

Application of a Method for the Mathematical Experimental Statistical Modeling Approach to Analyze Physical–Chemical Properties of Interpenetrating Polymer Network of Polyurethane and Unsaturated Polyester

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ABSTRACT: Modern statistical analysis methods were employed to investigate and evaluate the effect of chemical composition on mechanical properties of interpenetrating polymer network (IPN) formulations that had been synthesized of polyurethane and unsaturated polyester resin (cross-linked with styrene). Experiments run according to the mathematical plan made a basis for empirical models derived from the Sheffe polynomials. The models were utilized to optimize the chemical composition of IPN from the viewpoint of achievable mechanical parameters, to assess changes of those properties over the whole theoretically possible scope of quantitative compositions, and to investigate the effects of individual components and their possible

interactions. The findings supported a thesis on complex interactions between polymeric components of IPN; they can be the reason for tangled polyurethane, unsaturated polyester, and linear polystyrene polymer networks, and ultimately they can be responsible for the formation of immiscible phases within the plastics produced. Data were also obtained which make it possible to evaluate potential mechanical properties of synthesized IPN compounds as coating materials and engineering plastics. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1855–1867, 2005

Key words: polyurethanes; polyesters; interpenetrating networks (IPN); mechanical properties; modeling

INTRODUCTION

Interpenetrating polymer network (IPN) compositions as first obtained in the 1980s of are mixtures of two or more polymers wherein at least one component has undergone polymerization or cross-linking in the presence of other components. The essence of that structure is interpenetration of polymer network chains and knots, with polymers frequently presenting inverse hydrophobic performance, e.g., polyacrylate and polyurethane¹. Hence, those systems form separate and frequently interpenetrating spatial networks and there are no covalent bonds between them.^{2–5} Those materials are polymeric analogues of inorganic solid alloys as represented, for example, by alum crystallization systems. Formation of such polymer networks is advantageous for macroscopic homogenization of polymer mixes since it overcomes typical thermodynamic immiscibility of polymers and produces a single homogeneous phase, at least at the macroscopic level. That is satisfactory in many cases to

obtain advantageous processing and performance properties.

Despite apparent homogeneity, phase separation usually does take place in IPN systems and it can be observed at the molecular level, which results from different types of chemical structures in polymers and strongly diversified sizes of domains of flexible and rigid segments that are present in both networks. Physical–mechanical properties of such multicomponent systems are dependent on the morphology of polymer structures within those systems, on the degree of phase separation, and on size, shape, and arrangement of microregions produced. All those structural factors are decisive physical–mechanical properties of a specific IPN composite and are important for applicability of that composite. It is very hard to find good correlation between said properties and the structures of polymer segments and/or polymer supermolecular structure because of complexity of such multicomponent systems. In our opinion, one possible approach to solving that problem is developing empirical models for selected IPN systems that would describe the dependence: *chemical composition–properties*, and only then additional structural investigations could support the efforts intended to more

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precisely explain and interpret the correlations observed.

Our interest has been aimed at obtaining IPNs from unsaturated polyester resin (UP) and polyurethane (PU). This results from the fact that UPs have been widely employed as coating materials and engineering plastics. The products can be manufactured by casting or as glass-reinforced composite materials and SMC molding compounds.^{6–8} Molding really big elements of glass laminates is possible owing to low-viscosity specifications of those resins and their good wetting performance; glass fiber mats can thus be quickly impregnated with UP resin. However, the products so obtained are characterized by high molding shrinkage and brittleness. These are considerable drawbacks for their use as engineering plastics and in particular as casting resins or modern BMC molding compounds.^{9,10} One applicable method for improving the impact resistance and flexibility of UP resins is chemical modification, namely introducing polyurethanes to those resins. A few possible aspects are worth noting as follows:

- preparation of oligomeric unsaturated polyester, which also involves acrylic structures, with terminal groups capable of reacting with isocyanate prepolymers, applicable, for example, as an efficient binder for multilayer glass-reinforced composites,^{11,12}
- synthesis of polymer products in the reactions of high-molecular-weight, branched, unsaturated polyesters, which have –OH terminal groups, with diisocyanates, said products to be utilized, for example, in reaction injection molding;^{13–15}
- production of unsaturated polyesters, which are thickened with diisocyanates and not, as is the usual practice, with MgO or CaO; these are applicable as SMC molding compounds in sheet press molding processes;^{16,17}
- manufacture of polyurethane-modified alkyd resins that can be cross-linked with styrene in the free-radical cross-linking reaction, with improved strength and lower contraction in volume, to be utilized as coatings and in particular as glass-reinforced composite materials.¹¹

This report covers the production method for polyurethane–polyester interpenetrating polymer networks. This method makes it possible to obtain insulating foamed materials applicable in civil engineering, e.g., special panels made of multilayer composite materials that can be employed as thermal insulation or acoustic insulation elements.¹⁸

With the above concerns in mind, we undertook a study on the synthesis of IPN systems on the basis of commercially available selected polyurethane raw materials (polyols and diisocyanates) and alkyds derived

from unsaturated acids or anhydrides, cross-linked with styrene (and radical-type initiators).¹⁹ The synthesis processes were planned and executed according to mathematical experimental design method to minimize the number of tests required. That number, however, should be satisfactory to obtain, from appropriate calculations within the assumed scope of investigation, quantitative correlations between some specified chemical compositions of IPN compounds and a series of their mechanical properties. The choice of chemical compositions was affected by quantitative aspects and by structural factors that resulted from the substrates employed and that influenced the structures of IPNs. Also, possible tangling of chains within the networks produced and supermolecular structures of polymers were taken into consideration. The experimental design had to be more complex for that reason than, for example, a plan required for the optimization of composition of a typical physical mixture like ethylene-octene copolymer + polypropylene + auxiliary additives.^{20–23}

EXPERIMENTAL

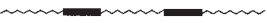
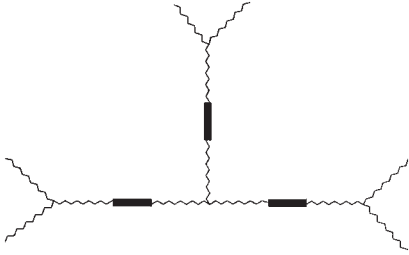

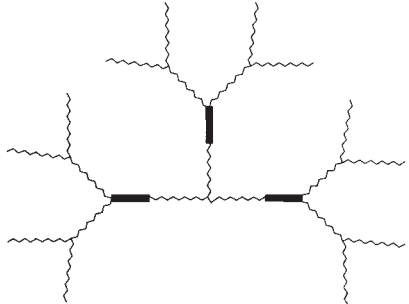
Raw materials and intermediates employed in the study

- 2,4- and 2,6-toluylene diisocyanate (2,4- and 2,6-TDI) (for industrial use); a mixture of these isomers at a ratio of 80 and 20%, respectively (from Aldrich)
- Polyoxyethylene glycol ($M_n = 2000$) (Rokopol D2002) and poly(oxyethylenepropylene) triol (Rokopol R330) from Zakłady Chemiczne Rokita S.A. in Brzeg Dolny (Poland) (dried under vacuum in nitrogen, at 120°C and during 2 h)
- Butane-1,4-diol (BD), trimethylolpropane (TMP), and styrene (ST) from Allied Signal Riedel de Haën (Germany)
- 1,4-Diazobicyclo-[2,2,2]-octane (DABCO) (Fluka)
- UP (Polimal 103), which was obtained by reacting maleic anhydride, phthalic anhydride, 1,3-propylene glycol and diethylene glycol
- Cobalt naphthenate (CoNa) as initiator in the form of 1% solution in dibutyl phthalate; commercial products available from Zakłady Chemiczne Nowa Sarzyna (Poland)
- Methyl ethyl ketone peroxide (MEKPO) from Atochem Deutschland GmbH

Synthesis of PU

The PU component was obtained in a two-stage polyaddition process in a solvent. The reaction of polyether polyols (Rokopol D2002, Rokopol R330) with TDI was conducted in styrene (i.e., in solution) at 80°C. DABCO (0.10 wt %) was the polyaddition cata-

TABLE I
Schematic Structures of PUR Used versus Raw Materials Applied in Their Synthesis

Type of extension agent	Type of polyol	
	"Rokopol D2002"	"Rokopol R330"
1,4-Butanodiol	 (symbol PU D2002-BD) used for IPN $m = 4$	 (symbol PU R330-BD) used for IPN $m = 2$
Trimethylolpropane	 (symbol PU D2002-TMP) used for IPN $m = 3$	 (symbol PU R330-TMP) used for IPN $m = 1$

lyst and an inert gas atmosphere was adopted to protect the reaction mixture against atmospheric humidity. The volumes of feedstocks were adjusted in such a way as to reach an initial molar ratio of $-NCO$ and $-OH$ groups of 2:1 for the first stage. The obtained isocyanate prepolymer was further extended at the subsequent stage by means of BD, to produce linear PU, or alternatively with TMP, to produce branched PU. The ratio of $-NCO$ and $-OH$ was maintained close to equimolar (1:1.1) for the second stage. The PU synthesis reaction was usually stopped after 6–8 h, when the content of $-NCO$ groups was below 0.3%.

Table 1 presents the structures of obtained PUs versus polyol types used.

Chemical composition of unsaturated polyester resin

Solutions of POLIMAL 103 in styrene made up the polyester component of IPN. The concentrations of those solutions amounted to 60–90 wt % polymer and they resulted from assumed weight ratios for PU, UP, and ST in the final IPN compositions. Since the volume of ST used was different in the synthesised compositions, the ratio of double bonds derived from the cross-linking agent (styrene) to those derived from polyester resin was also changing, illustrated in Table 2. The equivalent weight of "C=C" bonds for UP is 392.0 g/C=C.

Preparation of IPN compositions

After the concentration of the solution of UP in ST (solution II) was adjusted as required, the solution (I), i.e., PU resin in ST, with known and controlled concentration, was added thereto and those components were subjected to homogenization. Then, the hardening system, composed of 4 wt % MEKPO (initiator) and 0.4 wt% CoNa (accelerator), was introduced. The amounts of those components were referred to the total weight of alkyd and styrene in the mixture. Chemical compositions of prepared IPN compositions are presented in Table 2.

After the initiator and accelerator were introduced, all components were mixed thoroughly. Care was taken not to entrap air in the viscous material since there was no time for deaeration; the applicable life time of those compositions was relatively short, max. 5 min. The liquid compositions were poured into prepared PTFE molds with silicone separator plates, which gave adequate shapes to test pieces. The hardening process involved the following regime: minimum 12 h at room temperature, then 1 h at 60°C and 1 h at 70°C, and another 24 h at 80°C, and then the test pieces were subjected to seasoning for at least 24 h at room temperature. Four IPN systems were synthesized and then subjected to mechanical tests.

Samples for tests were synthesized according to the factor design which was based on 12 experiments for

TABLE II
Chemical Compositions of IPNs

Share of ST in IPN (wt %)	Share of PU in IPN (wt %)	Weight ratio of PUR components: (UP + ST)	Conditions for synthesis process			
			PU content (wt%) in solution I	UP content (wt%) in solution II	Weight ratio : PU : UP	Molar ratio of C=C of ST and C=C of UP
10	10	10 : 90	90	90	0.1	0.42
	20	20 : 80			0.3	
	30	30 : 70			0.5	
20	10	10 : 90	80	80	0.1	0.94
	20	20 : 80			0.3	
	30	30 : 70			0.6	
30	10	10 : 90	70	70	0.2	1.61
	20	20 : 80			0.4	
	30	30 : 70			0.8	
40	10	10 : 90	60	60	0.2	2.50
	20	20 : 80			0.5	
	30	30 : 70			1.0	

every IPN system, and formal allowance was made for three components in each IPN system: PU (q_1), ST (q_2), and UP (q_3) (Table 3). Adopted denotation convention for independent variables is advantageous for interpretation of findings but it gives no room for the additional (basic) amount of ST, which is contained in POLIMAL 103 resin and which is introduced in the commercial process together with polyester alkyd. The area for the planned experiment was limited by the concentrations q_1 , q_2 , and q_3 , and it can be presented as a parallelogram inscribed into an equilateral triangle with the vertices $q_1 = q_2 = q_3 = 1.0$ (Fig. 1). The complete experiment plan covered 12 samples for each IPN composition studied (Table 3).

It was possible in practice to prepare IPN systems with compositions outside the scope adopted for our experiment since we had 100% UP available (alkyd with no styrene). It was also possible to synthesize polyurethanes from the same isocyanate and polyol components in bulk, i.e., with no styrene. However, our earlier investigation revealed that it was very hard

to prepare some extreme compositions. Hence, we decided to make use of styrene and put limits to its concentration from 10 to 40%; that more or less corresponded to that monomer content in the standard polyester resin (35% max.).¹⁹ It is known from literature reports²⁴ that the properties of polyester resins reach their optimum values just within that scope of concentration for the cross-linking monomer, and thus it was no use to employ more styrene, above 40%. On the other hand, the viscosity of IPN systems before cross-linking was too high if the styrene share was reduced below 10% and that had a negative effect on the preparation of test pieces, which were molded as cast elements — the resin failed to map perfectly the shape of a mold and the cast elements happened to have air bubbles entrapped in them (precise deaeration of a viscous resin was very hard to do since its gelation time was too short).

TABLE III
Plan of Experiment

Experiment no.	Independent variables		
	q_1	q_2	q_3
1	0.1	0.1	0.8
2	0.1	0.2	0.7
3	0.1	0.3	0.6
4	0.1	0.4	0.5
5	0.2	0.1	0.7
6	0.2	0.2	0.6
7	0.2	0.3	0.5
8	0.2	0.4	0.4
9	0.3	0.1	0.6
10	0.3	0.2	0.5
11	0.3	0.3	0.4
12	0.3	0.4	0.3

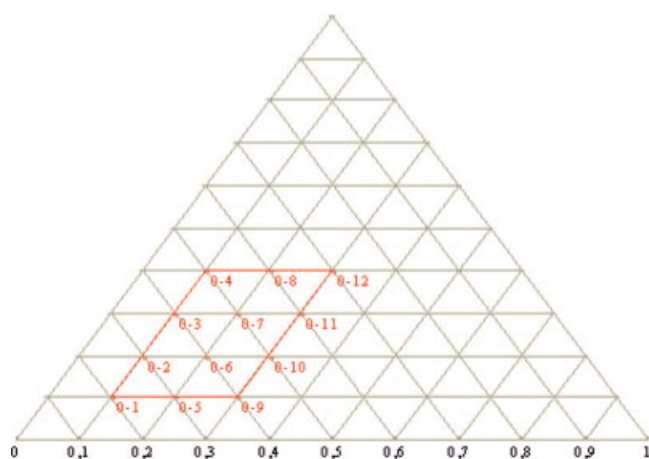


Figure 1 Planned area of experiments and experiment selected. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Points of Interpolation

No.	q_1	q_2	q_3
Point no. 1	0.1	0.1	0.8
Point no. 2	0.3	0.2	0.5
Point no. 3	0.2	0.2	0.6
Point no. 4	0.3	0.1	0.6

METHODS OF TESTS

Tensile strength (Y_1)

Strength tests of IPN materials were carried out with the use of a testing machine type Fp-100 from Heckert (Germany), in accordance with a standard procedure.²⁵ The sample holder travel speed was 5 mm/min and the measurements were taken over a distance of 100 mm. The measurements were controlled by the software LaborPoint 10.01. The tensile force versus sample tensile strain was recorded. That relation was computer processed and presented in charts as functions of tensile stress versus sample elongation.

Tensile strength in MPa was calculated from the formula

$$Y_1 = \frac{F_b}{w \times b}, \tag{1}$$

where F_b is the force recorded at rupture (N), w is the width of measuring length (mm), and b is the thickness of measuring length (mm).

Unit elongation (Y_2)

Ultimate elongation (ϵ) was calculated from the relation

$$Y_2 = \frac{L_b - L_0}{L_0} \times 100\%, \tag{2}$$

where L_b is the measuring length at rupture (mm) and L_0 is the initial measuring length (mm).

Impact resistance (Y_3)

Impact resistance of IPN samples was found with the use of standard Charpy method²⁶ and a pendulum machine from Ohst (Germany). The test pieces with no notch had the shape of small beams with the following dimensions: length $l = 50 \pm 1$, width $b = 6 \pm 0.2$, gauge $t = 4 \pm 0.0$ mm. The supports were arranged at a distance of $d = 40$ mm, and the striking energy was 1.0 J.

The impact resistance (Y_3) in kJ/m² was calculated from the formula

$$Y_3 = \frac{A_n}{b \times t} \times 10^4, \tag{3}$$

where A_n is the breaking energy required to break a test piece (J), b is the width of the test piece (mm), and t is the gauge of test piece (mm).

Hardness (Y_4)

A Shore hardness tester from Zorn (Germany) was employed in accordance with a standard²⁷ to test IPN compositions. Hardness in \hat{S} hA was read directly from the instrument after 15 s.

Mathematical methods for processing the findings

Computation of the experimental results done using software package STAT-SENS.²³ This package allows us to determine the different tasks at ESMA method-

TABLE V
Experimental Data for IPN Type R330

No.	TMP				BD			
	Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4
1	18.23	8.50	1.008	93.5	16.15	10.80	1.055	92.5
2	21.75	5.50	1.146	93.0	24.94	7.72	2.672	93.5
3	32.35	5.05	1.461	91.0	27.36	5.94	1.509	94.0
4	24.77	4.74	1.016	94.5	35.13	4.49	0.972	95.0
5	13.50	6.70	1.005	92.5	13.02	4.40	2.587	92.0
6	14.83	5.16	0.912	93.0	13.87	5.10	0.997	86.0
7	16.22	4.50	0.847	93.5	14.82	4.00	0.854	92.0
8	18.17	8.50	0.765	83.0	17.56	3.46	0.956	92.0
9	1.43	2.63	0.863	89.5	1.10	2.50	0.612	90.0
10	1.57	2.06	0.896	79.9	1.32	1.43	0.870	81.3
11	1.50	1.80	0.958	60.0	0.43	1.40	0.791	80.6
12	No data	No data	1.323	56.0	No data	No data	0.808	72.0

TABLE VI
Experimental Data for IPN Type D2002

No.	TMP				BD			
	Y ₁	Y ₂	Y ₃	Y ₄	Y ₁	Y ₂	Y ₃	Y ₄
1	16.23	7.80	0.883	96.5	22.00	8.15	0.670	95.5
2	27.55	4.80	1.027	96.0	36.20	5.70	1.008	93.5
3	26.46	4.47	1.041	90.0	31.86	4.51	0.689	90.0
4	28.31	4.30	0.549	96.5	19.92	4.05	0.572	93.5
5	15.53	6.48	1.032	96.0	15.50	5.46	0.638	96.0
6	16.36	4.20	0.828	95.0	12.47	4.11	0.710	87.0
7	17.67	5.00	0.717	89.2	2.27	1.15	0.630	93.0
8	1.70	1.60	1.431	86.5	2.03	1.24	0.995	85.6
9	4.14	3.46	0.825	90.6	4.11	3.90	0.616	92.0
10	1.52	2.90	0.688	89.1	1.43	1.51	0.632	82.8
11	0.70	2.20	0.592	64.2	0.69	1.11	0.588	61.0
12	No data	No data	No data	60.6	0.61	1.36	No data	79.3

ology. Because the linear model with only three parameters ($y_{nm}=a_{1m} q_1 + a_{2m} q_2 + a_{3m} q_3$) was not adequate for the goodness of the fit, a more complex model, the incomplete cubic model (Sheffe equation), was utilized to describe the dependencies of the mechanical properties studied (Y_1 – Y_4) versus chemical compositions of 4 IPN compounds.

The model view is

$$y_{nm} = a_{1m}q_1 + a_{2m}q_2 + a_{3m}q_3 + a_{4m}q_1q_2 + a_{5m}q_1q_3 + a_{6m}q_2q_3 + a_{7m}q_1q_2q_3, \quad (4)$$

where y_{nm} is the calculated mechanical parameters ($n = 1$ – 4) for the m th IPN composition IPN ($m = 1$ – 4); q_1, q_2, q_3 are variables with the following meaning: q_1 , polyurethane content; q_2 , styrene content; q_3 , polyester content, by Table 3; and a_{im} is the coefficient for the i th factor in that polynomial ($i = 1$ – 7), wherein

$$q_1 + q_2 + q_3 = 1. \quad (5)$$

It was a priori established that there isn't strengthened joint action among the same coefficients $q_1, q_2,$ and q_3 so q_1^2, q_2^2, q_3^2 and $q_1^3, q_2^3, q_3^3, a_3^3$ are absent in model (4). It was finally determined that this statement was correct.

Each equation within model (4) was understood to be statistically significant if the calculated Fisher criterion satisfied — depending on the assumed confidence levels α — the following conditions:

$$F_t > F = 6.16 \quad \text{for } \alpha = 0.05 \quad \text{and} \\ F_t > F = 4.01 \quad \text{for } \alpha = 0.10. \quad (6)$$

When model (4) is adopted, the coefficients a_{im} can be construed as follows.

TABLE VII
Factors in Sheffe Eq (4)

Type of IPN by TABLE I	m	y_{nm}	a_{1m}	a_{2m}	a_{3m}	a_{4m}	a_{5m}	a_{6m}	a_{7m}	Ft	Ad 5%	Ad 10%
1	y_1	-405.91	-119.01	-14.04	1168.40	649.36	395.11	-1796.10	16.536	+	+	
	y_2	-130.17	45.69	12.70	171.07	170.42	-106.54	-5.48	8.028	+	+	
	y_3	-3.475	-10.892	-0.454	58.857	12.340	28.002	-130.010	5.728	+	+	
	y_4	-302.1	193.9	74.7	-198.2	634.6	-146.7	791.6	13.946	+	+	
2	y_1	-181.77	58.37	3.71	114.16	271.81	95.85	-521.93	69.361	+	+	
	y_2	28.10	32.14	24.88	-192.97	-120.81	-93.39	460.60	18.795	+	+	
	y_3	-51.418	-30.575	-3.503	201.190	94.643	66.583	-303.620	1.185	-	-	
	y_4	8.4	228.2	96.7	-520.8	100.0	-221.8	854.8	7.391	+	+	
3	y_1	-193.12	-152.48	-13.17	434.78	327.94	467.36	-777.04	9.978	+	+	
	y_2	7.07	33.69	15.52	-203.85	-47.07	-86.77	486.74	3.560	-	+/-	
	y_3	-26.908	-8.469	-1.123	106.170	49.981	20.305	-169.030	0.614	-	-	
	y_4	-72.8	276.6	101.2	-812.3	230.6	-341.2	1572.5	9.984	+	+	
4	y_1	-117.01	-367.51	-10.68	1553.00	272.34	913.59	-3703.40	25.446	+	+	
	y_2	15.85	7.21	13.12	7.39	-29.51	-10.49	-200.45	27.066	+	+	
	y_3	-9.968	-4.683	-0.046	46.487	18.033	10.976	-69.869	0.296	-	-	
	y_4	-375.7	118.5	66.2	818.5	860.4	44.0	-1661.5	2.672	-	+/-	

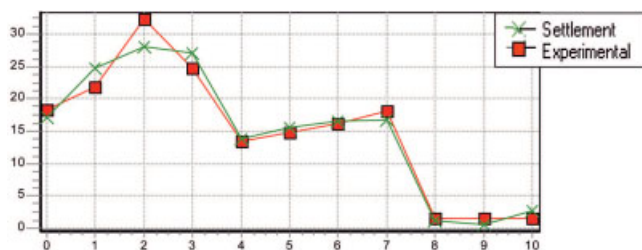


Figure 2 Comparison of experimental values Y_1 and model values y_1 at analyzed points in the chemical composition of IPN system 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The values of a_{1m} , a_{2m} , and a_{3m} characterize the effects of individual components, PU, ST, and UP, respectively; the values of a_{4m} , a_{5m} , and a_{6m} describe possible joint contribution from pairs of those substrates, PU + ST, PU + UP, ST + UP, respectively; and a_{7m} represents a joint effect of all three components: PU + ST + UP on the properties tested of m th IPN composition.

Four points were selected then which were specific for the considered area of experiment, as outlined by the parallelogram presented in Fig. 1:

$$P_j(q_1, q_2, q_3) \quad (j = 1-4). \quad (7)$$

Their precise coordinates can be found in Table 4. The interpolation method was then used to calculate the values of parameters y_{nm} for those compositions and those were compared with Y_{nm} , which were found in practice from measurements.

For each of the values of parameters y_{nm} the relative error $(\delta y_{nm})_k$ was calculated from the formula

$$(\delta y_{nm})_k = \left\{ \frac{(y_{nm})_k - (Y_{nm})_k}{(Y_{nm})_k} \right\} \times 100\%, \quad (8)$$

where $(y_{nm})_k$ is the calculated mechanical parameters ($n = 1-4$) for the k th sample of the m th IPN composition IPN ($m = 1-4, k = 1-12$); $(Y_{nm})_k$ is the experimental value of mechanical parameters ($n = 1-4$) for the k th sample of the m th IPN composition IPN ($m = 1-4, k = 1-12$).

The obtained results were utilized in optimization calculations and to determine, keeping in mind the analyzed mechanical properties, compromise chemical compositions for all four synthesized IPN systems.

RESULTS AND DISCUSSION

Tables 5 and 6 show the mechanical properties Y_1 – Y_4 as found for samples 1–12 (Table 3). Those samples were IPN systems for the synthesis of which PUs were used, which had been obtained from Rokopol 330 or Rokopol D2002. In Table 7, the factors a_{im} for polynomials (4) were provided, which had been found with

the use of the least-squares method, and also the values for the Fisher criterion $F_{i'}$, which were applicable to successive model equations, as well as the general evaluation for statistical significance for every equation. The sign of “+” was employed to mark the equations that were statistically significant and the sign of “–” was used for those that were statistically insignificant, while the polynomials marked with “+ / –” were, in our opinion, close to the border line. The presented data prove that, for the confidence level of $\alpha = 0.05$, tensile strength (y_1) is statistically significant for all IPN compositions studied (Table 1). Unit elongation (y_2) was also found to be statistically significant (except for IPN system 3, since for $\alpha = 0.10$ that equation was close to the border line). Moreover, impact resistance (y_3) and hardness (y_4) (except for IPN system 1) fell close to the border line. The above should be taken into consideration when formulating general conclusions and when providing interpretation for further optimization calculations.

In general, the functions for all the mechanical parameters analyzed are statistically significant only for IPN system 1, with the highest level of cross-linking. For example, consistence of experimental findings Y_{ni} and their corresponding values y_{ni} calculated from model (4) for that IPN system are illustrated in Figures 2–5.

The coefficients for polynomials were subjected to more detailed interpretation in Table 8. The approximate values for those coefficients as per Table 7 were utilized for further analysis, after they had been normalized by dividing the values of a_4 , a_5 , and a_6 by 10 and the value of a_7 by 100. This normalization enabled us to estimate the share of each coefficient in selected polynomial (4). The coefficients were then organized into two groups: those implying in our opinion the positive effect and those responsible for the negative effect on each property studied, depending on their + or – signs. If no coefficient is present in a given equation, that component or group of components has certainly no effect on the parameter described. Then, sums were found for all normalized coefficients that could be referred to the same mechanical feature y_n .

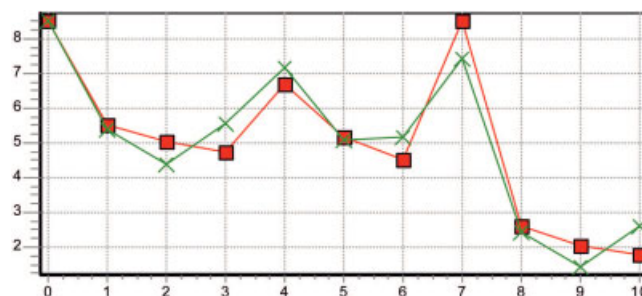


Figure 3 Comparison of experimental values Y_2 and model values y_2 at analyzed points in the chemical composition of IPN system 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

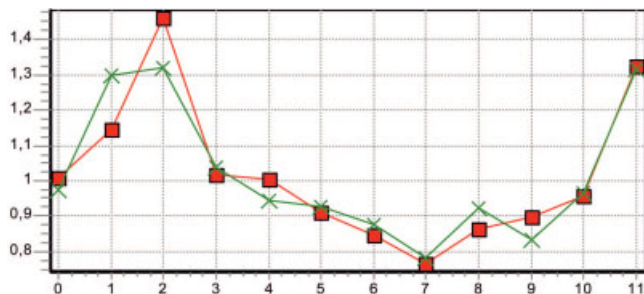


Figure 4 Comparison of experimental values Y_3 and model values y_3 at analyzed points in the chemical composition of IPN system 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$W_{y_n} = \sum_{m=1}^4 \left(\sum_{i=1}^3 a_{im} + \sum_{i=4}^6 0.1a_{im} + 0.01a_{7m} \right), \quad (9)$$

and shares (%) were calculated for every coefficient that pertains to every mechanical feature considered,

$$w_{a1(z)} = \frac{\sum_{m=1}^4 a_{1m}}{W_z} \times 100\% \quad (10)$$

$$w_{a2(z)} = \frac{\sum_{m=1}^4 a_{2m}}{W_z} \times 100\% \quad (11)$$

$$w_{a(z)} = \frac{\sum_{m=1}^4 a_{3m}}{W_z} \times 100\% \quad (12)$$

$$w_{a4(z)} = \frac{\sum_{m=1}^4 0.1 \times a_{4m}}{W_z} \times 100\% \quad (13)$$

$$w_{a5(z)} = \frac{\sum_{m=1}^4 0.1 \times a_{5m}}{W_z} \times 100\% \quad (14)$$

$$w_{a6(z)} = \frac{\sum_{m=1}^4 0.1 \times a_{6m}}{W_z} \times 100\% \quad (15)$$

$$w_{a7(z)} = \frac{\sum_{m=1}^4 0.01 \times a_{7m}}{W_z} \times 100\%, \quad (16)$$

where $z = y_1, y_2, y_3, y_4$.

Those shares were assumed to make quantitative measures for potential effects from individual components $w_{a1(z)}$, $w_{a2(z)}$, and $w_{a3(z)}$, combined effects from their pairs $w_{a4(z)}$, $w_{a5(z)}$, and $w_{a6(z)}$, or a combined effect from all three components $w_{a7(z)}$, which had been employed to synthesize the IPN systems and which influenced in a complex way the mechanical properties of the materials investigated.

Following that way of thinking, one can conclude from the data presented in Table 8 that the highest positive effect on strength at break is exerted by all three pairs of substrates, PU + ST, PU + UP, and ST + UP, and their relative efficiencies are 44.8:20.9:25.8. On the other hand, the opposite effect can be expected predominantly from individual substrates, PU and ST, and their efficiencies are also high, i.e., 54.7:38.9. The influences from other combinations are negligible. A supposition is hence justified that those components formed a few separate polymer phases in the IPN systems studied; the phases are more or less rigid and they are not miscible with each other, but they are decisive for the mechanical performance of the plastic.

It is hard to find an equally good explanation for changes in unit elongation, which is representative of the flexibility of a material. In any case, much higher effects have been exerted by individual components, PU, ST, and UP, than by their sequences, although some small negative joint action can be observed from two pairs, PU + ST and ST + UP. More quantitative data can be found in Table 8.

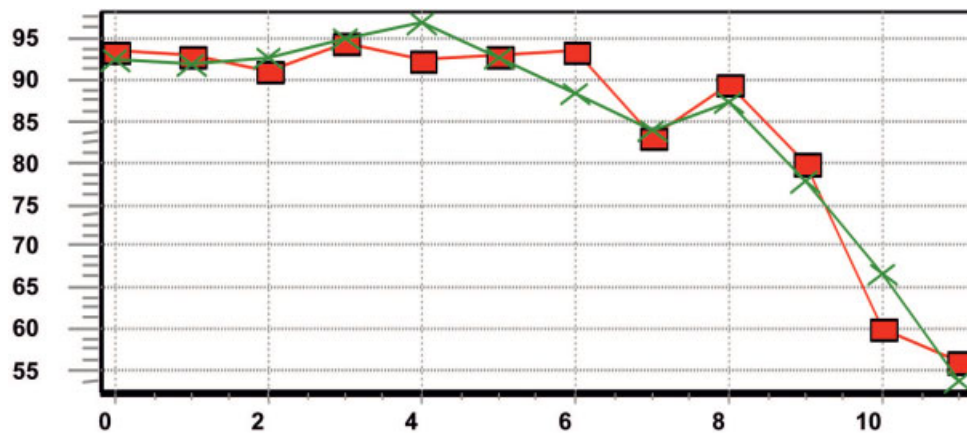


Figure 5 Comparison of experimental values Y_4 and model values y_4 at analyzed points in the chemical composition of IPN system 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VIII
Analysis of Effect from Chemical Composition on Mechanical Properties of IPN

Type of IPN <i>m</i>	<i>a_{im}</i>	Positive effect				Negative effect			
		Mechanical property							
		<i>y_{1m}</i>	<i>y_{2m}</i>	<i>y_{3m}</i>	<i>y_{4m}</i>	<i>y_{1m}</i>	<i>y_{2m}</i>	<i>y_{3m}</i>	<i>y</i>
(Approximate values for factors in eq. (4) as per Table VII)									
1	<i>a₁₁</i>					406	130	3	302
	<i>a₂₁</i>		46		194	119		11	
	<i>a₃₁</i>		13		7.5	14		0.5	
	0.1 <i>a₄₁</i>	117	17	6					20
	0.1 <i>a₅₁</i>	65	17	1	63				
	0.1 <i>a₆₁</i>	40		3			11		15
	0.1 <i>a₇₁</i>				8	18	0	1	
2	<i>a₁₂</i>		28	—	8	182		—	
	<i>a₂₂</i>	58	32	—	228			—	
	<i>a₃₂</i>	4	25	—	97			—	
	0.1 <i>a₄₂</i>	11		—			19	—	52
	0.1 <i>a₅₂</i>	27		—	10		12	—	
	0.1 <i>a₆₂</i>	10		—			9	—	22
	0.01 <i>a₇₂</i>		5	—	8.5	5		—	
3	<i>a₁₃</i>		7	—		193		—	73
	<i>a₂₃</i>		34	—	277	152		—	
	<i>a₃₃</i>		16	—	101	13		—	
	0.1 <i>a₄₃</i>	43		—			20	—	81
	0.1 <i>a₅₃</i>	33		—	23		5	—	
	0.1 <i>a₆₃</i>	47		—			9	—	34
	0.01 <i>a₇₃</i>		5	—		8		—	
4	<i>a₁₄</i>		16	—		117		—	376
	<i>a₂₄</i>		7	—	119	368		—	
	<i>a₃₄</i>		13	—	66	11		—	
	0.1 <i>a₄₄</i>	155	1	—	82			—	
	0.1 <i>a₅₄</i>	27		—	86		3	—	
	0.1 <i>a₆₄</i>	91		—	4		1	—	
	0.01 <i>a₇₄</i>			—		37	2	—	17
<i>W_{ym}</i> eq. (9)		728	282	10	1382	1643	221	15.5	992
Share[%]	<i>w_{a1}(y_n)</i> eq. (10)	0.0	18.1	0.0	0.6	54.7	58.8	19.4	75.7
	<i>w_{a2}(y_n)</i> eq. (11)	8.0	42.2	0.0	59.2	38.9	0.0	71.0	0.0
	<i>w_{a3}(y_n)</i> eq. (12)	0.5	23.8	0.0	19.1	2.3	0.0	3.2	0.0
	<i>w_{a4}(y_n)</i> eq. (13)	44.8	6.4	60.0	5.9	0.0	17.6	0.0	15.4
	<i>w_{a5}(y_n)</i> eq. (14)	20.9	6.0	10.0	13.2	0.0	9.0	0.0	0.0
	<i>w_{a6}(y_n)</i> eq. (15)	25.8	0.0	30.0	0.3	0.0	13.6	0.0	7.2
	<i>w_{a7}(y_n)</i> eq. (16)	0.0	3.5	0.0	1.7	4.1	1.0	6.4	1.7

— Model equation, which is statistically insignificant.

TABLE IX
Results of Optimization

Type of IPN	max <i>y₁</i>						min <i>y₁</i>						max <i>y₂</i>						min <i>y₂</i>					
	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₁</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₁</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₂</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₂</i>
	<i>q₁</i>	<i>q₂</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>
1	0.10	0.33	0.57	0.11	0.58	28.24	0.29	0.17	0.54	0.41	0.31	2.22	0.11	0.10	0.79	0.12	0.13	8.50	0.29	0.20	0.51	0.41	0.39	1.96
2	0.10	0.39	0.51	0.11	0.76	33.47	0.29	0.27	0.44	0.41	0.61	1.70	0.10	0.10	0.80	0.11	0.13	10.54	0.29	0.39	0.32	0.41	1.22	0.62
3	0.10	0.28	0.62	0.11	0.45	29.97	0.29	0.39	0.32	0.41	1.22	*	0.10	0.10	0.80	0.11	0.13	7.63	0.29	0.39	0.32	0.41	1.22	*
4	0.10	0.24	0.66	0.11	0.36	34.34	0.24	0.39	0.37	0.32	1.05	*	0.10	0.10	0.80	0.11	0.13	8.07	0.29	0.32	0.39	0.41	0.82	0.80

Type of IPN	max <i>y₃</i>						min <i>y₃</i>						max <i>y₄</i>						min <i>y₄</i>					
	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₃</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₃</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₄</i>	<i>q₁</i>		$\frac{q_1}{1-q_1}$		<i>q₂</i>	<i>y₄</i>
	<i>q₁</i>	<i>q₂</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>	<i>q₃</i>
1	0.10	0.26	0.64	0.11	0.41	1.35	0.19	0.39	0.42	0.23	0.93	0.79	0.18	0.10	0.72	0.22	0.14	97.2	0.29	0.39	0.32	0.41	1.22	58.8
2	0.10	0.22	0.68	0.11	0.32	2.03	0.29	0.27	0.44	0.41	0.61	0.57	0.10	0.39	0.51	0.11	0.76	96.8	0.29	0.39	0.32	0.41	1.22	76.0
3	0.29	0.39	0.32	0.41	1.22	1.60	0.29	0.20	0.51	0.41	0.39	0.55	0.16	0.10	0.74	0.19	0.14	98.6	0.29	0.39	0.32	0.41	1.22	63.0
4	0.29	0.39	0.32	0.41	1.22	1.04	0.29	0.16	0.55	0.41	0.29	0.55	0.19	0.10	0.71	0.23	0.14	99.8	0.29	0.31	0.40	0.41	0.78	73.3

Incorrect results are marked as *, but, possibly, the optimum points are true.

TABLE X
Scopes of Mechanical Properties for IPN Systems Studied

y_n	The best	The worst	Limits for output variables	
			Low	High
y_1	35	1	15	35
y_2	11	1	1	6
y_3	3	0.5	0.6	3
y_4	96	55	80	100

Impact resistance of IPN systems studied was found to be enhanced by joint action of the three pairs of components, PU + ST, PU + UP, and ST + UP, at a proportion of 6:1:3. The adverse effect has been observed from ST solely; the increasing amount of that component probably causes formation of a rigid phase, which contains homopolymer (polystyrene).

Hardness of the investigated compositions is principally controlled by ST, which is easy to understand. The negative effects, which can also be expected, comes from PU. To some extent, negative contribution is also brought in by a less rigid two-component phase, PU + ST.

The developed model was then utilized to calculate the maximum and minimum values for the parameters analyzed, y_1 – y_4 , specific for the synthesized IPN systems, over the considered scope of experiments (Table 9). In Table 9 two important factors that characterize the structure of IPN systems were presented: weight ratio PU to ST/UP ($q_1/1-q_1$) as the weight ratio of the two polymer networks and weight ratio ST to UP q_2/q_3 as a proportional parameter to the molar ratio of ST to UP C=C bonds.

Calculated maximum and minimum values for the parameters y_1 – y_4 make it possible to assess the dispersion for those parameters, which can be expected in practice from the materials studied (Table 10). Table 10 also provides the scopes for those values that have been adopted for optimization calculations. In other words, that information covers the scatter of properties for the materials investigated, i.e., that information makes some general specification for those materials as potential engineering plastics. The obtained model equations were further utilized to find chemical

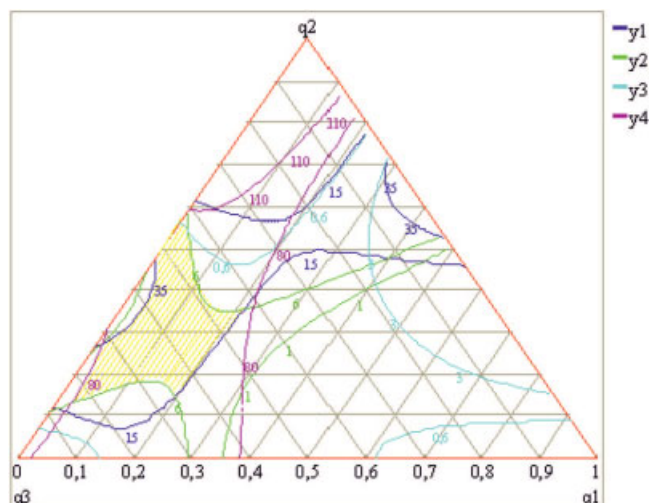


Figure 6 Compromise area for R330 + TMP (IPN, $m = 1$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compositions of IPN systems, $m = 1$ –4, which provide the compromise (within the scopes as defined in Table 10) for the mechanical properties considered (Table 11). Table 11 shows that the most advantageous properties were achieved in the case of IPN system 2, i.e., when PU has been synthesized from the isocyanate prepolymer obtained from trifunctional Rokopol 330. However, its extension to produce a branched PU system will require the use of difunctional BD. It is important that the model equations that describe mechanical properties of just that IPN system were the most statistically significant. It is also important that the compromise chemical composition for each IPN system falls within the investigated area as defined by the parallelogram presented in Figure 1. The factors in model equations (4) as specified in Table 7 were utilized to develop two-dimensional and three-dimensional diagrams of mechanical properties,

$$y_{nm} = f_{nm}(q_1, q_2, q_3). \quad (17)$$

These diagrams cover the whole theoretically possible area of compositions as defined by the equilateral triangle of Figure 1.

TABLE XI
Compromise Points Search Results

IPN type m	q_1	q_2	q_3	$\frac{q_1}{1-q_1}$	$\frac{q_2}{q_3}$	y_{1m}	y_{2m}	y_{3m}	y_{4m}
1	0.10	0.16	0.74	0.11	0.22	22.80	6.13	1.227	91.9
2	0.10	0.21	0.69	0.11	0.30	24.48	7.48	2.024	91.7
3	0.12	0.14	0.74	0.14	0.19	20.91	6.50	0.978	95.9
4	0.10	0.15	0.75	0.11	0.20	30.00	6.97	0.764	92.9

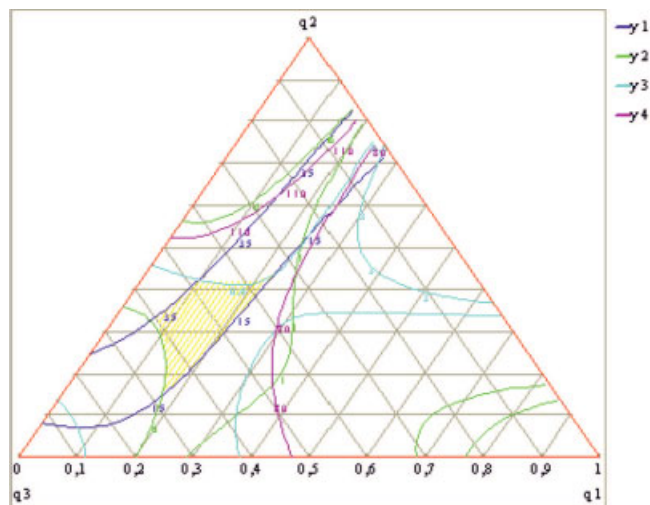


Figure 7 Compromise area for R330 + BD (IPN, $m = 2$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

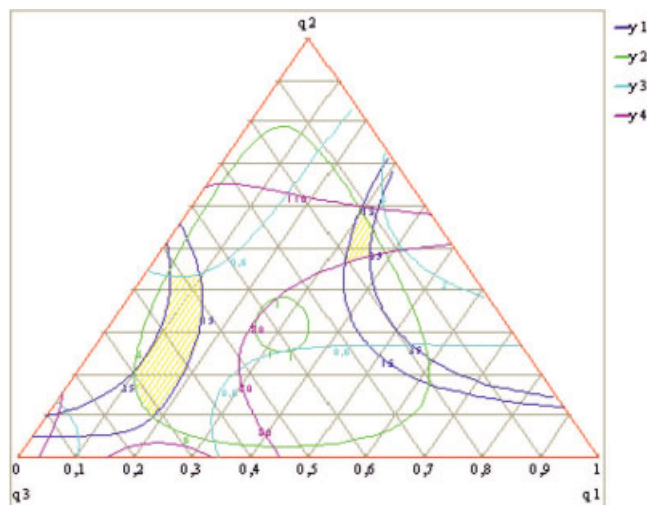


Figure 9 Compromise area for D2002 + BD (IPN, $m = 4$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The compromise areas for successive IPN systems were indicated in two-dimensional diagrams presented in Figs. 6–9. It is apparent that those areas fit fairly well into the parallelogram which defines the borders for our experiments. Only for the IPN formulation No 1 with the highest level of cross-linking, interesting mechanical properties are offered also by IPNs with the PU content below 10%.

It can hence be assumed that the optimum compositions of other IPN systems overlap the scope of concentrations covered with our experiments. The compromise compositions calculated for all IPN systems studied with the use of developed mathematical models can be generally understood to have been

experimentally verified, although their scopes are much more narrow than the scope of our experiment. Possibly narrowing the scope of our investigations would make the findings presented herein more reli-

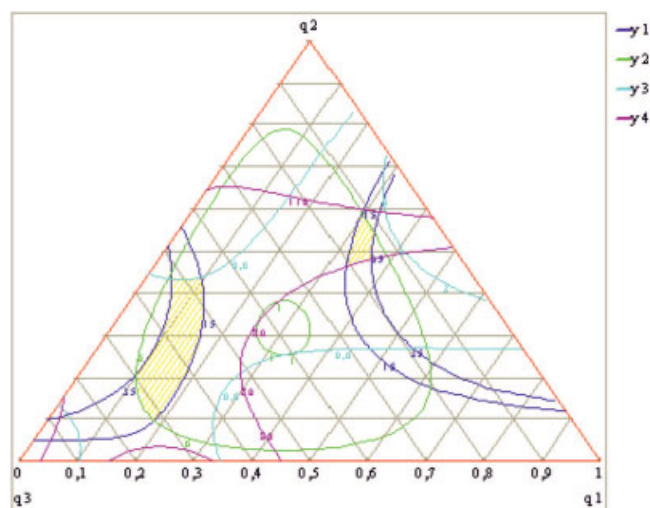


Figure 8 Compromise area for D2002 + TMP (IPN, $m = 3$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

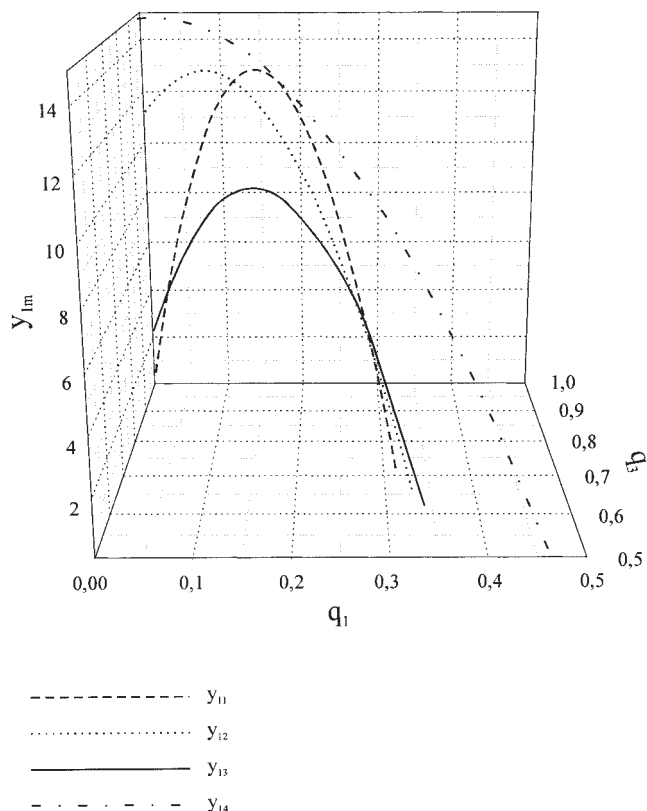


Figure 10 Profiles for changes in mechanical strength ($y_{1,m}$) for four IPN systems ($m = 1-4$) for which the share of styrene has been set up as $q_2 = 0.05$.

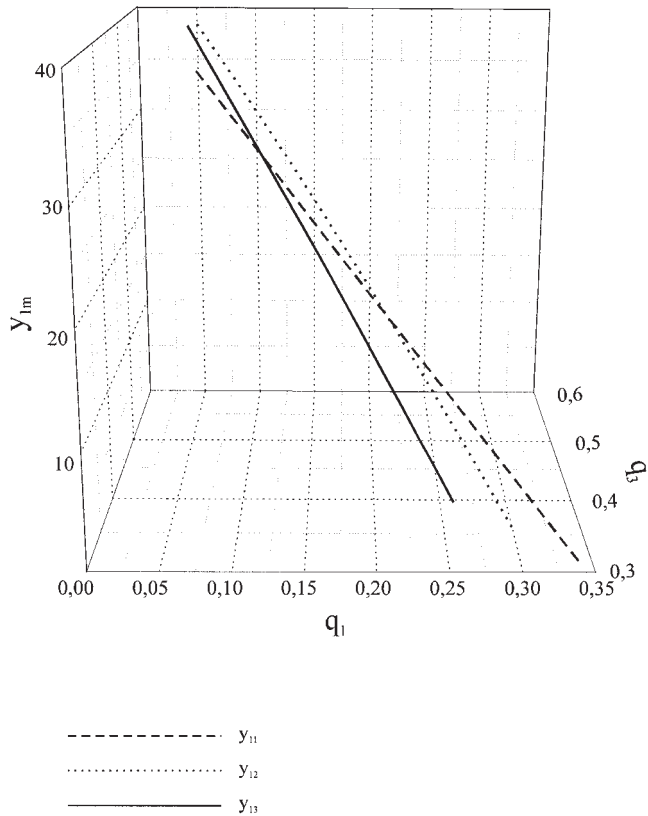


Figure 11 Profiles for changes in mechanical strength (y_{1m}) for four IPN systems ($m = 1-4$) for which the share of styrene has been set up as $q_2 = 0.35$.

able. That can be significant when considering individual applicability issues. In other words, changing the qualitative-quantitative compositions of synthesized IPN systems will not yield any superior mechanical parameters for the substrates employed by us than those provided in Table 10.

There is still one question that needs to be answered: What are the changes of the properties studied over the whole theoretically permissible compositions of IPN systems 1-4 as defined by the surface area of the equilateral triangle shown in Figure 1? That information is achievable by extrapolation of developed model equations outside the scope of that which has already been investigated.

Figures 10 and 11 show tensile strength values (y_{1m}) for IPN systems that have been synthesized ($m = 1-4$) with the styrene content fixed at the level of $q_2 = 0.05$ or 0.35 . The scopes of PU and UP concentrations as specified on the q_1 and q_3 axes result from the dependence (5). Depending on the styrene content, the tensile strength value reaches its maximum $y_{1m} = 12-14$ MPa for ($q_1 = 0.15, q_2 = 0.05, q_3 = 0.80$). In the case of the IPN system with a higher styrene content ($q_2 = 0.35$) a linear decrease of tensile strength can be observed for increasing PU content and decreasing UP content, starting from 40 MPa for $q_3 = 0.64$ and going to 0.5 MPa for $q_3 = 0.35$.

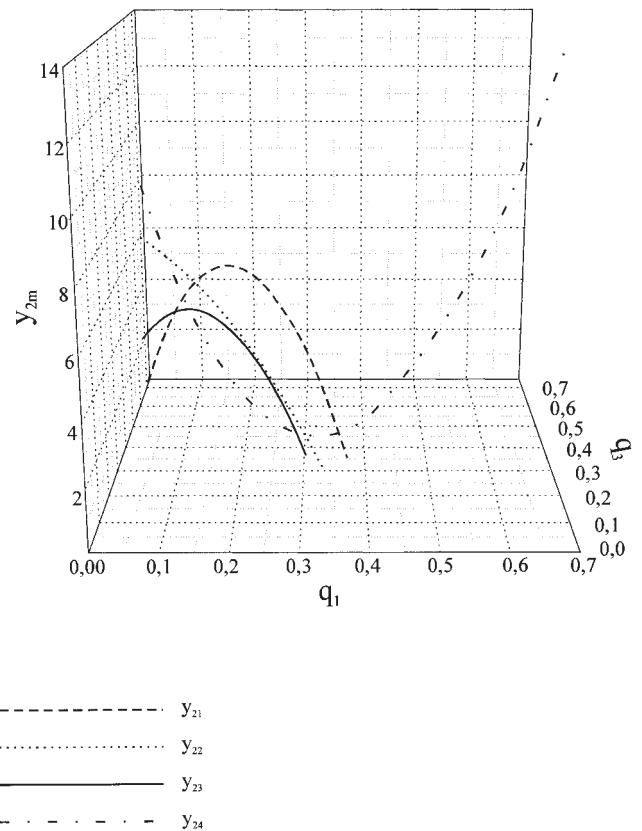


Figure 12 Profiles for changes in unit elongation (y_{2m}) for four IPN systems ($m = 1-4$) for which the share of styrene has been set up as $q_2 = 0.35$.

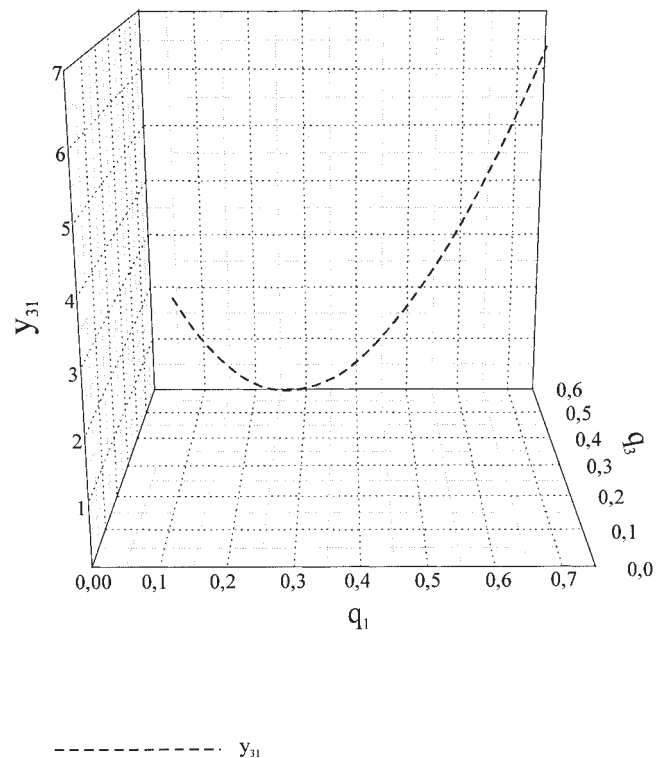


Figure 13 Profiles for changes in impact resistance (y_{3m}) for an IPN system ($m = 1$) for which the share of styrene has been set up as $q_2 = 0.35$.

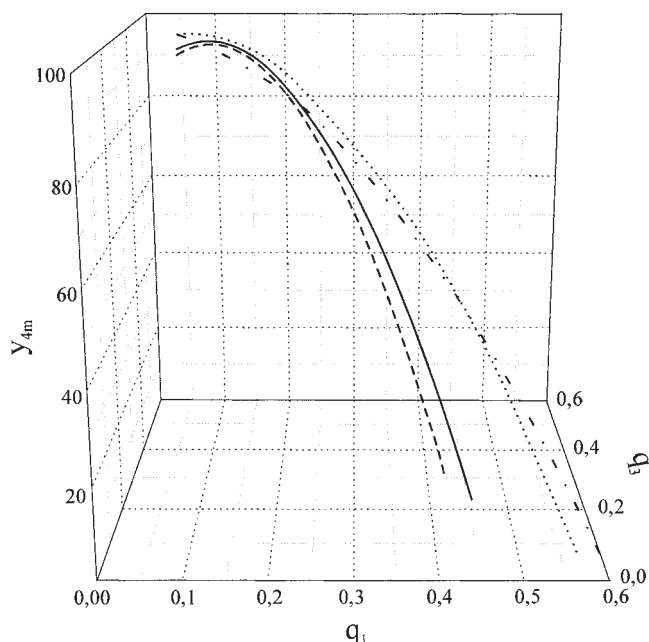


Figure 14 Profiles for changes in hardness (y_{4m}) for four IPN systems ($m = 1-4$) for which the share of styrene has been set up as $q_2 = 0.35$.

As shown in Fig. 12, changes in unit elongation for IPN compositions with constant styrene content $q_2 = 0.35$ are strongly dependent on qualitative composition of the material and more precisely on the polymer cross-linking level (Table 1). Only in the case of the IPN system with the lowest cross-linking level ($m = 4$) does its unit elongation y_{24} go to the minimum, which is close to zero, and then it climbs back to over 14%. The maximum elongation for other IPN systems reaches about 8–10%. A statistically significant model equation for impact resistance (y_3) was obtained only for the IPN system ($m = 1$) (Fig. 13). The calculations show that the impact resistance reaches its minimum $y_{31} = 0.83 \text{ kJ/m}^2$ for the IPN composition with the composition ($q_1 = 0.22$, $q_2 = 0.35$, $q_3 = 0.44$).

Using results from charts plotted in Fig. 14, the hardness of IPNs studied with styrene content of $q_2 = 0.35$ increases together with the UP content from its initial value of about 20° ($q_3 = 0.12$) to about 95° Sh A ($q_3 = 0.67$), which is connected with the simultaneous reduction of PU content from $q_1 = 0.53$ to nearly zero.

CONCLUSIONS

The observed effects of individual components on the mechanical properties of synthesized IPN systems prove the complexity of interactions among those components that can result from the formation of tangled polymer networks, PU, UP, and linear polystyrene. The conclusions set forth on the basis of our findings and covering the formation of immiscible

phases in the materials obtained are only hypothetical at the present stage of investigations. Those conclusions must be verified and confirmed in further investigations with the use of independent structural analysis methods like DSC, WAX, and AFM, which are useful in the analysis of supermolecular structures.

The study made it possible to develop chemical compositions of IPN systems on the basis of polyurethanes and unsaturated styrene–polyester resins. The compositions were optimized from the viewpoint of their mechanical properties, which were important for the applicability of those systems. Also, a more extensive evaluation was made for the obtained plastics as potential engineering plastics and/or coating materials.

The employed statistical procedure is general enough that it makes it possible to analyze and evaluate effects from numerous structural and process-related factors on the properties of polymer compositions. The procedure was demonstrated to be particularly useful in studying IPN systems with complex structures.

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