Effect of Composition on Behavior of Tricomponent Polymer Blends.   Study by Means of Simplex Lattice Planning of the Experiment

K. DIMOV, E. DILOVA, and S. STOYANOV,

Higher Institute of Chemical Technology, Sofia 56, Bulgaria

Synopsis

Some indicators of tricomponent polymer mixtures are investigated in dilute solution, in concentrated solution, and in the solid state.   The method used is that of simplex lattice planning of the experiment for an experimental mathematical description of these indicators of the composition of polymer mixtures.   The dependences are described by regression equations of the fourth power.   Lines of equal values are constructed of the investigated indicators, according to the equations obtained.   The character of the outline surfaces corresponds to the complex interaction between the supramolecular formations in the transitions from a dilute into a concentrated solution and in the solid state.   Compositions of optimum regions were determined wherein films and probably fibers of optimum physicomechanical indicators can be obtained.   These optimum regions outline the zones of improved structural compatibility among the components.

INTRODUCTION

The presence of a copolymer in dicomponent polymer blends may, as is known, improve their compatibility.   A triangular diagram of composition versus property is a convenient means of determining the effect of the composition of tricomponent polymer blends on compatibility.[1–4]   In previous studies, a number of experimental points were determined empirically.   The probable course of lines of constant values of the studied properties can be plotted from these points.   However, no attempts have been made as yet to mathematically describe the properties of the composition of polymer blends or to find a field of composition of optimum compatibility of the components.

Investigating certain indicators of tricomponent polymer blends both in a dilute and in a concentrated solution, as well as in the solid state, we have attempted to describe them mathematically as a function of the ratio of the components in the polymer blend.   Proceeding from the mathematical descriptions, we have tried to find a common denominator in the polymers' behavior in dilute solution, in concentrated solution, and in the solid state, as well as to determine the optimum regions of the compositions in which solutions, films, or fibers of properties desired beforehand can be obtained from tricomponent polymers.   An experimental statistical method employing the simplex lattice plans of Scheffe[5,6] was used for the purpose.   Far more precise than former methods of studying

the diagrams of composition versus property, this method enables one to obtain data within strictly planned points of the diagram and to deduce mathematical dependences of the composition's properties.

METHOD

The polymer blends PAN-PMMA-ANVS (polyacrylonitrile, poly(methyl methacrylate), acrylnitrile–vinylsulfonate) and PAN-ANMMA-ANVS (ANMMA = acrylnitrile–methylmethacrylate, with 94.5% AN and 5.5% MMA) were investigated. This particular selection permits to trace the effect of the quantity and the type of the active functional sets (i.e., cyano, methacrylate, and sulfonic groups) on the compatibility of PAN with its copolymers and other homopolymers. Data on the molecular weight and on the chemical composition of these polymers are given in Table I. DMF (dimethylformamide) was used as solvent. The fractions x_1, x_2, and x_3, as shown in the simplex diagram (Fig. 1),

TABLE I
Indicators of Initial Polymers

No.	Polymer	Mol wt	N_2, %	AN, %	MMA, %	VS, %
1	PAN	54,000	26	100	—	—
2	PMMA	150,000	—	—	100	—
3	ANVS	45,500	25.1	96.5	—	3.5
4	ANMMA	49,800	24.5	94.5	5.5	—

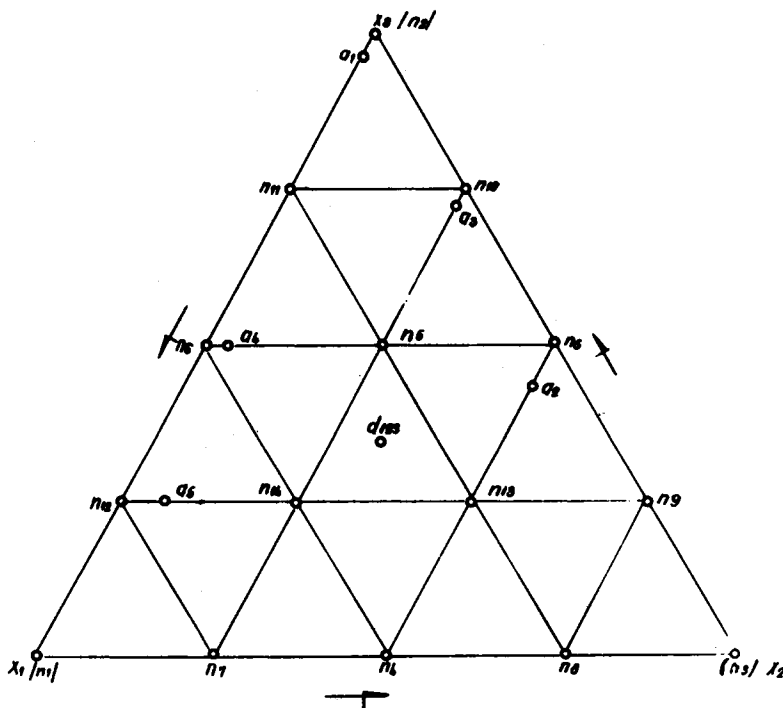ª N_2 = Nitrogen; AN = acrylonitrile; MMA = methyl methacrylate; VS = vinyl sulfonate.

Fig. 1. Simplex lattice of planned experiments; a_1, a_2, a_3, a_4, a_5, d_{123} = control points.

are those of the three components of the polymer blends. The condition $\sum_{i=1}^{3} x_i = 1.0$ is fulfilled for each point of the diagram.

The indicators adopted for study characterize the condition and the behavior of the polymer blends in dilute solution, in concentrated solution, and in the solid state.

Y_1, the viscosity of a 1% solution (η) of the pure components and the polymer blends in DMF, was studied as dilute solution.[7] The structure of the polymer, determined by its molecular nature, is known to manifest itself in the rheological characteristics of the investigated system. Their change permits to assess the spinning possibilities of the concentrated polymer solutions. The rheological characteristics K and n were appropriately used for the dicomponent polymer blend PAN-PMMA[13] in order to trace its spinning possibilities.

The curve of flow of the 19% solutions within certain limits is successfully described by the exponential model of Ostwald, $\tau = K \cdot \gamma^n$, as shown by our preliminary investigations.[8,9] The behavior of the concentrated solutions and the rheological characteristics K and n were selected for description. Y_2 is a rheological characteristic (n), describing the deviation of concentrated solutions from Newtonian behavior. Y_3 is the consistency coefficient in the exponential model (K), which is linked with the viscosity of the concentrated solution and reflects the interaction of the supramolecular structural formations.

The following essential physicomechanical indicators of the polymer blends in the solid state were determined: Y_4, the shearing strength of the film L (m), i.e., the length of film at which it breaks due to its own weight,[4,10] was determined, along with the relative extension at breaking, on a Shopper dynamometer as an arithmetic mean of ten specimens; Y_5, the stability of multiple deformations up to breaking, RMD in number;[10] and Y_6, the relative extension at breaking, l (m). These indicators were determined by means of methods used in determining analogous indicators in the paperboard industry.[4,10] They yield much information on the structural compatibility of the components in polymer blends.

The plan of the experiments on the simplex diagram was made so that its progressive complication permits to check the adequacy of the equations obtained and of raising the power to the fourth order (Fig. 1).[5,6] The matrix of the planned experiments and the results for the polymer blend PAN-PMMA-ANVS are given in Table II.

EXPERIMENTAL

The regression equations $y_i = f(x_1, x_2,$ and $x_3)$, where $i = 1, 2, 3, 4, 5,$ and 6 for the two polymer blends as polynomials of the second, the incomplete third, and the fourth order were deduced from the results obtained in Table II. The polynomials of the fourth order proved to be adequate mathematical models. The regression equation of the fourth order is as follows:

$$y = B_1 x_1 + B_2 x_2 + B_3 x_3 + C_1 x_1 x_2 + C_2 x_1 x_3 + C_3 x_2 x_3 + G_1 x_1 x_2 (x_1 - x_2)$$
$$+ G_2 x_1 x_3 (x_1 - x_3) + G_3 x_2 x_3 (x_2 - x_3) + D_1 x_1 x_2 (x_1 - x_2)^2 + D_2 x_1 x_3 (x_1 - x_3)^2$$
$$+ D_3 x_2 x_3 (x_2 - x_3)^2 + F_1 x_1^2 x_2 x_3 + F_2 x_1 x_2^2 x_3 + F_3 x_1 x_2 x_3^2.$$

TABLE II

Matrix of Planned Experiments to Obtain a Model of Fourth Power and Results for Polymer Blend PAN-PMMA-ANVS

No.	Exp.	PMMA (x_1)	ANVS (x_2)	PAN (x_3)	η (y_1)	n (y_2)	K (y_3)	L (y_4)	R.M.D. (y_5)	l (y_6)
1	n_1	1	0	0	0.2915	0.9116	26.17	2,685	1.0	3.30
2	n_2	0	0	1	2.137	0.9118	29.85	3,958	3224	15.10
3	n_3	0	1	0	1.561	0.6085	12.30	4,366	1818	6.83
4	n_4	0.5	0.5	0	0.944	0.8267	26.69	3,058	1.0	1.52
5	n_5	0	0.5	0.5	1.848	0.8761	23.42	4,150	2013	8.30
6	n_6	0.5	0	0.5	1.078	0.8843	15.02	2,430	1.0	2.55
7	n_7	0.75	0.25	0	0.588	0.9036	8.53	2,091	1.0	1.31
8	n_8	0.25	0.75	0	1.334	0.8034	25.46	3,008	1.0	2.78
9	n_9	0	0.75	0.25	1.896	0.8784	18.67	4,211	2560	9.200
10	n_{10}	0	0.25	0.75	2.044	0.8928	31.79	3,990	3600	12.26
11	n_{11}	0.25	0	0.75	1.567	0.9205	17.26	2,352	1.0	2.22
12	n_{12}	0.75	0	0.25	0.648	0.9325	7.89	2,072	1.0	2.13
13	n_{13}	0.25	0.5	0.25	1.443	0.8846	16.37	3,468	1.0	4.16
14	n_{14}	0.5	0.25	0.25	1.035	0.8554	25.31	2,454	1.0	1.92
15	n_{15}	0.25	0.25	0.5	1.5071	0.9112	16.49	3,601	1.0	9.95
16	d_{123}	0.333	0.333	0.333	1.32	0.826	28.4	3,673	1.0	6.02

TABLE III
Coefficients of Deduced Regression Equations

| No.		PAN-PMMA-ANVS						PAN-ANMMA-ANVS				
		η (y_1)	n (y_2)	K (y_3)	L (y_4)	l (y_5)	R.M.D. (y_6)	n (y_1)	K (y_2)	L (y_3)	l (y_4)	R.M.D. (y_6)
1	B_1	0.2951	0.9116	26.17	2,685	3.30	1.0	0.8718	24.49	2,438	42.28	4,856
2	B_2	1.560	0.6085	12.30	4,366	6.83	1,818	0.8628	15.26	4,244	7.51	1,269
3	B_3	2.137	0.9188	29.85	3,958	15.1	3,224	0.9506	14.93	4,124	13.05	2,870
4	C_1	0.070	0.2666	29.85	-5,490	-14.2	-3,634	-0.0544	-0.98	824	30.14	4,750
5	C_2	-0.545	-0.1096	-51.96	-3,566	-26.60	-6,466	-0.0120	-4.36	3,092	-29.86	6,144
6	C_3	-0.002	0.4638	9.38	-48.0	-10.66	-2,032	-0.0020	7.62	784	1.28	-226
7	G_1	-0.593	-0.2730	-127.2	-407.8	-1.56	4,844	-0.5390	20.76	1,285	10.79	8,933
8	G_1	0.018	0.0645	-40.2	1,900	31.01	8,592	0.2383	-8.12	250	30.31	-3,929
9	G_3	0.750	0.7318	-23.2	90.6	5.69	-1,796	0.0767	1.46	2,122	-24.42	-2,167
10	D_1	0.462	0.9269	-167.1	1,138	-7.61	-4,844	1.9301	-90.1	-5,897	-182.2	10,138
11	D_2	0.094	0.7539	-121.4	-9,402	-43.4	-8,592	0.0917	11.03	-10,935	55.1	15,078
12	D_3	2.588	0.8208	51.1	-1,119	37.67	20,048	-0.0549	-60.01	1,407	71.55	3,143
13	F_1	1.903	-4.1270	1531	-24,710	-235.8	19,403	1.4951	-38.68	-54,922	-389.5	-145,139
14	F_1	-1.190	-0.2040	-917.2	18,836	-155.7	-22,375	-0.3356	-155.0	-14,461	166.4	94,549
15	F_3	2.445	3.8850	-692.5	54,031	618.5	-40,506	1.0928	-108.37	50,428	-278.2	10,766
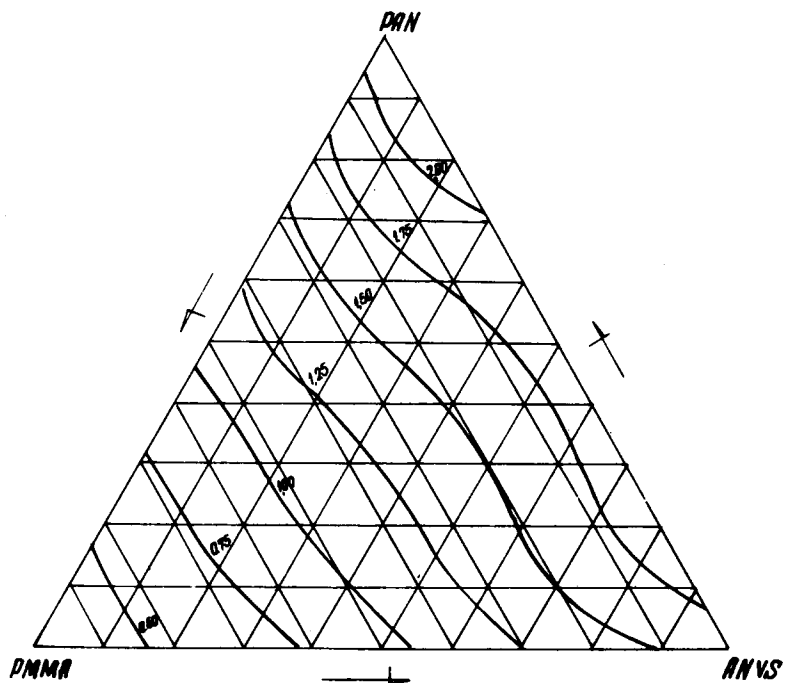
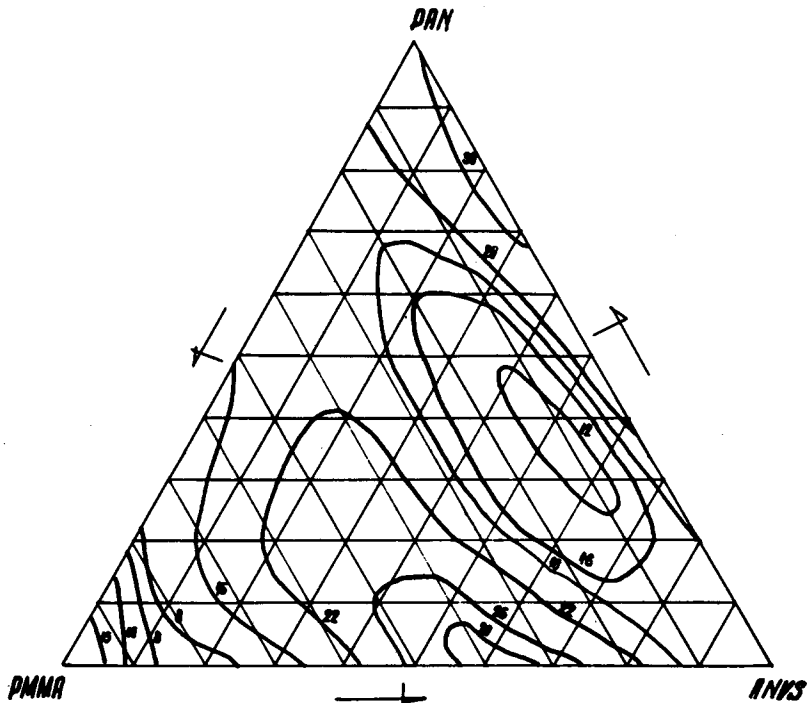Fig. 2. Lines of constant values of the viscosity (η) for polymer blend PAN-PMMA-ANVS.

Fig. 3. Lines of constanr values of the coefficient of consistency (K) for polymer blend PAN-PMMA-ANVS.
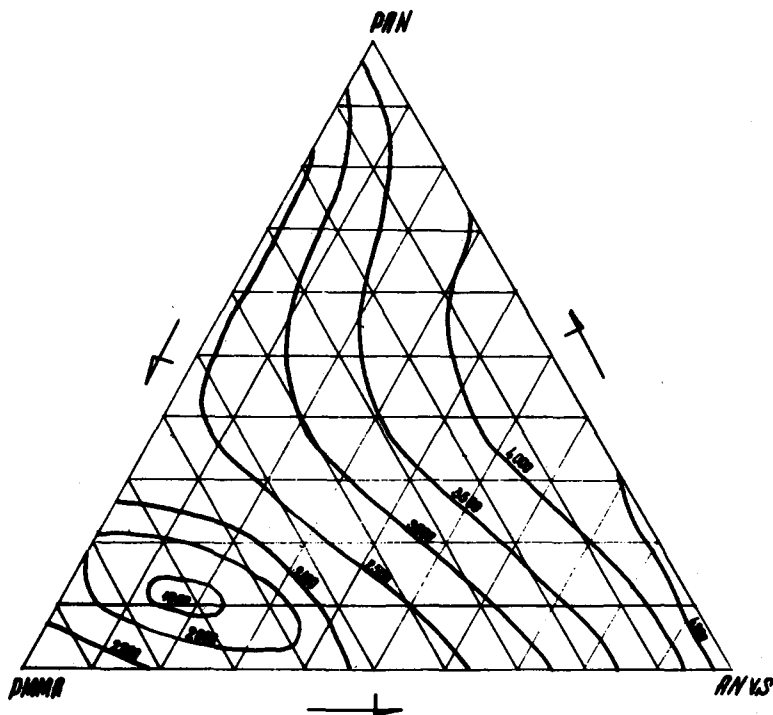
Fig. 4. Lines of constant values of rupture length L (m) for polymer blend PAN-PMMA-ANVS

The coefficients of the deduced regression equations are given in Table III. The adequacy of the equations was checked according to control points not participating in the experimental plan for deducing the corresponding equations—Student's t criterion.[14] The control points were selected beforehand so that most of them get into the probable region of anticipated optimum values of the indicators. For example, the coordinates of one of the investigated control points of a PAN-PMMA-ANVS blend, a_1, are: $x_1 = 0.02$; $x_2 = 0$; $x_3 = 0.98$, corresponding to a 2% PMMA content (RMD = 4000); for a_3: $x_1 = 0.05$ for 5% PMMA and RMD = 3200; and for a PAN-ANMMA-ANVS blend, $x_1 = 0.04$, $x_2 = 0.1$, and $x_3 = 0.5$. The adequate equations thus obtained allow computation of every one of the indicators, depending on the composition of the triple blend, for an arbitrary point of the simplex diagram. A scanning by simplex was made according to the equations, and the lines of the permanent values of the indicators were computed in order to determine the regions of their optimum values (Figs. 2, 3, and 4).[5,6]

DISCUSSION

The determined complex surfaces (Figs. 2, 3, and 4) accurately reflect the character of the interaction between the supramolecular structural formations of the tricomponent polymer blends both in a dilute and in a concentrated solution, as well as in the solid state. Figure 2 shows the lines of the viscosity values of the polymer blend PAN-PMMA-ANVS. The smooth course of the surfaces suggests a weaker physical interaction between the supramolecular formations in a

dilute solution. A slight decrease of viscosity with an increase of the PMMA content in the polymer blend up to 1.0 is observed; the ratio of the other two components has no effect on the viscosity. The role of PMMA as a "diluter" in a polymer blend which, in this case, consists of three components is thus once again demonstrated.[11]

The transition from a dilute to a concentrated solution, as seen in Figures 2 and 3, leads to a more complex character of interaction, which we assess by the rheological characteristic K (Fig. 3). The dependence of K on the composition is a complex surface and reflects the degree of structural interaction. This is also apparent from the values of K in Table II. K has a high value for pure PMMA (19% solution), in which homogeneous macromolecules interact strongly. A strong decrease of K is observed when the PMMA content in the polymer blend exceeds 70%. A similar region with a well-defined tendency of that kind is outlined for a PMMA content between 10% and 20%. In regions having a 0–5% and 30–60% PMMA content, K increases between 28 and 30.

This complex pattern suggests that none of the components of the polymer blend has a dominant effect in a given region. This is probably due to the specific features of the interaction of homogeneous and heterogeneous active functional groups. This specificity determines the intermolecular interaction of the supramolecular structural formations on the contact surface between them. In case of a pronounced change of K, the interaction between the heterogeneous groups, which results in a weakening of the internal molecular interaction, probably plays the predominant role. The considerable accumulation of homogeneous functional groups, on the other hand, decreases the possibilities of a specific interaction.

The plasticizing action of PMMA macromolecules also produces a great effect in a concentrated solution. The consistency coefficient K for a ca. 70% PMMA content has the lowest values. In the solid state, the PMMA content up to 8% acts as an interstructural plasticizer: RMD grows, as shown by our experiment with a dicomponent PAN blend. A greater PMMA content in the polymer blend leads to the disappearance of RMD and to the decrease of the rupture length and rupture extension (min. ca. 70%), owing to the predominant PMM content as a separate phase in the polymer blend, which manifests its strength indicators (Fig. 4). It can therefore be assumed that the concentrated solution preserves its structure in the solid state.

This is explained by PMMA's changed role in a solid polymer solution. PAN or its copolymer has a predominant effect on the physicomechanical indicators when the PMMA content is up to 8%. They are the dispersion medium, while PMMA is the dispersion phase. The dispersion particles of PMMA are in a quasi-dissolved state. With a higher PMMA content in polymer blends, its specific indicators become manifest. Compared with PAN and ANVS, PMMA has much poorer physicomechanical indicators. Polymers, as a rule, do not form a common crystal lattice. The films obtained are heterogeneous. The degree of their homogeneity and their physicomechanical indicators is determined by the size of the diffusion layer of the supramolecular formations' interface. A high content of more voluminous methacrylate groups makes for microvoids which, according to Griffith's theory, appear as microdefects.

The plasticizing effect of PMMA macromolecules (up to 8% content) is explained by the fact that, penetrating between the structural elements of PAN

and its copolymer ANVS, they decrease the interaction between the polar nitrile (CN) groups. The nitrile and the methacrylate groups are close in polarity and mutually repel each other. This lends greater elasticity to the macromolecular chains of PAN.[11] Due to their close polarity, the polymers should be compatible, but the shape of the macromolecule interferes here as a factor.

The polymers are structurally compatible within the range of 0–8% PMMA content. Most of PMMA is in a quasi-dissolved state. Above this percentage, PMMA differentiates as a separate phase. At this stage, there appears a change in the blend's entropy as well as a greater number of microdefects of the void. The film becomes more heterogeneous. As a result, its physicomechanical indicators deteriorate.

These conclusions are analogous to the corresponding ones for the dicomponent blend PAN-PMMA.[11] PAN and its copolymers, as compared to PMMA, are closer in nature and behavior.

The properties of the tricomponent heterogeneous polymer blends are determined by the properties of their components as well as by the interaction of the interphase surface. Double contacts between the phases are established in every tricomponent polymer blend. There are also triple contacts between the phases of the type $x_1-x_2-x_3$. It may therefore be assumed that the tricomponent three-phase blend has qualitatively the same microheterogeneous structure as the dicomponent blend of these polymers. The difference is only in the number of phases in the blend. The tricomponent heterogeneous blends may therefore be considered as blends of three couples of polymers. The very particles and the interface undergo no essential changes in comparison with corresponding binary blends. That is why the properties of the three-phase blend of a certain composition are determined by the corresponding properties in dicomponent blends and by their ratio in the tricomponent blend.

A generalized analysis of the results reveals that only the elements of supramolecular structural formations are formed in a dilute solution. The PMMA macromolecules are compact globules. Owing to the weak intermolecular interaction in a dilute solution and to their great elasticity, they do not open up, while the increasing PMMA percentage up to 1.0 leads to a decrease of the viscosity. In a concentrated solution, the possibilities of intermolecular interaction and of a decrease of the dipole interaction between the nitrile groups increase. The behavior of the concentrated solution then depends on the structure of the supramolecular formations and on their molecular interaction on the interface.[12]

The concentrated solution of polymer blends structurally represents a heterogeneous system, so that a qualitative expression of the interactions actually existing on a supramolecular level can be given only by the structural compatibility. The passing of such structurally microheterogeneous systems into the solid state leads to a peculiar distribution of the polymers on the basis of the supramolecular structures previously formed in a concentrated solution. This is confirmed by the above data on the polymer blends investigated by us. Consequently, their behavior in dilute solution, in concentrated solution, and in the solid state must be taken into account when delineating the optimum zones of structural compatibility of the investigated polymer blends.

In determining the optimum regions, use was made of the method of plotting the contour lines of the target parameters (Figs. 5 and 6). The undesired region
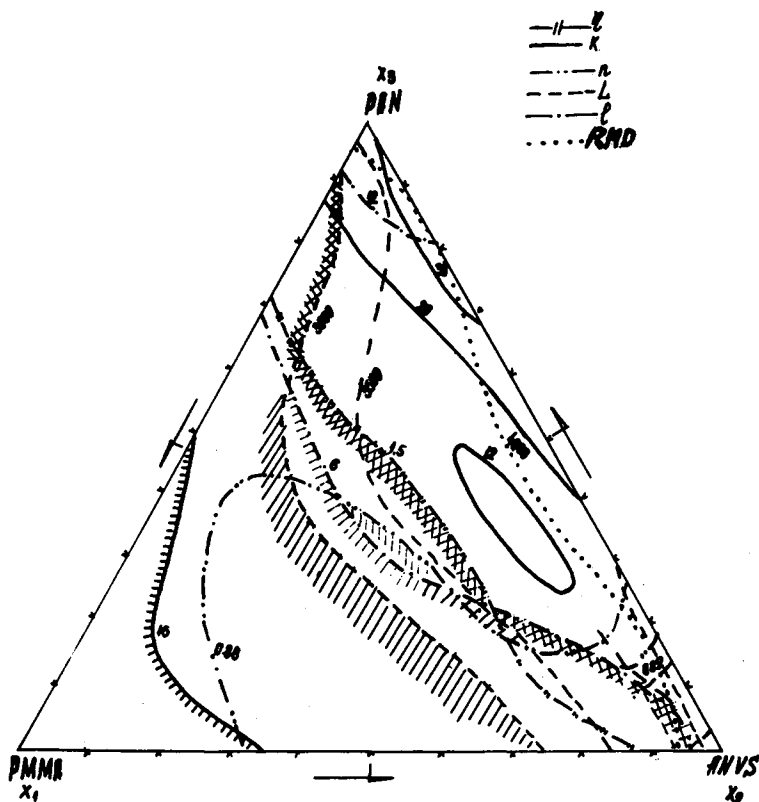
Fig. 5. Region of optimum composition and properties for polymer blend PAN-PMMA-ANVS.

of each target parameter, Y = from 1 to 6, has been shaded. Thus, recording the state of tricomponent blends in dilute and in concentrated solution as well as in the solid state, the coordinates of the optimum regions of polymer blends were determined. When delineating the optimum regions, values were selected among the investigated indicators which ensure optimum physicomechanical indicators in the solid state as a guaranty of improved structural compatibility. For instance, K and n should vary within certain limits, as these rheological characteristics are directly connected with energy consumption in the transport and spinning of polymer solutions. With increase in K, the productivity of the fillers also increases, while energy consumption goes down. But K should not have values that are too low, for the physicomechanical indicators of films from these solutions deteriorate considerably. The other rheological characteristic, n, should likewise range within certain limits. Its values should not exceed nor be much smaller than one, for then a strong structuralization appears in the concentrated polymer solution. The contour of the optimum region broadens whenever some physicomechanical features of the obtained products (depending on their use) can be neglected.

In some cases recourse is had to a compromise determination of some of its sectors. For instance, for PAN-PMMA-ANVS (Fig. 5), if great film elasticity is not required, the optimum region is much larger in area. But if RMD is an important indicator (say, for films and fibers), the optimum region is strongly displaced to the right, toward the PAN-ANVS line, where RMD is over 4000 c/s.
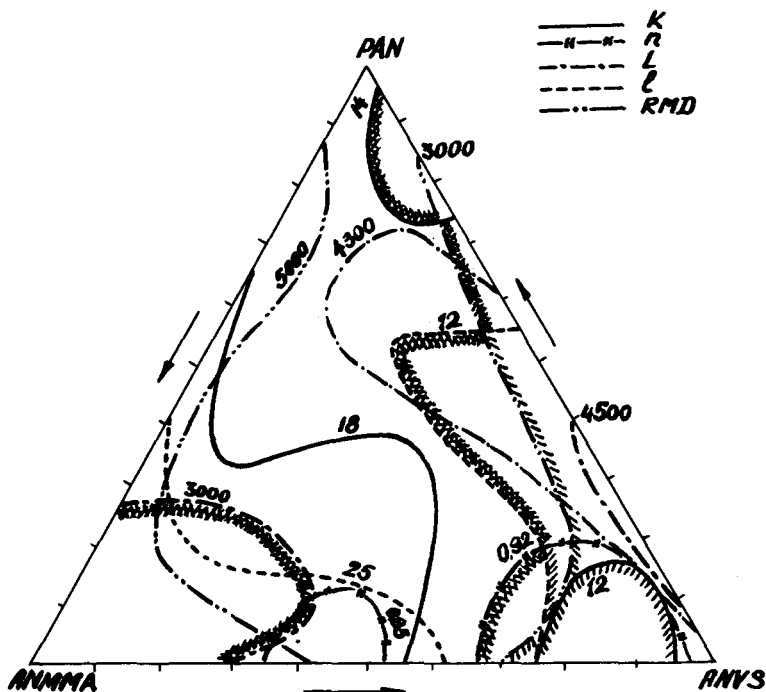
Fig. 6. Region of optimum composition and properties for polymer blend PAN-ANMMA ANVS.

The coordinates of this region are: $x_1 = 0$–0.1; $x_2 = 0.9$–1.0; $x_3 = 0$–1.0. The corresponding limits of the optimum values of its investigated indicators are: viscosity (1, 1.75–2.13), $n = 0.92$; $K = 20$–30; $L =$ greater than 4000 m, extension $l = 6$–13×10^{-3} m; RMD $= 4000$ c/s. The optimum region of the PAN-ANMMA-ANVS polymer blend (Fig. 6) was delineated by analogous considerations. Its coordinates are: $x_1 = 0$–75; $x_2 = 0.3$–0.65; $x_3 = 0$–1.0, and the corresponding limits of the optimum values of the indicators are: viscosity $= 1.70$–2.15; $n = 0.85$–0.95; $K = 20$; $L = 3000$–4500 m; RMD $= 3000$–5000 c/s; and extension $l = 12$–15×10^{-3} m.

The substitution of a copolymer for a homopolymer is known to lead to an improvement of compatibility in the polymer blend. This is also confirmed by the results obtained for the PAN-ANMMA-ANVS polymer blend and for the change of η, K, L, l, and RMD.

The described optimum regions of the two polymer blends define the limits in which the different components can vary and in which their behavior in dilute solution, in concentrated solution, and in the solid state is fairly close. Within these limits, the interaction between the supramolecular formations ensures optimum values of all the investigated indicators. Consequently, the optimum region delineates the zone of improved structural compatibility between the components of the investigated polymer blends.

CONCLUSIONS

1. The dependences established between the composition of polymer blends in solutions and the investigated properties of the products obtained from them are described by regression equations of the fourth order.

2.   Lines of equal values of the investigated indicators were plotted on the simplex diagram according to the obtained equations.

3.   The regions of the composition of polymer blends, in which films and probably also fibers of optimum basic physicomechanical characteristics can be obtained, were determined by the method of plotting the contour lines of the target parameters.

4.   A structural connection probably exists between the polymer blends investigated by us both in dilute and in concentrated solution, as well as in the solid state.

5.   Our investigations confirm the structural compatibility in the PMMA-ANVS and PAN-ANMMA-ANVS tricomponent polymer blends for the obtained optimum regions.   They also confirm that a copolymer in the polymer blend improves the compatibility of the homopolymers.

References

1. A. Dobry and Boyer-Kawenoky, *Polym. Sci.*, **1**, 95 (1947).

2. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).

3. J. Muller, Thesis, Strasbourg, 1968.

4. V. Cornelia, *Cell. Chem. Technol.*, **1**, 597 (1971).

5. H. Scheffe, Experiments with Mixtures, *J. Royal Statist. Soc.*, **B 20** 344 (1971).

6. J. W. Gorman and J. E. Himman, *Technometrics*, **4**, 463 (1964).

7. C. Jezzy and M. Laezkowski, *Faserforsch. Textiltech.*, **14**, 265 (1963).

8. S. Middleman, *The Flow of High Polymers*, Chem. Eng. Dept., University of Rochester, Rochester, N. Y., 1968.

9. F. Mauraux, *Ind. Chim. Belg.*, **35**, 891 (1970).

10. Scan. Pat. P16:65; Scan. Pat. P17:66.

11. K. Dimov and E. Dilova, *Chim. Volokna*, **6**, 21 (1971).

12. V. N. Mihailov, *Viskomol. Soedin.*, **13**, 395 (1972).

13. K. Dimov, E. Dilova, and G. Peev, *Angew. Makromol. Chem.*, **36**, 18 (1974).

14. G. A. Chemleva and N. G. Mikeshina, *New Ideas in Planning an Experiment* (in Russian), Nauka, Moscow, 1969, p. 191.