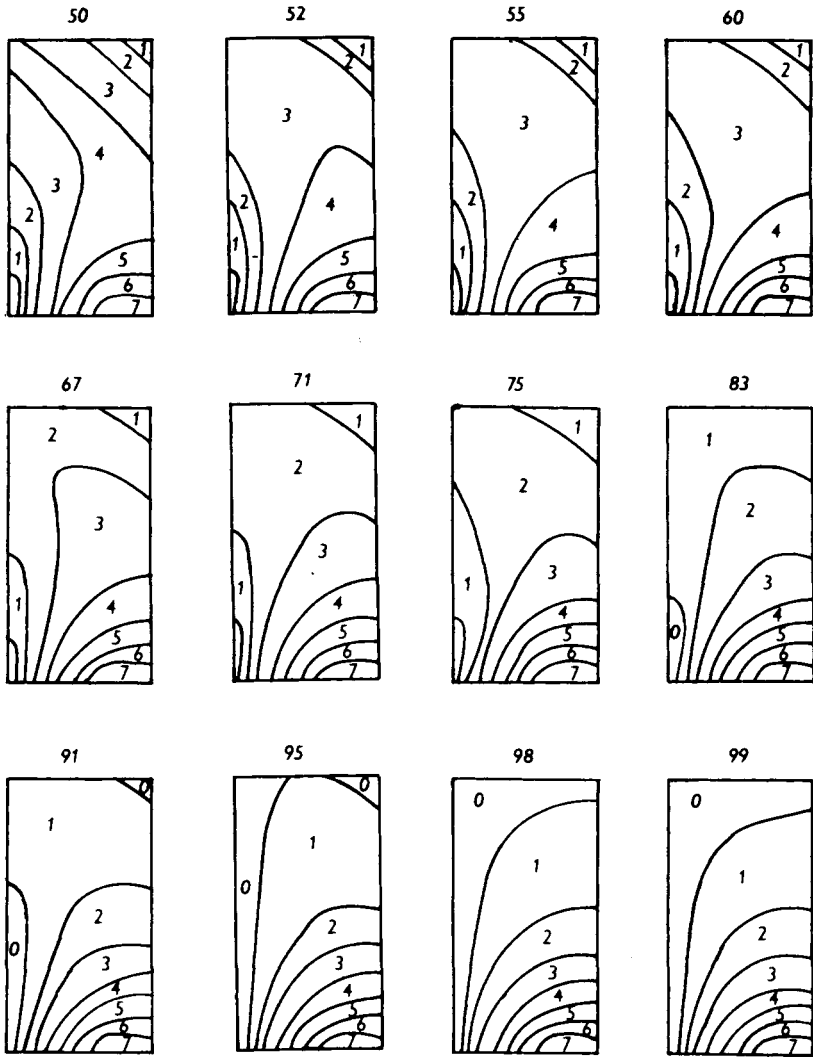


Fig. 6. Model diagrams with chemical interaction dominating. Same model as in Figure 5.

The method of graphic modeling has furnished the mathematical solution of the model equation.

For the sake of completeness, the contact model as per assumption (2) was also explored (Fig. 7), but was found unsatisfactory.

The so-called concentration model was also studied where the interaction product was assumed to depend merely on the concentrations of fillers A and B introduced, rather than on the contact surface areas K_{LS} obtained, i.e.,

$$\Pi = f(C_A, C_B, \varphi)$$

A modified interaction model equation was set up for this model as well. However, it has been confirmed beyond all doubt that the concentration model is a misfit and that the behavior of real rubbers or compounds is adequately described by the contact model only.

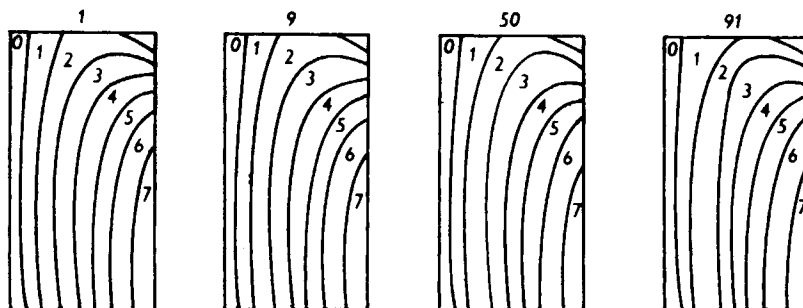


Fig. 7. Contact model diagrams ($R = 0.16$), η_A decreasing progressively, η_B decreasing regressively with increasing filler concentration.

CONCLUSION

In an attempt to elucidate the relations in real systems comprising a silicone polymer and fillers, physical considerations were employed to derive the probable variants of the concentration dependence of the polymer–filler contact surface area. The components of the total interfacial area present in the system were defined as function of filler concentration for both theoretical and real fillers. The interaction processes necessary for the system to acquire satisfactory properties after cure can only proceed at the polymer–filler interface but are blocked at the other component interfaces which contribute nothing to the overall interaction product.

The nature of the polymer–filler interaction has been rendered more accessible to experimental study by the application of an uncommon filler, grade D 330 ferrite, chemically inactive against the polymer, which has stopped the chemical interaction mechanisms normally at play when using the common silica filler (Aerosil).

A mathematical model of the interaction was proposed in an effort to quantify the relative contributions of the chemical and physical components of the polymer–filler interaction.

These contributions were quantified by confrontation of experimental diagrams describing the properties of the three-component system polymer–Aerosil–ferrite with model diagrams computed using the interaction model equation proposed. It has been confirmed that the contribution of the physical interaction in shaping the rubber properties, particularly strength, is $96 \pm 3\%$, whereas that of the chemical interaction does not exceed 7%.

It has been made clear by model exploration that the properties of filled silicone rubbers are only influenced indirectly by filler concentration. Rather than concentration, it is the polymer–filler contact surface area established in the system which directly decides its properties. The availability of the surface of Aerosil 130 for polymer–filler contacts drops rapidly with increasing overall concentration of fillers already in the range of low concentrations, whereas the availability of the surface of ferrite powder for the same type of contacts remains high up to medium concentrations and decreases rapidly afterwards.

Thus, the fact that silica was identified by the model as a high structure filler in contrast to the “inert” metal powder fillers, serves as an independent proof of the model.

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