Vulcanization of Liquid Carboxyl-Terminated Rubber Filled with Leather Buffing Dust

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SYNOPSIS

Vulcanization of the system of liquid carboxyl-terminated rubber–triepoxide–diisocyanate–chromium catalyst–leather buffing dust has been investigated. Using the method of statistical planning of experiments, regression equations were obtained, describing the effects of the components weight ratio on the vulcanization parameters and on the physical properties of the vulcanized rubber. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Leather production is characterized by a large quantity of collagenous wastes and, therefore, the investigation of their utilization is necessary. In past years, we dealt[1,2] with the grafting of hydrophylic acrylates onto refuse chrome-tanned collagen fibers. Among the leather production wastes that have not yet found effective utilization is, besides fibrous material, leather buffing dust. Attempts were made to utilize it as a filler of thermosetting plastics (e.g., Ref. 3); however, products on this base have not significantly asserted themselves in practice. Also, the use of buffing dust for the manufacture of a feeding hydrolyzate has not asserted itself because of the residual chromium toxicity in the feedstuff. Utilization of waste leather buffing dust in the preparation of composites with rubber latexes appears to be possible.[4] We are not aware of any new approaches in the utilization of this waste that have been used in practice.

In this article, we attempted to utilize waste leather buffing dust as a filler of rubber. However, because it would be very difficult to incorporate a larger quantity of buffing dust into solid rubber and because the use of rubber latexes is complicated by the following drying, we examined the possibility of using reactive liquid polymers as a basic substrate. We selected liquid rubber terminated by carboxyl groups, whose chain can be extended with the help of diepoxides. The efficient selective catalysts of this reaction are chromium complexes.[5–8] Selectively controlled branching or cross-linking can be effected either by the addition of the multifunctional epoxide or by the reaction of a bifunctional agent with the hydroxyl groups generated during the chain extension. In our work, we selected a combination of both possibilities, and besides trifunctional epoxide, we used diisocyanate onto which the polyhydroxylated chains are added, forming the urethane bonds. The stated conception is expressed in a simplified manner in Figure 1.

Diisocyanate can also react with free carboxyl groups of liquid rubber and yield[9] a thermally unstable mixed anhydride, decomposing to polyamide and carbon dioxide. However, it is expected that in the presence of a selective chromium catalyst the reaction of carboxyl groups with epoxides will take precedence and diisocyanate will assert itself as a cross-linking agent of the primarily formed polyol. It is also more probable, on the basis of our experience (contrary to the literature,[10]), that, in the presence of a selective chromium catalyst, a very significant homopolymerization of epoxide will not occur. We have also presumed that it is not possible to exclude the participation of diisocyanate and triepoxide as coupling agents between the polymer network and the filler (protein with sufficient quantity of carboxyl, amino, and hydroxyl groups).
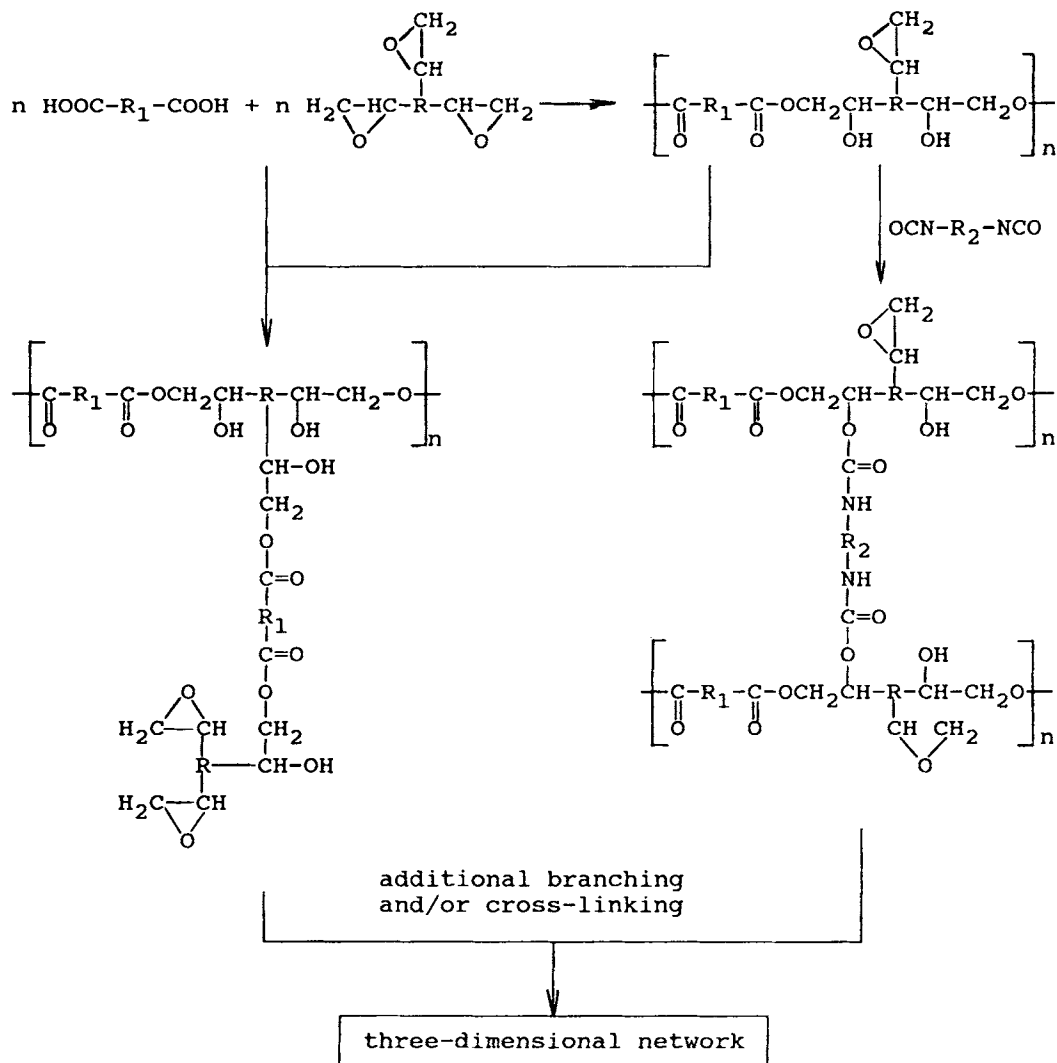
Figure 1   Scheme of some possible chemical reactions taking place during vulcanization of the reaction mixture under investigation.

EXPERIMENTAL

Materials

Liquid rubber OBNK-30 (Russia) is a copolymer of butadiene and acrylonitrile (30%) terminated by carboxyl groups. Its average molecular weight is 2935 g mol^{-1}; carboxyl group content, $6.56 \cdot 10^{-4}$ mol g^{-1}; and functionality, 1.925. Epoxide ECHD (Russia) is a chlorinated tetraglycidyl derivative of 4,4-diphenylmethane diamine, but has an average molecular weight of only 482 g mol^{-1}; epoxide group content, $6.044 \cdot 10^{-3}$ mol g^{-1}; and mean functionality, 2.91. A 4,4-diphenylmethane diisocyanate (MDI) from Bayer (Germany) was used, and complex chromium octoate (catalyst) was prepared according to the literature.[8] Buffing dust from chrome-tanned

leather (4.51% Cr) was obtained from a local tannery and used as a filler after drying to a constant humidity at 20°C. The content of free carboxyl, hydroxyl, and amino groups has not been determined.

Preparation of Samples

Components were mixed in a ratio determined by the specification of the planned experiment (Table I) in a 0.2 dm^3 laboratory mixer Werner-Pfleiderer. At first, epoxide and liquid rubber were mixed together. Then, a catalyst and buffing dust were added, and after further mixing, diisocyanate was added the laboratory temperature. Vulcanization of the compound was executed in a manual press at a temperature of 150°C; the vulcanization time was de-

Table I   Relation Between Original and Coded Independent Variables

Factor	Unit	x_i Level				
		−2	−1	0	1	2
x_1	mol mol^{-1}	0.4	0.6	0.8	1.0	1.2
x_2	phr	40	55	70	85	100
x_3	phr	0	0.25	0.5	0.75	1.0
x_4	phr	0	5	10	15	20

termined from the results of the vulcanization parameters' measuring (vulcameter, Cone-Monsanto).

The test pieces were prepared by cutting out from plates of 2 mm thickness and physical properties were determined using the usual methods. Cold extraction of vulcanized compounds by chloroform was used to determine the gel content, the latter being recalculated to the polymer phase content without filler. The method of biparametric nonlinear regression was used for determining the values of the rate constant of vulcanization and the maximal modulus from the course of the vulcanization curves. The first-order kinetic equation with the induction period was selected as a regressive function. The values of the induction period were read directly from the graphic record of the vulcanization curve. The values of the maximal modulus are presented in direct proportional heights of the vulcanization curves.

Evaluation

The method of a planned experiment[11,12] was used to evaluate the dependence of vulcanization characteristics, gel content, and physical properties of the compounds on their composition. A second-degree polynomial for four factors in form (1) was used as a mathematical model:

$$y_i = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{11} x_1^2$$
$$+ b_{22} x_2^2 + b_{33} x_3^2 + b_{44} x_4^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3$$
$$+ b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4 \quad (1)$$

where x_i are coded levels of the factors x_i characterizing the compound composition. The relation between coded x_i and actual x_i values is given in Table I; the meaning of values x_i are the following:

x_1 molar ratio (MR) of COOH/epoxy groups (mol mol^{-1})

x_2 content of filler (phr)

x_3 content of catalyst (phr)

x_4 content of MDI (phr).

The following characteristics for dependent variables y_i were used:

y_1 maximal modulus (height of the vulcanization curve in cm)

y_2 rate constant of vulcanization (min^{-1})

y_3 induction period (min)

y_4 optimal vulcanization $\tau_{95\%}$ (min)

y_5 hardness (Shore A)

y_6 elasticity (%)

y_7 elongation (%)

y_8 tensile strength (MPa)

y_9 elongation at break (%)

y_{10} energy of rupture (J)

y_{11} actual strength (MPa)

y_{12} gel content (%).

The measured values of these dependent variables are given in Table II. The values of the regression coefficients b_{ij} and indexes of multiple correlation $I_{x,y}$ are given in Table III.

RESULTS AND DISCUSSION

We used the MR of carboxyl and epoxide groups in the system (x_1) and relative quantities (phr) of buffing dust (x_2), chromium catalyst (x_3), and MDI (x_4) as factors that can affect the behavior of the selected reaction system. The limits of the independent variables (Table I) were estimated on the basis of logical considerations and verifying experiments.

By giving the experimental results (Table II) into the regressive function (1), the values of the regression coefficients b_{ij} were calculated (Table III). As the values of the indexes of multiple correlation $I_{x,y}$ show, the mathematical model describes the effects

Table II   Results of Experiments

No.	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
1	0.6	55	0.25	5	32.67	0.179	0.3	17.04
2	1.0	55	0.25	5	18.99	0.778	0.3	4.15
3	0.6	85	0.25	5	18.09	0.562	0.5	5.83
4	1.0	85	0.25	5	9.96	0.619	0.9	5.79
5	0.6	55	0.75	5	13.75	0.826	0.4	4.02
6	1.0	55	0.75	5	10.62	0.781	0.5	4.44
7	0.6	85	0.75	5	14.03	0.907	0.3	3.60
8	1.0	85	0.75	5	11.12	1.076	0.2	3.03
9	0.6	55	0.25	15	17.17	0.493	0.4	6.48
10	1.0	55	0.25	15	11.26	0.431	1.0	7.95
11	0.6	85	0.25	15	21.06	0.918	0.6	3.86
12	1.0	85	0.25	15	19.47	0.659	0.6	5.15
13	0.6	55	0.75	15	27.23	0.810	0.3	3.00
14	1.0	55	0.75	15	15.36	0.884	0.5	3.89
15	0.6	85	0.75	15	28.88	1.035	0.3	3.19
16	1.0	85	0.75	15	22.06	0.888	0.3	3.67
17	0.4	70	0.50	10	22.76	0.920	0.6	3.86
18	1.2	70	0.50	10	14.13	0.984	0.7	3.74
19	0.8	40	0.50	10	16.34	0.417	0.9	8.08
20	0.8	100	0.50	10	24.08	0.927	0.5	3.73
21	0.8	70	0	10	6.19	0.430	1.2	8.16
22	0.8	70	1.00	10	20.94	0.894	0.1	3.50
23	0.8	70	0.50	0	18.44	0.528	0.9	6.62
24	0.8	70	0.50	20	13.96	1.509	0.6	2.64
25	0.8	70	0.50	10	22.79	0.546	0.7	6.19
26	0.8	70	0.50	10	19.01	0.627	0.7	5.48
27	0.8	70	0.50	10	19.59	0.587	0.8	5.96
28	0.8	70	0.50	10	23.20	0.706	0.7	4.04
29	0.8	70	0.50	10	22.77	0.664	0.7	5.26
30	0.8	70	0.50	10	22.04	0.719	0.7	4.87
31	0.8	70	0.50	10	26.00	0.732	0.4	4.49

of the system composition on its characteristics in an extremely fitting manner. An exception is the case of elongation at break (y_9) where the value of $I_{x,y}$ is low. For this reason, we shall no longer concern ourselves with this property.

As is apparent from Table III, the MR of COOH/ epoxy (x_1) significantly influences the maximal modulus and optimal vulcanization, whereas the rate constant of vulcanization is influenced to a substantially lesser degree by this factor and the induction period is not influenced at all. Because the filler also contains an unknown amount of carboxyl groups, the real values of the MR are different of those presented in this article and have a linear growth with the increase of the filler content. The filler content (x_2) affects mainly the rate constant of vulcanization, and that in a positive manner, and has a significant negative effect on the optimal vulcanization. There are probably two causes: The first

one is physical—by increasing the quantity of the filler, the viscosity of the compound increases, which causes dissipation energy to grow in the course of mixing, and partial cross-linking may have occurred already in this phase. The second one (chemical) is based on the catalytic action[5,6] of undefined chromium complexes bound to the protein macromolecules of the buffing dust from chrome-tanned leather. This hypothesis was supported by an experiment in which a mixture of liquid rubber and triepoxide remained liquid at an MR of 0.8 even after 2 h of heating at 150°C, if it contained no catalyst. Following the addition of 100 phr of buffing dust to this mixture, vulcanization occurred with a rate constant of 0.38 min^{-1}.

A change of the catalyst content (x_3) in the mixture has, according to presumption, a statistically significant response in all the characteristics of vulcanization. Acceleration of the reaction of the car-

No.	y_5	y_6	y_7	y_8	y_9	y_{10}	y_{11}	y_{12}
1	90	28	38.3	13.6	3.5	1.13	18.8	91.2
2	85	31	20.7	10.8	2.0	0.36	13.1	89.2
3	91	30	25.5	13.3	5.0	0.97	16.6	90.2
4	91	33	16.1	8.5	3.0	0.38	9.9	80.1
5	88	27	51.2	15.4	7.5	1.63	23.9	90.8
6	88	33	33.9	13.2	4.0	1.01	17.4	88.1
7	94	32	24.7	12.7	3.5	0.73	15.7	89.1
8	91	33	26.4	13.3	6.0	0.79	16.6	85.2
9	91	27	39.9	15.2	5.0	1.20	21.3	94.0
10	91	33	31.8	12.2	2.5	0.86	16.1	87.0
11	94	32	28.9	16.0	4.0	1.22	20.6	93.5
12	89	35	20.8	12.7	4.0	0.79	15.2	85.9
13	89	27	39.7	17.0	4.0	1.82	23.8	95.3
14	92	30	42.3	14.6	6.5	1.39	20.7	89.3
15	90	30	25.5	17.1	5.5	1.28	21.4	90.4
16	90	34	21.4	12.7	5.0	0.85	15.4	87.6
17	91	27	43.4	16.2	7.0	1.78	23.2	91.4
18	87	30	24.1	10.6	6.5	0.64	13.1	93.8
19	89	28	43.7	13.7	6.0	1.03	19.7	92.8
20	94	32	17.4	11.2	6.0	0.57	13.1	89.4
21	92	32	23.5	11.2	6.0	0.70	13.9	88.8
22	86	29	23.4	8.5	4.0	0.44	12.1	90.7
23	90	30	37.7	8.8	4.0	1.47	20.8	89.3
24	91	33	27.7	15.9	4.0	1.47	20.8	93.2
25	88	32	24.9	10.7	6.5	0.65	13.4	89.2
26	89	33	28.0	13.1	6.0	0.96	16.8	90.7
27	87	34	23.7	11.4	8.0	0.71	14.1	91.1
28	88	32	28.4	13.6	5.0	1.01	17.4	91.1
29	87	32	35.4	12.7	7.5	0.89	17.1	91.6
30	87	32	25.2	13.4	4.5	0.78	16.8	90.8
31	86	32	22.1	12.2	8.0	0.96	14.9	91.5

boxyl groups with the epoxide groups manifests itself a shortened induction period and optimal vulcanization and an increase in the rate constant. The dosage of MDI (x_4) influences significantly only the rate constant and the optimal vulcanization, which is in accordance with the growth of network density. The fact that MDI concentration, in effect, does not influence the induction period correlates with the theoretical assumption that the reaction of carboxyl groups with epoxide is primary. Diisocyanate does not participate significantly in this reaction, but reacts, consequently, with the formed hydroxyderivative. It is worth noting the high values of combining regressive coefficients for filler, catalyst, and MDI in the case of maximal modulus, which points to the synergism of the mentioned effects.

If we observe the effects of the individual factors on the complex of physical properties (y_5–y_{11}), we come to the conclusion that the decisive factors are the MR of COOH/epoxy (x_1) and the filler content (x_2). The effect of filler content conforms, in general, with the assumption ensuing from the laws of the behavior of filled compounds. The effect of catalyst concentration (x_3) is relatively small. However, due to this fact, it asserts itself significantly in the vulcanization characteristics, thus enabling control of the kinetic relations of the mixture during vulcanization without affecting the physical properties. Only the hardness and energy of rupture are more significantly influenced by the catalyst concentration. The decrease in hardness is most probably caused by the fact that the chromium octoate acts in the compound simultaneously as a plasticizer and a lubricant. This not only directly affects the hardness, but also improves the flow properties of the compound. As a result of this, those defects of material on which local concentrations of stress occur can be bypassed by the plastic flow of the polymer.

Table III Coefficients of Regression Equation Type (1)[a]

Regression Coefficient	Dependent Variables					
	y_1	y_2	y_3	y_4	y_5	y_6
b_0	22.202	0.656	0.686	5.243	87.430	32.429
b_1	−2.962	0.021	0.063	−0.429	−0.750	1.458
b_2	0.537	0.104	−0.029	−1.102	1.083	1.292
b_3	1.003	0.146	−0.163	−1.492	−0.500	−0.375
b_4	1.021	0.098	−0.004	−0.734	0.417	0.292
b_{11}	−0.749	0.059	−0.049	−0.305	0.433	−0.847
b_{22}	−0.308	−0.010	−0.036	0.222	1.058	−0.472
b_{33}	−1.969	−0.013	−0.042	0.203	0.433	−0.347
b_{44}	−1.310	0.076	−0.011	0.098	0.808	−0.097
b_{12}	0.934	−0.047	−0.031	0.773	−0.375	−0.438
b_{13}	0.299	−0.014	−0.050	0.644	0.625	−0.063
b_{14}	0.115	−0.073	0.019	1.019	0.375	0.188
b_{23}	1.278	−0.017	−0.075	0.765	0	0.063
b_{24}	2.695	0.018	−0.056	0.304	−1.000	0.313
b_{34}	3.437	−0.021	−0.038	0.571	−0.500	−0.563
Index of Correlation						
$I_{x,y}$	0.843	0.866	0.741	0.859	0.845	0.914

Regression Coefficient	Dependent Variables					
	y_7	y_8	y_9	y_{10}	y_{11}	y_{12}
b_0	26.829	12.433	6.500	0.857	15.786	90.838
b_1	−4.133	−1.408	−0.250	−0.238	−2.384	−1.550
b_2	−6.717	−0.442	0.042	−0.138	−1.513	−1.248
b_3	1.783	0.358	0.375	0.079	0.663	0.359
b_4	−0.917	1.283	0.083	0.163	1.688	1.126
b_{11}	1.742	0.506	−0.104	0.101	0.939	0.109
b_{22}	0.942	0.268	−0.292	0.001	0.497	−0.276
b_{33}	−0.833	−0.382	−0.542	−0.061	−0.553	0.605
b_{44}	1.729	0.256	−0.792	0.089	0.509	−0.230
b_{12}	1.263	−0.088	0.313	0.044	0.169	−0.419
b_{13}	1.638	0.363	0.438	0.031	0.556	0.711
b_{14}	1.563	−0.263	0.250	0.031	−0.144	−0.293
b_{23}	−1.863	0.200	−0.313	−0.119	−0.569	0.044
b_{24}	−0.338	0.300	0	0.006	0.281	0.393
b_{34}	−1.763	0.175	−0.125	−0.006	−0.406	−0.012
Index of Correlation						
$I_{x,y}$	0.933	0.852	0.697	0.918	0.892	0.746

[a] Values printed in italics are, according to the absolute value of T criterion,[12] statistically insignificant.

It causes more even distribution of stress, thus preventing the initiation of a crack growth.

Addition of MDI (x_4) into the system increases hardness, tensile strength, actual strength, energy of rupture, and gel content. These changes are influenced by the growth of network density as a consequence of cross-linking reactions of diisocyanate with hydroxyl groups of the adduct (Fig. 1).

Contour diagrams of sections of a quint-dimensional experimental space provide a more illustrative image than does a polynomial expression. For reasons of easier programmability and greater illustratability, we selected contour diagrams of the dependent variables on two factors at constant values of two further factors. As a result of the high number of possible combinations, we shall limit ourselves

only to those that we consider to be significant and illustrative. Some further relationships are described without illustrations but by analogy.

The dependencies of the maximal modulus (y_1) on the molar ratio COOH/epoxy and the catalyst concentration for two various levels of MDI are illustrated in Figure 2. In both cases, the value of the maximal modulus increases with decrease of the MR. However, at a constant MR and a growing concentration of the catalyst, the maximal modulus decreases if no MDI is present, but permanently grows in its presence. It is apparent that in the absence of MDI the immediate effect of the catalyst manifests itself, not only accelerating the reaction, but also plasticizing and lubricating, changing the structure of the compound toward less dense networks. A higher concentration of catalyst generates a higher concentration of hydroxyl groups at a certain time. If a sufficient quantity of MDI is also present at the same time, it reacts with these hydroxyl groups and increases the network density in direct proportion to their concentration (and thus also to the concentration of the catalyst).

This explanation conforms to the high statistical significance of the interaction coefficient b_{34}, and also of b_{24} (catalytic effect of chromium complexes in the buffing dust). A practically identical relationship as in Figure 2 is gained if, instead of catalyst concentration, the concentration of MDI is plotted on the vertical axis. The maximal modulus decreases with the growing content of MDI if the system does not contain a selective catalyst (respectively, only a small quantity present in the buffing dust) and other reactions (e.g., homoaddition) take place. A sufficient quantity of lateral hydroxyl groups is not generated and no formation of cross-linking with MDI can occur. The latter then reacts with pollutants without creating of a network and thus behaves in the compound as an indifferent additive.

These results also show that the proportion of addition reactions of liquid rubber carboxyl groups on diisocyanate is, in comparison with the addition of hydroxyl groups, negligible. However, if the system contains a sufficient quantity of a selective catalyst, the density of the polymer network grows in proportion to the MDI concentration and the value of the maximal modulus grows. Inasmuch as the growth of MDI concentration manifests itself favorably on the value of the maximal modulus with the increase of the filler content, it is necessary to admit that the filler also participates in the cross-linking reactions with diisocyanate.

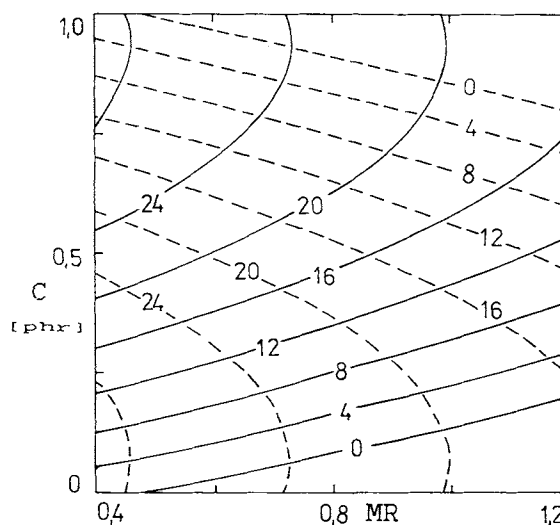The rate constant of vulcanization is significantly influenced by all the reaction parameters. Its de-

Figure 2 Dependence of maximal modulus $(y_1$, approximated as height of vulcanization curve in cm) on molar ratio COOH/epoxy (MR) and catalyst concentration (C) at constant levels of filler (70 phr) and MDI (——— 20 phr, – – – 0 phr).

pendence on the catalyst and the filler concentrations (Fig. 3) shows that both factors accelerate the reaction in a linear way, whereas the effect of the buffing dust content is more pronounced for greater surpluses of epoxide in the mixture. This trend is further proof of the assumption of the catalytic active centers' presence in the buffing dust, whether it be the specific effect of chromium complexes bonded to collagen or the nonspecific effect of other sites, e.g., of amino groups. The dependence of the rate constant on the MDI and filler contents are shown on Figure 4. For lower values of the MR of COOH/epoxy (i.e., in an excess of epoxide), the mentioned variable is almost linearly proportional to both parameters. The course of dependence substantially changes in an excess of carboxylated liquid rubber, where the rate constant is practically independent of both factors. This again shows that the share of addition reactions of carboxyl groups on diisocyanate are negligible. Understandably, the rate constant is directly proportional to the concentration of the catalyst under all circumstances, and, also, its minimal value in the proximity of an MR of COOH/epoxy of 1.0 is expected.

The length of the induction period (y_3) is significantly influenced only by the concentration of the catalyst. An illustration of this simple case is in a plane shown on Figure 5.

Both dependent variables discussed above are projected into optimal vulcanization (y_4), which is then influenced to a certain extent by all parameters

and that in the interaction members. It is apparent from Figure 6 that there is a decrease of the optimal vulcanization with increase of the dosage of the filler, which is first and foremost caused by its catalytic effect, but perhaps also by the increased dissipation energy in the course of mixing a more viscous mixture. The first possibility is evidently dominant inasmuch as the dependence of the optimal vulcanization on the molar ratio and concentration of the catalyst shows also the same course as in Figure 6. The MR of COOH/epoxy influences the optimal vulcanization in a more complicated manner. This is given by the statistical significance of the interaction members b_{12}, b_{13}, and b_{14}, and it is almost impossible to deduce the causes of the suggested trends unambiguously from a data file.

It ensues from the dependence of the hardness (y_5) on the filler content and the MR of COOH/epoxy (Fig. 7) that at a constant dosing of the buffing dust the hardness increases monotonously with the decreasing of the MR, i.e., with increase of epoxide excess. This is rather surprising, because for nonfilled mixtures of rubber OBNK and epoxide ECHD, but also for their carbon black-filled compounds, the values of hardness, tensile strength, and gel content are, in our experience, maximum in the proximity of the MR value of 0.8 if a selective chromium catalyst is used. Thus, it is evident that besides the reaction of epoxide with carboxyl groups other reactions must be taking place, mainly homoaddition of epoxide. Because at 150°C temperature and with the absence of a catalyst practically no cross-linking occurs, this effect can be caused by nonspecific ca-
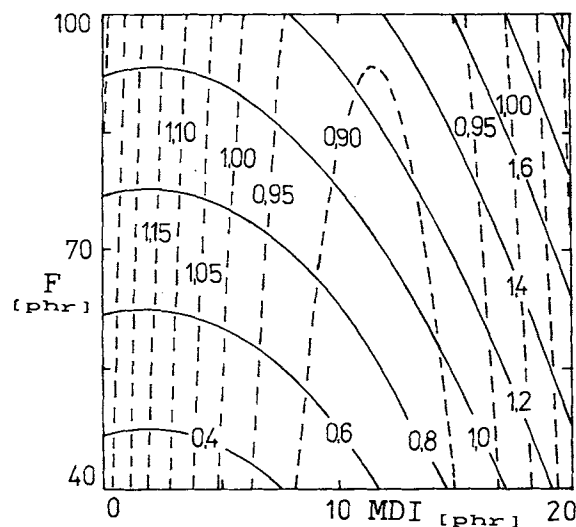

Figure 4 Dependence of rate constant of vulcanization (y_2, min^{-1}) on MDI and filler (F) concentrations at constant levels of catalyst concentration (0.5 phr) and molar ratio COOH/epoxy (——— 0.4, – – – 1.2).

talysis on active sites in the buffing dust. This is evident by the fact that the growth of hardness with the falling of the MR is substantially steeper in the absence of a catalyst. An excess of epoxide has, in fact, a substantially greater positive influence on the growth of hardness resulting from the presence of networks created by homoaddition. In selective catalysis, on the other hand, its reaction with carboxyl groups brings about a fall in hardness. Inasmuch as the growth of the hardness with the growth of epoxide excess is in the presence of a catalyst sub-
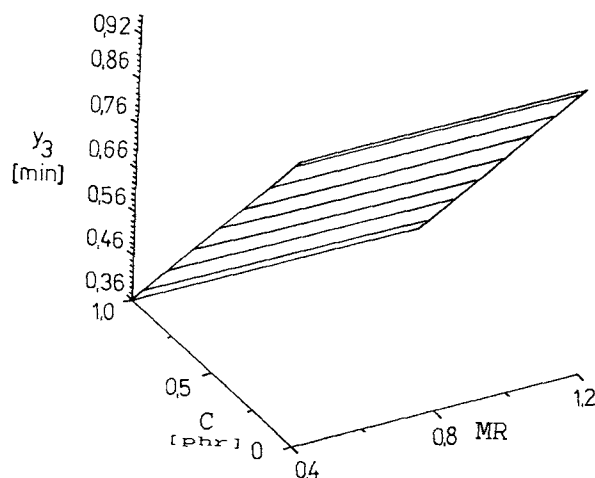

Figure 3 Dependence of rate constant of vulcanization (y_2, min^{-1}) on catalyst (C) and filler (F) concentrations at constant levels of MDI (10 phr) and molar ratio COOH/epoxy (——— 0.4, – – – 0.8).

Figure 5 Dependence of induction period (y_3, min) on the molar ratio COOH/epoxy (MR) and catalyst concentration (C) at constant levels of filler (70 phr) and MDI (10 phr).
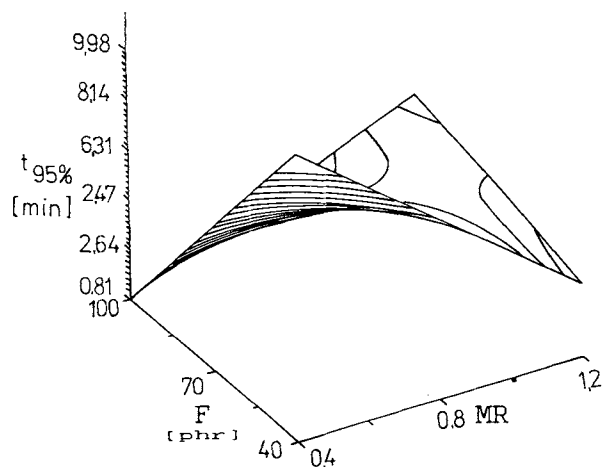
Figure 6 Dependence of optimal vulcanization (y_4, min) on molar ratio COOH/epoxy (MR) and filler content (F) at constant levels of catalyst (0.5 phr) and MDI (10 dsk).

stantially lower, it is possible to expect a partial compensation of the two above-described conflicting tendencies. The optimal filler content for attainment of maximal hardness is approximately 60 phr. Figure 8 illustrates the analogic dependencies on two further variables (MDI and catalyst concentrations). The dependencies have again the shape of a trough. Whereas for an excess of epoxide (MR 0.4 and 0.8) the hardness increases toward a zero catalyst content, at an excess of carboxyl groups (MR 1.2), the direction of the trough is turned around. This phenomenon is in agreement with the anticipated presence of competing nonselective active sites in the filler, causing homoaddition of epoxide. In an excess of carboxylated liquid rubber, no homoaddition of epoxide can occur to a greater extent, because it is consumed in rapid reaction with the carboxyl groups.

Thus, in these circumstances, the greatest hardness is manifested in the regular network given by the high conversion of functional groups in the presence of a sufficient quantity of selective catalyst.

Less explicit is the explanation of why at a constant concentration of catalyst the hardness first falls with the growth of MDI concentration and then grows rapidly from the approximate value 7 phr of MDI. The growth of hardness in the second part of the dependence is caused by the growth of network density as a consequence of the transversal urethane-bond formation. The fall in the first part of the dependence can be caused by the closeness of experimental points interpolated through the regression plane. Another possibility is the reaction of some isocyanate groups with low molecular contaminants (mainly residual humidity in the buffing dust). Thus, an increase of the rubber phase content and a fall in the hardness would occur, and only at higher concentration of MDI would the effect of network density dominate. This explanation conforms to the course of hardness dependence on filler content (Fig. 7), where the decrease of hardness during dosage to approximately 60 phr of buffing dust would have been caused by the described effect, whereas for a higher filler content, its hardening effect would be dominant.

The dependence of elasticity (y_6) on the MR of COOH/epoxy and the filler content manifests a maximum with the coordinates of the MR of 1.0 and 90 phr of filler (Fig. 9). The greatest elasticity is thus manifested in systems with equimolar abundance of carboxyl and epoxy groups. This is understandable, because it is these very systems that have the most regular elastic network. Dense networks, occurring in the excess of epoxide, deform nonre-
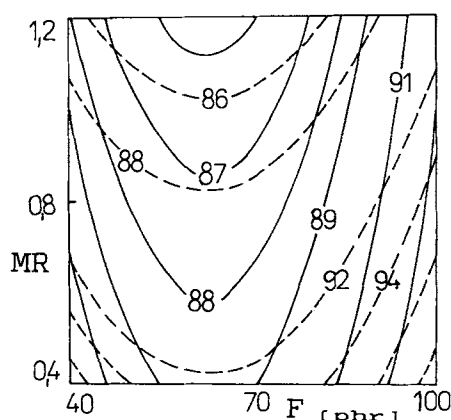

Figure 7 Dependence of hardness (y_5, Shore A) on filler content (F) and molar ratio COOH/epoxy (MR) at constant levels of MDI (10 phr) and catalyst (——— 0.5 phr, – – – 0 phr).
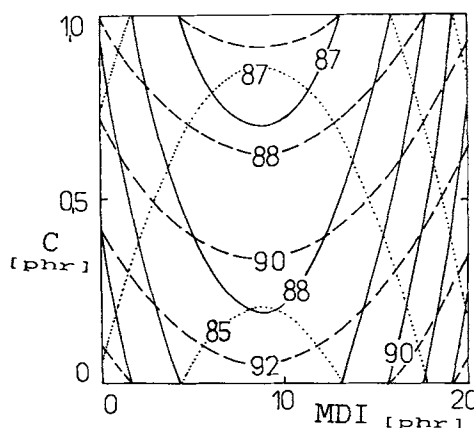

Figure 8 Dependence of hardness (y_5, Shore A) on filler content (F) and molar ratio of COOH/epoxy (MR) at constant levels of filler (70 phr) and molar ratio COOH/epoxy (——— 0.8, – – – 0.4, · · · · · 1.2).

versably and their dynamic properties are poor. It is interesting to know that increasing the filler content improves the elasticity to a certain extent, which could be given by the specific character of the buffing dust, differing from the usual particle-type fillers. The concentrations of catalyst and MDI do not have a significant effect on the elasticity.

Elongation (y_7) is also significantly influenced only by the value of the MR of COOH/epoxy and the filler content (Fig. 10). The resulting area is a plane falling in the direction of the growth of the filler content and also of the value of the MR. On changing the catalyst and the MDI concentrations, the dependence has an identical course. With increasing filler content, the elongation decreases in linear form, because the rubber phase content is smaller. This trend, however, can be compensated by increasing of the epoxide content without diisocyanate addition. It is convenient to compare this dependence with that of Figure 11, where the growth in tensile strength (y_8) is apparent with the fall in value of the MR. The increased strength enables the polymer network to approach more closely the theoretical value of its potential elongation. Networks created at a higher MR value have admittedly a greater potential elongation, but thanks to their small strength, they are far from attaining it. The monotonous growth of tensile strength conforming to the increase of MDI concentration can be seen in Figure 11. This growth is influenced by three mechanisms: The first of them is the increase of the network density, the second is the contribution of the urethane bonds polarity (hydrogen bridges), and the third is the reaction of diisocyanate with the active hydrogens of filler polypeptide chains, which
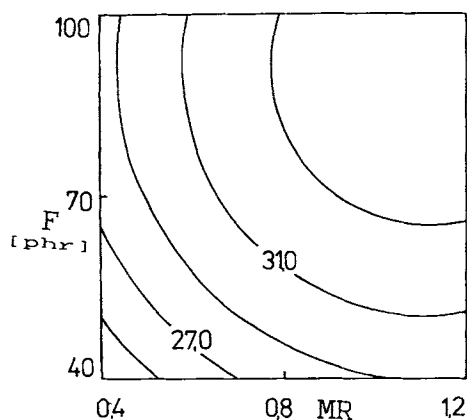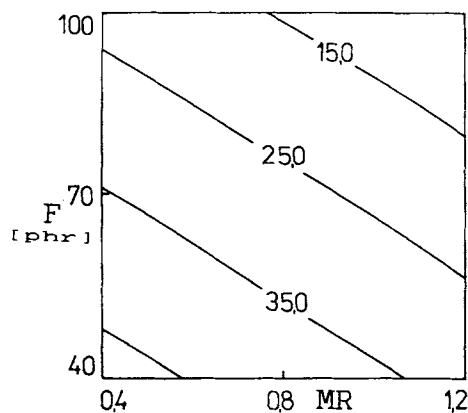

Figure 10   Dependence of elongation (y_7, %) on molar ratio COOH/epoxy (MR) and filler content (F) at constant levels of catalyst (0.5 phr) and MDI (10 phr).

brings about the interconnection of the polymer and collagen networks.

The energy of rupture (y_{10}) is significantly influenced by all the independent variables, but their interactions, with the exception of that of the filler–catalyst, does not significantly assert itself. On assessment of the effect of filler and catalyst concentrations (Fig. 12), it can be seen that the system behaves in a different way for high and low concentrations of the catalyst. In the first case, the energy of rupture is dependent to a great extent on the degree of filling and decreases with its growth, which is analogical to the behavior of high molecular rubbers filled with inactive fillers or superfilled with carbon black. For a low concentration of catalyst, the energy of rupture remains constant for variously filled systems and relatively small, and the system is at the limit of rubber elasticity. Practically, for the entire extent of the experiment, the energy of rupture grows with the increasing concentrations of MDI and epoxide. We have already discussed a similar dependence in the case of hardness. An increase of the modulus and strength occurs, resulting in comparable elongations in the increase of the energy of rupture.

The actual strength (y_{11}) is defined as the stress at rupture related to the cross section at the moment of rupture. It is, accordingly, a characteristic close to the energy of rupture and the found dependencies y_{10} and y_{11} have an adequate course. In Figure 13, this dependence is demonstrated by the effect of the MR of COOH/epoxy and MDI concentration.

All the independent variables significantly influence the gel content (y_{12}), which is a sensitive indicator of the quality of the polymer network created from reactive multifunctional components. Its de-

Figure 9   Dependence of elasticity (y_6, %) on molar ratio COOH/epoxy (MR) and filler content (F) at constant levels of catalyst (0.5 phr) and MDI (10 phr).
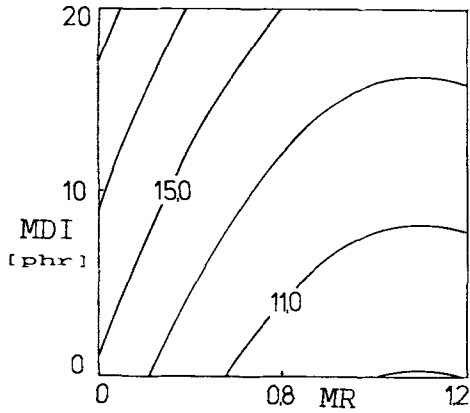
Figure 11 Dependence of tensile strength (y_8, MPa) on molar ratio COOH/epoxy (MR) and MDI concentration at constant levels of filler (70 phr) and catalyst (0.5 phr).
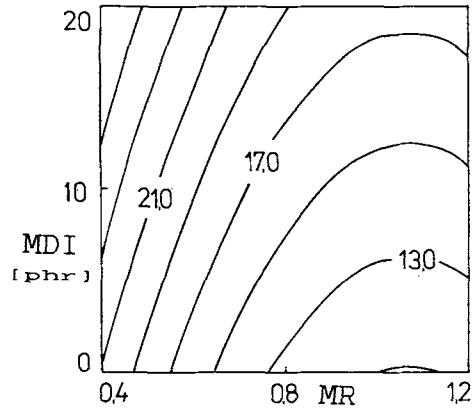

Figure 13 Dependence of actual strength (y_{11}, MPa) on molar ratio COOH/epoxy (MR) and MDI concentration at constant levels of filler (70 phr) and catalyst (0.5 phr).

pendence on the MR of COOH/epoxy and the filler content is simple (Fig. 14). The gel content has a linear growth with the increase of epoxide concentration and decreasing content of filler. In the absence of a catalyst, the dependence on the epoxide concentration is steeper, because in these conditions, the homoaddition reactions of epoxide are preferred. In the presence of a sufficient quantity of catalyst, these reactions are suppressed and a more regular but less dense network is created. The increase of the network density occurs also with the growth of MDI content, as shown in Figure 15. The same effect can be available by increasing of the epoxide content without diisocyanate addition. It can be noted that the dependence of the gel content on the composition of the compound is, according to an assumption,

analogical to the dependence of the maximal modulus.

CONCLUSION

The presented interpretations of the effects of the investigated system composition on the vulcanization parameters and the physical properties of prepared compounds show that all components assert themselves statistically significantly on all measured responses. The obtained data file enables selection of the mixture composition in such a way as to achieve optimal values of vulcanization parameters. However, these values are but ancillary criteria, because from the aspect of practical application, the
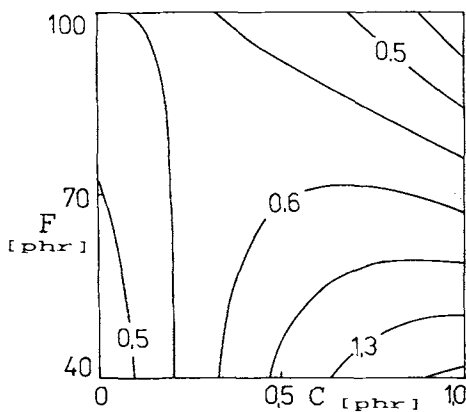

Figure 12 Dependence of energy of rupture (y_{10}, J) on catalyst (C) and filler (F) concentrations at constant level of molar ratio COOH/epoxy (0.8) and in the absence of MDI.
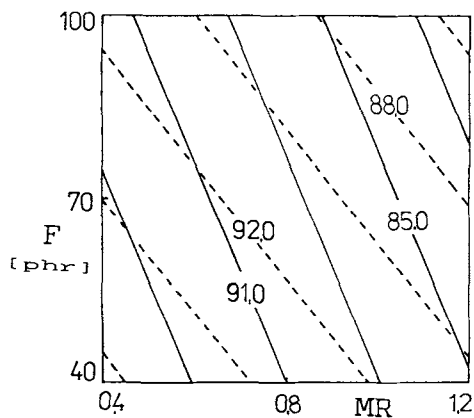

Figure 14 Dependence of gel content (y_{12}, %) on molar ratio COOH/epoxy (MR) and filler content (F) at constant levels of MDI (10 phr) and catalyst (———— 0 phr, – – – 0.5 phr).
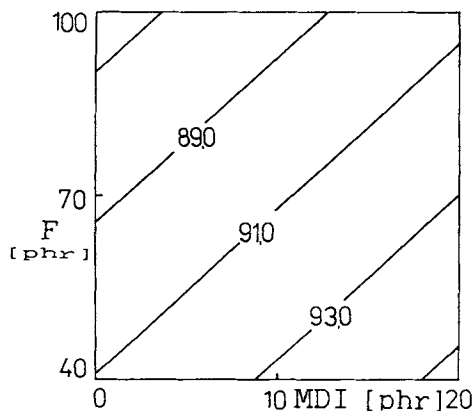
Figure 15 Dependence of gel content (y_{12}, %) on MDI and filler (F) concentrations at constant molar ratio COOH/epoxy (0.8) and catalyst concentration (0.5 phr).

physical properties of compounds are decisive. How can they be influenced purposefully is indicated in a survey of graphic illustration of all relationships and the accompanying commentary. On the basis of the results of the complex planned experiment, it is possible to reach the following practical conclusions:

- Leather buffing dust can be used without any further processing except for drying as a filler of rubber elastomers.

- The use of liquid carboxyl-terminated rubber as a precursor of the elastomer network enables the mixing of more than 100 phr of buffing dust into the compound.

- The reaction of liquid carboxyl-terminated rubber with triepoxide is catalyzed by the filler itself; however, to achieve greater selectivity and regularity of the network, it is necessary to use a chromium catalyst.

- It is possible to utilize MDI or another diiso-cyanate as a suitable supplementary cross-linking agent.

- The properties of the compounds can be purposefully influenced by a change of the mixture composition in accordance with the derivated regression function.

- The material obtained by the above-stated processing of the waste buffing dust from the chrome-tanned leather is potentially applicable on cemented soles, wrapping sheets, lagging and noise damping materials, sealing materials, antivibration pads, etc.

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