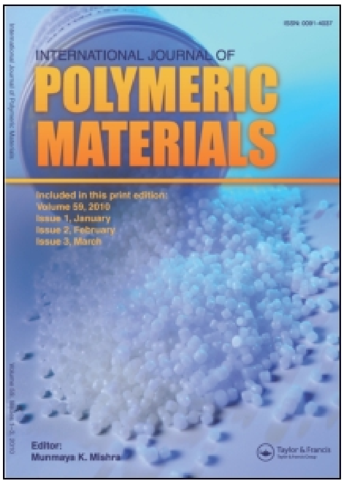

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Effect of the Sequence of Introduction of the Plasticizers and Their Mixtures on the Dynamic–Mechanical Behaviour of Polyvinylchloride Compositions at Low Temperatures

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The sequence of introduction of plasticizers in relation to the other components, and mainly in relation to the stabilizers, in PVC-compositions has a marked effect on the compatibility and efficiency of the action of plasticizers, and hence on the whole complex of their physical and mechanical properties.

The impact strength, determined by the work required for the destruction of the standard sample in the standard diagram of impact loading is extremely sensitive to material brittleness. Its variation reflects the effect of the sequence of plasticizer introduction on the dynamic–mechanical behaviour of PVC-compositions and the problem is treated in relation to the effect of plasticizer nature, the amount of plasticizer introduced into the composition, and testing temperature.

INTRODUCTION

Present PVC-compositions are multi-component systems consisting of mixtures of plasticizers, stabilizers, lubricants and high-melting dispersion additives.

The sequence of introduction of plasticizers and their mixtures in PVC-compositions has a considerable effect on their compatibility and efficiency, particularly in cases when the stabilizers are structurally active high-melting dispersion additives. The introduction of plasticizers, differing in nature and in amount, at a varied sequence in relation to the other components of the composition (in a special case stabilizers only) has a marked effect on the whole complex of physical and mechanical properties of PVC-composition.[1]

The investigation of the problem in relation to the increase of cold resistance of PVC-compositions is of high practical interest in view of the reliable exploitation of polymers and polymer materials at low temperatures.[3]

The impact strength, determined by the work required for the destruction of the standard sample in the standard diagram of impact loading (Dinstat method) is sensitive to material brittleness and has a direct relation with the cold resistance of the polymer materials.[3]

There are premises, based on thermomechanical investigations and investigations on the temperature dependence of tangent on the angle of mechanical losses (coefficient of mechanical losses), permitting the forecast for improved mechanical behaviour of PVC-compositions at low temperatures. At these conditions, strong influence is to be expected for the sequence of introduction of the components in PVC at low additives concentrations, and a slight manifestation of this effect at 40 wt% of plasticizer.[2]

The investigations made by the authors earlier, at concentration range of 1–15 wt% of plasticizer and separately at 40 wt% of plasticizer give grounds for the assumption for common regularities related to the sequence of introduction of the components and its effect on the impact strength at low temperatures in the whole concentration range, i.e. from 0.25 to 40 wt%.[4,5]

It is the aim of the present work to disclose the common regularities in the effect of sequence of components introdution in a three-component system (polyvinylchloride-stabilizer-plasticizer) on impact strength at low temperatures, and hence indirectly on cold resistance of PVC-composition.

EXPERIMENTAL PROCEDURE

Polyvinylchloride composition based on suspension polyvinylchloride with $K_s = 68$ is the object of investigation. Three-basic lead sulphate ($3PbO.PbSO_4.H_2O$) is used as a stabilizer. The amount of its introduction, i.e. 1 wt%, is chosen on the basis of earlier investigations[2] on the effect of three-basic lead sulphate on the efficiency of plasticizers and their mixtures in three-component PVC-compositions, this amount remaining constant throughout all tests—1 wt%.

Two plasticizers differing in chemical nature are chosen: Diizooctylphthalate (DIOP) and Dioctyladapinate (DOA), and their mixture of 1:1 ratio is used in line with them. The levels of variation of the amount of plasticizer introduced in PVC are chosen from three

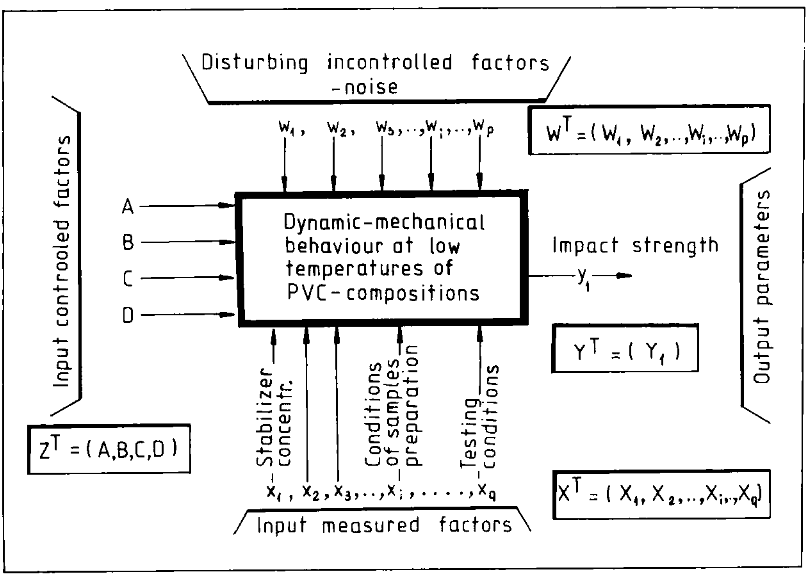

FIGURE 1 Diagram of the experiment carried out for investigation of the dynamic–mechanical behaviour of PVC-compositions at low temperatures.

TABLE I

Controllable factors

	Level of variation of the factors[b]		
Controllable factors[a]	Total number	Measure	Levels
1. Test temperature (A)	$i = 3$	°C	−40; −50; −60
2. Concentration of the plasticizer introduced (B)	$j = 4$	$wt\%$	0.25; 1; 15; 40
3. Sequence of plasticizer introduction as related to the stabilizer (C)	$k = 2$	—	stabilizer-plasticizer (straight); plasticizer-stabilizer (reverse)
4. Type of plasticizer (D)	$l = 3$	—	DOA; DIOP; DOA + DIOP (1 : 1)

[a] Control (controllable factor) is effected on the amount of the stabilizer introduced, being a constant value—1 wt%

[b] The reiterations for every test are five ($m = 5$).

characteristic concentration ranges, following,[2] i.e. 0.25–1 wt%; 1–15 wt%; and 15–40 wt%, thus covering completely the concentration range of 0.25–40 wt%.

Stabilizers and plasticizers are introduced in PVC at a varied sequence: PVC-stabilizer-plasticizer (straight sequence) and PVC-plasticizer-stabilizer (reverse sequence). The samples are prepared from a dryblend in which the components are introduced in the way already pointed out.

Impact strength is determined on standard samples at a single-bracket impact bending following Dinstat diagram, and test temperature varies so that it covers the cold resistance range.

At these conditions, a four-factor experiment is made following the diagram shown on Figure 1, with five observations for each test, with factors and levels of variation, enlisted in Table I.

The test data is processed using the method of the four-factor dispersion analysis with reiteration of tests.[6]

RESULTS AND DISCUSSION

Table II presents the results from impact strength tests, made at −40 down to −60°C temperatures following the scheme of the complete factor experiment. The average value of impact strength for each test is also given.

The results from the statistical analysis of the experimental results obtained are enlisted in Table III. The experiment as a whole is reproducible and this enables data processing by the method of the dispersion analysis, i.e. dispersions are homogeneous, and the model is reproducible in terms of factors and time.

The experiment scheme suggests not only a resultant experiment disclosing the effect of each of the major controllable factors, but also a possibility for disclosing the effect from the mutual influence of the independent factors.

The structure of the data in accordance with the method of the four-factor dispersion analysis with reiteration of tests could be expressed by the following:

$$X_{ijklm} = \mu + \alpha_i + \beta_j + \gamma_k + \delta_l + (\alpha\beta)_{ij} + (\alpha\gamma)_{ik} + (\alpha\delta)_{il} + (\beta\gamma)_{jk} + (\beta\delta)_{jl} + (\gamma\delta)_{kl} + (\alpha\beta\gamma)_{ijk} + (\gamma\delta\alpha)_{kli} + (\beta\gamma\delta)_{jkl} + (\delta\alpha\beta)_{lij} + (\alpha\beta\gamma\delta)_{ijlk} + e_{ijklm} \quad (1)$$

where μ is total average ($\bar{x}$); α_i, $\beta_j \ldots$ is the effect from the displacement $\bar{x}_i$, $\bar{x}_j$, $\bar{x}_k$ and $\bar{x}_l$ in relation to $\bar{\bar{x}}$ or $(\bar{x}_i - \bar{\bar{x}})$, etc.;
$(\alpha\beta)_{ij\ldots}$ is the effect from the interaction of two factors;
$(\alpha\beta\gamma)_{ijk\ldots}$ is the effect from the interaction of three factors;
$(\alpha\beta\gamma\delta)_{ijkl}$ is the effect from the interaction of four factors;
e_{ijklm} is error.

The dispersion analysis of the experimental data is presented on Table IV.

The effect of the major factors is significant at 1% level of significance (confidence probability 99%). Insignificant are the effects from the interaction of temperature-sequence of plasticizer introduction $(A \times C)$ and the interaction of temperature-concentration-sequence of plasticizer introduction $(A \times B \times C)$.

The verification of the statistical hypothesis for equal action of the major factors and interactions at 5% level of significance (confidence probability 95%) leads to a very interesting conclusion, Table V: the effect from the action of the major independent factors *A*, *B*, *C* and *D* is equivalent to 95% probability.

Another interesting result is obtained from the comparison of the effects from $(C \times D)$ and $(A \times B)$, as well as $(C \times D)$ and *B*. It is

TABLE II

Scheme of the experiment. Impact strength (following Dinstat), kJ/m^2

Stabilizer-plasticizer (straight sequence)	A($i = 3$) →	−40°C				−50°C				−60°C			
	B($j = 4$) →	0.25	1	15	40	0.25	1	15	40	0.25	1	15	40
DOA	y_1	32.606	20.690	17.675	16.767	17.865	19.433	16.079	19.361	32.689	19.926	17.559	13.072
	y_2	31.028	18.674	17.602	15.022	25.850	20.129	14.060	19.692	29.423	16.011	17.160	13.889
	y_3	35.046	21.830	17.571	17.737	20.998	16.511	17.679	15.332	28.739	24.083	13.651	12.015
	y_4	24.514	20.550	20.104	18.478	25.691	24.548	18.965	18.400	18.809	18.391	16.408	19.940
	y_5	24.910	19.506	19.912	21.403	28.187	22.934	19.915	14.286	22.249	16.044	17.017	15.251
	$\bar{y}$	29.621	20.251	18.573	17.881	23.718	20.711	17.340	17.414	26.382	18.891	16.359	14.833
DIOP	y_1	23.343	23.922	23.336	14.201	21.305	31.178	18.609	12.163	20.458	18.207	8.714	13.632
	y_2	25.423	28.860	17.669	11.850	20.689	19.066	18.549	13.073	16.026	20.563	11.633	13.531
	y_3	22.007	24.415	18.306	12.497	20.111	21.238	17.447	12.757	20.674	16.818	8.643	12.972
	y_4	25.596	25.517	14.076	12.799	21.086	31.734	12.284	12.219	21.348	17.623	13.884	13.429
	y_5	21.258	17.026	21.210	14.591	19.031	25.467	18.895	12.403	19.163	19.357	14.956	11.794
	$\bar{y}$	23.525	25.948	18.919	13.188	20.446	25.737	17.157	12.523	19.534	18.514	11.766	13.072
DOA + DIOP	y_1	30.189	17.306	7.819	13.008	18.454	20.534	12.678	11.358	20.218	22.311	14.864	11.209
	y_2	21.302	22.399	8.943	11.856	21.434	20.518	9.931	11.046	24.745	27.744	18.555	10.736
	y_3	22.672	24.007	6.019	11.674	16.913	28.197	11.749	10.957	21.039	19.240	14.816	13.478
	y_4	23.595	22.326	13.899	11.398	24.984	16.943	11.920	12.283	16.693	22.208	14.024	10.583
	y_5	31.103	28.470	10.989	19.010	13.046	24.952	14.136	11.323	21.073	30.441	15.036	13.145
	$\bar{y}$	25.772	22.902	9.534	13.389	18.966	22.229	12.083	11.393	20.754	24.389	15.459	11.830

Plasticizer-stabilizer (reverse sequence)													
DOA	y_1	28.326	17.842	19.186	21.179	15.575	32.985	21.485	22.465	16.058	18.403	18.788	12.579
	y_2	25.193	27.192	19.602	19.317	23.015	25.393	24.161	15.780	22.211	30.073	20.569	15.045
	y_3	30.189	18.088	19.086	18.660	14.795	33.315	21.416	16.086	23.891	25.091	19.919	14.354
	y_4	28.634	21.658	19.823	26.129	20.643	27.987	25.198	14.335	19.134	17.579	17.686	19.318
	y_5	29.026	12.847	20.061	26.844	17.730	18.414	25.027	22.465	18.762	20.136	18.021	16.911
	$\bar{y}$	28.274	19.525	19.552	22.426	18.352	27.719	23.457	18.226	20.011	22.256	18.997	15.645
DIOP	y_1	18.728	20.183	20.671	13.597	22.075	22.325	16.298	12.637	16.820	16.311	17.869	13.434
	y_2	13.064	18.146	17.509	13.395	22.913	20.209	19.503	12.001	19.231	20.451	17.004	10.814
	y_3	15.540	18.964	18.837	11.705	19.993	19.971	16.254	13.811	19.705	18.898	24.471	11.990
	y_4	18.823	24.650	19.677	14.158	19.480	16.621	18.285	14.285	20.827	22.342	18.385	13.400
	y_5	18.651	19.076	18.263	13.767	20.186	18.956	17.487	13.694	24.371	17.032	19.779	13.788
	$\bar{y}$	16.961	20.204	18.991	13.324	20.929	19.616	17.565	13.286	20.191	19.007	19.502	12.685
DIOP + DOA	y_1	30.446	22.203	19.104	19.860	25.890	27.303	23.052	11.787	23.860	31.689	18.986	13.687
	y_2	23.889	32.501	22.816	11.923	30.274	22.658	20.236	11.623	24.287	21.889	22.115	13.525
	y_3	21.744	33.506	20.492	13.586	26.154	18.436	20.983	11.058	27.237	23.884	24.838	11.308
	y_4	32.753	20.499	22.645	13.978	25.385	24.024	20.290	10.231	21.458	32.576	18.275	10.628
	y_5	30.068	22.125	18.364	20.082	27.168	14.767	24.014	12.595	31.392	25.678	20.673	10.221
	$\bar{y}$	27.780	26,167	20.684	15.886	26.974	21.438	21.715	11.459	25.647	27.143	20.977	11.873

$C(k = 2) \rightarrow$

$D(l = 3) \rightarrow$

TABLE III

Statistical analysis of the experimental data

1. Verification of the hypothesis for homogeneity of the order of dispersions (Cohren's Criterion) (G)	$G_n(72; 4) = 0.0317 < G(0.95; 72; 4) = 0.0419 < G(0.99; 72; 4) = 0.0489$
2. Assessment of dispersion for reproducibility (Sy^2)	$Sy^2 = 0.6893$ at $\Phi = 288$
3. Assessment of dispersion for average value ($S\bar{y}^2$)	$S\bar{y}^2 = 0.1379$ at $\Phi = 288$
4. Student's criterion (t)	$t(0.95; 5) = 2.57$
5. Deviation of the average value with 95% probability ($\Delta x_{0.95}$)	$\Delta x_{0.95} = \pm 0.427$ kJ/m^2

TABLE IV

Dispersion analysis of the experimental data

Source of variations	Sum of the squares, Q	Number of degrees of freedom, Φ	Non-displaced assessment of the dispersion of the general totality	Ratio of the dispersions	Fischer's criteria $F_{0.95}$	Fischer's criteria $F_{0.99}$
A	204.54	2	102.27	11.46	3.00	4.61
B	4407.20	3	1469.07	164.60	2.60	3.78
C	198.33	1	198.33	22.22	3.84	6.63
D	424.84	2	212.42	23.80	3.00	4.61
$A \times B$	199.51	6	33.25	3.72	2.10	2.80
$A \times C$[a]	17.91	2	8.96	1.00	3.00	4.61
$A \times D$	140.66	4	35.17	3.94	2.37	3.32
$B \times C$	376.54	3	125.51	14.06	2.60	3.78
$B \times D$	602.79	6	100.46	11.26	2.10	2.80
$C \times D$	348.70	2	174.35	19.53	3.00	4.61
$A \times B \times C$[a]	87.37	6	14.56	1.63	2.10	2.80
$B \times C \times D$	390.46	6	65.08	7.29	2.10	2.80
$C \times D \times A$	149.24	4	37.31	4.18	2.37	3.32
$A \times B \times C \times D$	794.98	12	66.25	7.42	1.75	2.18
Error E	2677.43	300	8.92	—	—	—
Total:	11020.53	359	—	—	—	—

[a] These effects of interaction occur to be insignificant for the conditions of the experiment, i.e. these dispersions compared to the intergroup error are negligible. They are not a source of variation in the system.

TABLE 5

Verification of the statistical hypothesis for uniform action of the major factors and interactions (confidence probability 95%)

Factors and interactions	A	B	C	D	$A\times B$	$A\times D$	$B\times C$	$B\times D$	$C\times D$	$B\times C\times D$	$D\times C\times A$	$A\times B\times C\times D$	$A\times B+B\times C+A\times D+B\times D$	$B\times C\times D+D\times C\times A$	Interactions
A	×	0[c]	0	0	0	0	0	0	0	0	0	0	0	0	0
B		×	0	0	θ[a]	θ	θ	θ	0	θ	θ	θ	θ	θ	θ
C			×	0	0	0	0	0	0	0	0	0	0	0	0
D				×	0	0	0	0	0	0	0	0	0	0	0
$A\times B$					×	0	0	0	0[b]	0	0	0	0	0	0
$A\times D$						×	0	0	0	0	0	0	0	0	0
$B\times C$							×	0	0	0	0	0	0	0	0
$B\times D$								×	0	0	0	0	0	0	0
$C\times D$									×	0	0	0	0	0	0
$B\times C\times D$										×	0	0	0	0	0
$D\times C\times A$											×	0	0	0	0
$A\times B\times C\times D$												×	0	0	0
$A\times B+B\times C+A\times D+B\times D$													×	0	0
$B\times C\times D+D\times C\times A$														×	0
Interactions															×

[a] The effect from the major factor B predominates that of interaction $A\times B$ at 95% probability.
[b] The effect from interaction $C\times D$ predominates that of interaction $A\times B$ at 95% probability.
[c] The effect from major factor B and that of major factor A are equal at 95% probability.

TABLE VI

Dispersion analysis of the experimental data—a model excluding temperature

Source of variation	Sum of the squares, Q	Number of degrees of freedom, Φ	Non-displaced assessment of the dispersion of the general totality	Ratio of the dispersions	Fischer's criteria, $F_{0.99}$
B	4407.20	3	1469.07	115.55	3.78
C	198.33	1	198.33	15.60	6.63
D	424.84	2	212.42	16.71	4.61
$B\times C$	376.54	3	125.51	9.87	3.78
$B\times D$	602.79	6	100.46	7.90	2.80
$C\times D$	348.70	2	174.35	13.71	4.61
$B\times C\times D$	390.46	6	65.08	5.12	2.80
Error E	4271.66	336	12.71	—	—
Total:	11020.53	359	—	—	—

quite evident that in selecting the plasticizer and the sequnce of introduction of the components a higher effect is obtained compared to the case of selection of the amount of plasticizer depending on material test temperature. Also, through a suitable selection of the plasticizer and the sequnce of its introduction the amount of plasticizer introduced in PVC-composition could be reduced, the efficiency of the plasticizer remaining the same.

On the basis of the model as-obtained a model is built for the effect investigated without the participation of samples test temperature, Table VI, where the established regularities are more clear. The model is obtained through including the effect of factor A into error E. Further, investigation is made for the basic sources of variability of the system, related to the problem under consideration.

All effects from the major independent factors and from the interactions are significant at a level of significance of 5% (confidence probability 95%), Table VI. The verification of the statistical hypothesis for equal action of the factors and the interactions is presented in Table VII.

The major conclusions from the investigation made could be summarized as follows:

The sequence of introduction of the plasticizer independent of its

TABLE VII

Verification of the statistical hypothesis for uniform action of the factors and the interactions (confidence probability 95%)—a model excluding temperature

Factors and interactions	B	C	D	$B\times C$	$B\times D$	$C\times D$	$B\times C\times D$	Interactions $B\times C+B\times D+C\times D+B\times C\times D$
B	×	0	0	θ	θ	0	θ	θ
C		×	0	0	0	0	0	0
D			×	0	0	0	0	0
$B\times C$				×	0	0	0	0
$B\times D$					×	0	0	0
$C\times D$						×	0	0
$B\times C\times D$							×	0
$B\times C+B\times D+C\times D+B\times C\times D$								×

chemical nature and its concentration (0.25 to 40 wt%) affects confidently the impact strength of PVC-composition at low temperatures (from −40 down to −60°C, in accordance with the investigation conditions).

The independent action of the sequence of introduction (C) of the plasticizers and their mixtures is equivalent to the independent effect of concentration (B) and of the chemical nature of the plasticizer (D), i.e. one more degree of freedom results for the control of the properties of PVC-composition, and this being of pure organizational nature.

The interaction ($B\times C$) of introduced plasticizer concentration and sequence of components introduction is equal in effect to the independent factors of plasticizer chemical nature (D) and introduction sequence (C). High plasticizer efficiency results at low concentration and reverse sequence of plasticizer introduced.

The interaction ($C\times D$) of chemical nature of plasticizer and introduction sequence in effect of influence is equal to the major independent factors. High efficiency results from the introduction of the mixture of both plasticizers DIOP+DOA (1:1) and at reverse plasticizer introduction sequence.

Very good are the characteristics obtained at low concentrations of the plasticizers DOA and DIOP+DOA, and this shows the effect from the action of ($B\times D$).

The regularities observed permit conclusions to be made for the sequence of introduction of plasticizers in the three-component system of PVC-stabilizer-plasticizer[4,5] to be spread for the whole concentration range of 0.24–40 wt%.

The properties of PVC-compositions (impact strength at low temperatures, cold resistance), in accordance with the investigation made, could be controlled also by the variation in the sequence of introduction of the plasticizers and their mixtures. Here, in the statistical model describing this effect there also will be present mixed members of second order and higher, and this shows that the choice of the components and the technology of introduction should follow an optimization procedure for searching a global extremum.

CONCLUSIONS

The investigations of the impact strength of PVC-compositions at low temperatures show the significance of the established effect of the sequence of components introduction into the composition which could be used for the control of their properties. It could be considered as one more possibility for regulating the properties of PVC-compositions and for the control of the efficiency of plasticizer action in a wide concentration range.

The present investigation directs our attention to the use of small amounts of plasticizers and mixtures of plasticizers through the variation in the sequence of components introduction with the ultimate goal of improvement of the properties of PVC-compositions.

It was found that the addition of the plasticizer before stabilizer introduction into the polymer composition results in higher plasticizer efficiency and a better dynamic-mechanical behaviour of the PVC-composition at low temperatures.

Considerable savings of plasticizers could be achieved at the same efficiency of the plasticizer, with a suitable choice of plasticizer, low concentration of plasticizer introduced and reverse plasticizer introduction sequence.

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References

1. T. S. Gancheva, Variation in the properties of PVC-compositions under the action of small amounts of additives, Doctor of science technique dissertation work, Sofia, (1982).
2. K. G. Bukovska, Plastication of PVC with mixture of plasticizers, Master of science technique dissertation work, Sofia, (1982).
3. B. I. Verkin and V. V. Pustovalov, *Low-temperature investigations for ductility and strength*, Moscow, Erergoizdat, (1982).
4. P. D. Dinev, D. L. Kostov and R. N. Boshnakova, Investigations on the effect of the sequence of introduction of some additives in PVC-compositions on their low-temperature impact strength, Varna, International Symposium "Polymers '83", (1983).
5. T. S. Gancheva, P. D. Dinev, D. L. Kostov and R. N. Boshnakova, Effect of the sequence of introduction of some additives in PVC-compositions on their dynamic deformation at low temperatures, Scientific Conference "Radio's Day '83", Sofia, (1983).