

Article

Application of Statistical Mixture Models for Ternary Polymer Blends

I. Nascimento, R. E. Bruns*, D. F. Siqueira, and S. P. Nunes

Instituto de Química, UNICAMP, Cidade Universitária Zeferino Vaz, Barão Geraldo,
Campinas - SP, Brazil

Received: August 16, 1996

Este trabalho mostra como modelos estatísticos podem ajudar na obtenção de misturas poliméricas complexas. Neste caso foram estudadas misturas poliméricas ternárias cujos valores de energia e tensão de ruptura foram medidos para treze amostras com proporções diferentes. As respostas foram tratadas estatisticamente usando modelos cúbicos especial e completo. O comportamento dos valores das respostas para toda a faixa de composição das blendas PS/PMMA/PVDF e PS/PBMA/PVDF foram adequadamente descrito pelo modelo cúbico completo. Diagramas ternários marcados por valores de curvas de nível são úteis para analisar como estas propriedades mecânicas mudam quando se varia a proporção dos componentes. Uma modelagem estatística correta para toda a faixa de proporção de componentes para a blenda PS/PEMA/PVDF requer modelos de misturas mais sofisticados.

The paper shows how statistical models can help tailor complex polymeric mixtures. Ternary polymer mixtures were studied. Energy and strength at break response values were measured for thirteen samples of varying component proportions. The responses were statistically treated using special and full cubic models. The behaviors of these response values for the whole range of compositions of the PS/PMMA/PVDF and for PS/PBMA/PVDF blends are adequately described by full cubic models. Ternary diagrams marked by isoresponse value contour lines are useful for analyzing how these mechanical properties change with varying component proportions. Successful statistical modeling of the whole range of component proportions of the PS/PEMA/PVDF blends evidently requires more sophisticated mixture models.

Keywords: *statistical mixture models, polymer blends, full cubic models, polymethacrylates, polystyrene, poly(vinylidene fluoride)*

Introduction

Polymeric materials used in all kinds of technological applications are almost always a complex mixture of polymeric components and several additives. Polymer blending has been established as a current way of achieving desired properties¹. However, many aspects should be considered to predict the final properties of a wide range of possible formulations even if only few components are considered. Suitable mechanical properties are usually one of the main goals of mixing polymers. Immiscible polymer blends are frequently prepared (or developed) to supply a more attractive commercial product in the sense of price or processability, but in detriment of their mechanical properties,

which sometimes have to be recovered by adding a third component, a compatibilizer. Block copolymers are normally chosen for this purpose, but homopolymers can also be useful for compatibilization². If the degree of miscibility between the homopolymer compatibilizing agent C and each of the blend polymer components (A and B) is low but still higher than the one between A and B, C may be located at the A/B interface. When the degree of miscibility between C and at least one of the polymer components is considerably high, it dissolves into A and B rich phases. In any case the compatibilizer acts by decreasing the interfacial tension and therefore improving dispersion and interface adhesion among the polymer blend components.

Here statistical modeling of a limited number of experiments is shown to be helpful in describing properties of polymer blends with wide composition ranges. The mechanical properties of ternary polymer blends with Poly(vinylidene fluoride) (PVDF), Polystyrene (PS) and poly(methacrylates) were investigated and discussed using different models. PVDF and PS are immiscible polymers. The introduction of polymethacrylates (PXMA) (X = methyl, ethyl or butyl) into PVDF/PS has a compatibilizing function. PVDF/PMMA and PVDF/PEMA are known as miscible pairs. PVDF and PMMA have a lower critical solution temperature (LCST) at 330 °C and an upper critical solution temperature (UCST) at 140 °C. Between these temperatures the blend is miscible in the melt state over the entire range of compositions. Miscibility is probably due to H-bond formation between the carbonyl groups of PMMA and the acidic hydrogens of PVDF, with an enthalpy of mixing of -1.9 kJ/mol for blends containing 50% of each polymer and with the Flory-Huggins parameter, χ , varying from -0.7 to -0.1³⁻⁷. PVDF and atactic PEMA are also miscible with a LCST between 220 and 250 °C, with a χ = -0.34^{8,9}. PS and PMMA are not miscible, but the χ value is low, χ = 0.01^{2,10}.

Statistical Mixture Modeling

Experimental mixture designs and models permit the determination of optimum values of ingredient proportions with the execution of a minimum number of experiments^{11,12}. The mixture models are derived from the general polynomial equation used in response surface analysis

$$\hat{y} = b_0 + \sum_{i=1}^q b_i x_i + \sum_{i=1}^q \sum_{\substack{j=1 \\ i \leq j}}^q b_{ij} x_i x_j + \sum_{i=1}^q \sum_{i=1}^q \sum_{\substack{k=1 \\ i \leq j \leq k}}^q b_{ijk} x_i x_j x_k \dots \quad (1)$$

that expresses how a predicted response value, \hat{y} , changes with varying values of the q experimental factors being investigated. For mixtures the q factor values, or ingredient proportions, x_i , are related by

$$\sum_{i=1}^q x_i = 1 \quad (2)$$

since the proportions of the ingredients in mixtures always sum to 1 (or 100%). Substitution of this equation into Eq. 1 results in the mixture model for three ingredients ($q = 3$) with redefined coefficients indicated with asterisks.

$$\begin{aligned} \hat{y} = & b_1^* x_1 + b_2^* x_2 + b_3^* x_3 + b_{12}^* x_1 x_2 + b_{13}^* x_1 x_3 + \\ & + b_{23}^* x_2 x_3 + b_{123}^* x_1 x_2 x_3 + d_{12}^* x_1 x_2 (x_1 - x_2) + \\ & + d_{13}^* x_1 x_3 (x_1 - x_3) + d_{23}^* x_2 x_3 (x_2 - x_3) \end{aligned} \quad (3)$$

The first three terms form the **linear mixture model**. Its b_i^* coefficients ($i = 1, 2, 3$) can be determined by simply performing response measurements on the pure components of the mixture being investigated. These pure components are represented by points at the vertices of the mixture concentration triangle in Fig. 1. The **quadratic model** includes the next three terms that have b_{ij} coefficients indicating synergic or antagonistic interaction effects on the response values between two of the mixture ingredients. To determine these effects, experiments on binary mixtures are necessary. Using a multi-variant statistical criterion, the binary 50/50 mixtures shown in Figure 1 are the most appropriate ones to be investigated for precise model determination. If the $b_{123}^* x_1 x_2 x_3$ term is added to the quadratic model, the result is a **special cubic model** already used by the authors to model mechanical resistance of a PS/PMMA/PVDF ternary blend¹³. A response measurement on at least one ternary mixture is necessary to evaluate b_{123}^* , with best choice being the (33/33/33) mixture, indicated at the center of the concentration triangle in Fig. 1. This design results in the smallest statistical uncertainties in the mixture model parameter values.

If the response dependence on the ingredient proportions is too complex to be described by the above models the **full cubic model** containing all the terms in Eq. 3 can be used. Besides the ternary mixture, binary 33/66 mixtures, also shown in Fig. 1, rather than the 50/50 mixtures, are recommended for model determination. Since it is not possible to know *a priori* which model will best represent the experimental data, experiments in our investigation were performed for all the mixtures indicated in Fig. 1. The

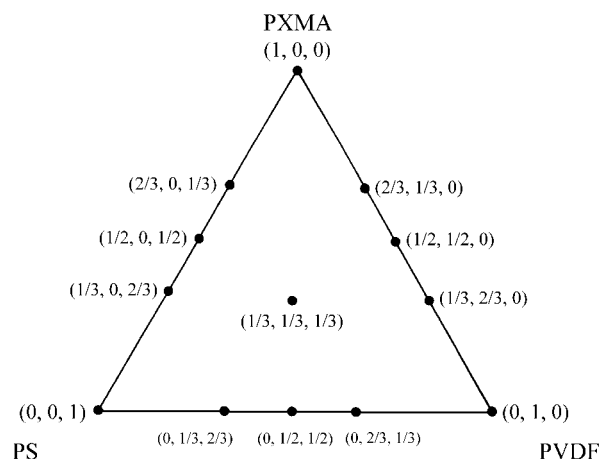


Figure 1. Component proportions of PXMA (X = M, B, E), PVDF and PS used in the thirteen mixtures investigated in this work.

models tested in this work contain a maximum of ten parameters (the full cubic model for three ingredients) and the thirteen distinct mixtures used permit an analysis of variance (ANOVA) of residuals which provide statistical F indices of regression significance and lack of fit to all contemplated models. Replicate determinations for each mixture were performed so that experimental error could also be estimated.

Experimental

Materials

Poly(vinylidene fluoride) (PVDF) (18270-2), poly(ethyl methacrylate) (PEMA) (9003-42-3); poly(butyl methacrylate) (PBMA) (9003-63-8) and poly(methyl methacrylate) (PMMA) (9011-14-7) were purchased from Aldrich. Polystyrene (PS) ($M_w = 3.0 \times 10^5$ g/mol and $M_w/M_n = 1.9$) was kindly supplied by Proquigel, São Paulo, Brazil.

Mechanical tests

Polymer mixtures were extruded in a Custom Scientific Instruments CS 194 mixing extruder, with rotor temperature at 150 °C and rotor rate of 220 rpm. The extruded rods were then cut into pellets and re-extruded to assure mixing efficiency. Sheets of 8 x 0.4 mm were obtained. Sheets 60 mm long were used for the mechanical tests in a EMIC tensile machine with rate of 5 mm/min. The tensile strength at break and the energy absorbed by the sample before breaking (integral of the stress-strain curve) were measured.

X-Ray diffraction

The sample crystallinity was evaluated using a Shimadzu X-Ray diffractometer with Cu K_α radiation.

Results and Discussion

Values of tensile strength at break are presented in Tables 1-3. For the statistical models a minimum number of formulations were chosen following the experimental design of Fig. 1. The area below the stress-strain curve gives the energy that the sample is able to absorb before breaking. It is related to the impact resistance. Quite low values were measured for binary PS/PVDF blends (0.007-0.08 J). Addition of polymethacrylates increased the energy values considerably to 0.3-1.3 (for 33/33/33 blends) showing their efficiency in improving phase adhesion and dispersion in the multicomponent system. The effect was much more evident in the case of blends with PEMA. The interaction parameters for ternary blends are usually given by B,

$$B_{123} = \frac{(B_{12} \phi_2)^2}{(1 - \phi_1)} + \frac{(B_{13} \phi_3)^2}{(1 - \phi_1)} + \Delta B \left[\frac{\phi_3 \phi_2}{(1 - \phi_1)^2} \right] \quad (4)$$

where $B_{ij} = RT\chi_{ij}/V$, $\Delta B = B_{21} + B_{13} - B_{32}$ with χ_{ij} representing the Flory-Huggins interaction parameter between i and j , ϕ_i is the i^{th} volume fraction and V is the base molar volume. Although B is strictly valid for non polar systems in equilibrium, the concept has been widely used in the field of polymer blends¹⁴.

Table 1. Average energy and strength at break values and their standard deviations for the mixture design of the PS/PMMA/PVDF blends^a.

| Composition | Energy at break (J) | Strength at break (MPa) |
|-----------------------|---------------------|-------------------------|
| PMMA | 0.256 ± 0.072 | 23.430 ± 2.99 |
| PVDF | 3.895 ± 0.601 | 64.400 ± 3.96 |
| PS | 0.635 ± 0.007 | 24.05 ± 0.07 |
| PMMA/PVDF 50/50 | 17.110 ± 2.348 | 89.025 ± 24.81 |
| PMMA/PS 50/50 | 0.149 ± 0.054 | 25.728 ± 4.07 |
| PVDF/PS 50/50 | 0.060 ± 0.014 | 24.620 ± 6.25 |
| PMMA/PVDF 66/33 | 1.448 ± 0.731 | 39.563 ± 11.91 |
| PMMA/PVDF 33/66 | 35.150 ± 3.482 | 213.942 ± 38.76 |
| PMMA/PS 66/33 | 0.311 ± 0.124 | 29.207 ± 8.79 |
| PMMA/PS 33/66 | 0.092 ± 0.022 | 15.718 ± 2.80 |
| PVDF/PS 66/33 | 0.083 ± 0.012 | 8.412 ± 1.48 |
| PVDF/PS 33/66 | 0.006 ± 0.000 | 0.87 ± 0.07 |
| PS/PMMA/PVDF 33/33/33 | 0.269 ± 0.056 | 20.955 ± 2.24 |

a) Standard deviations were calculated from replicate measurements for each of the above mixtures. The energy and strength at break values given are averages of these determinations.

Table 2. Average energy and strength at break values and their standard deviations for the mixture design of the PS/PBMA/PVDF blends^a.

| Composition | Energy at break (J) | Strength at break (MPa) |
|-----------------------|---------------------|-------------------------|
| PBMA | 0.515 ± 0.064 | 6.520 ± 1.24 |
| PVDF | 3.895 ± 0.601 | 64.400 ± 3.96 |
| PS | 0.635 ± 0.007 | 24.05 ± 0.07 |
| PBMA/PVDF 50/50 | 0.309 ± 0.076 | 4.298 ± 0.50 |
| PBMA/PS 50/50 | 1.201 ± 0.068 | 12.467 ± 1.97 |
| PVDF/PS 50/50 | 0.060 ± 0.014 | 24.620 ± 6.22 |
| PBMA/PVDF 66/33 | 0.716 ± 0.035 | 8.070 ± 0.229 |
| PBMA/PVDF 33/66 | 0.178 ± 0.021 | 5.720 ± 0.75 |
| PBMA/PS 66/33 | 3.042 ± 0.077 | 6.535 ± 0.16 |
| PBMA/PS 33/66 | 0.625 ± 0.013 | 23.33 ± 11.63 |
| PVDF/PS 66/33 | 0.078 ± 0.015 | 8.412 ± 1.47 |
| PVDF/PS 33/66 | 0.007 ± 0.000 | 0.870 ± 0.07 |
| PS/PBMA/PVDF 33/33/33 | 0.470 ± 0.090 | 10.775 ± 1.00 |

a) See Table 1.

Table 3. Average energy and strength at break values and their standard deviations for the mixture design of the PS/PEMA/PVDF blends^a.

| Composition | Energy at break (J) | Strength at break (MPa) |
|-----------------------|---------------------|-------------------------|
| PEMA | 0.950 ± 0.141 | 46.528 ± 2.69 |
| PVDF | 3.895 ± 0.601 | 64.400 ± 3.96 |
| PS | 0.635 ± 0.007 | 24.050 ± 0.07 |
| PEMA/PVDF 50/50 | 1.70 ± 0.042 | 104.80 ± 2.12 |
| PEMA/PS 50/50 | 0.615 ± 0.247 | 39.10 ± 0.17 |
| PVDF/PS 50/50 | 0.0600 ± 0.014 | 24.6 ± 6.22 |
| PEMA/PVDF 66/33 | 21.848 ± 2.613 | 180.63 ± 16.75 |
| PEMA/PVDF 33/66 | 41.995 ± 6.541 | 236.05 ± 19.66 |
| PEMA/PS 66/33 | 0.915 ± 0.109 | 26.488 ± 2.11 |
| PEMA/PS 33/66 | 0.564 ± 0.064 | 9.350 ± 0.65 |
| PVDF/PS 66/33 | 0.083 ± 0.012 | 8.412 ± 1.48 |
| PVDF/PS 33/66 | 0.00570 ± 0.000 | 1.405 ± 0.09 |
| PS/PEMA/PVDF 33/33/33 | 1.335 ± 0.163 | 37.175 ± 2.98 |

a) See Table 1.

For PVDF/PS, $B = 18 \times 10^6 \text{ J/m}^3$; for PVDF/PEMA, $B = -12.8 \times 10^6 \text{ J/m}^3$; and for PS/PEMA, $B = 5.0 \times 10^6 \text{ J/m}^3$. Using Eq. 4 the B_{123} values can be estimated for PS/PEMA/PVDF. The B values tend to decrease (miscibility increases) as the PEMA content increases, as shown in Table 4. Blends with lower B values are also able to absorb more energy before breaking, as shown in Table 4. For PVDF/PEMA, $B = -17.3 \times 10^6 \text{ J/m}^3$ and for PEMA/PS, $B = 0.2 \times 10^6 \text{ J/m}^3$.

Considering only the binary PVDF/PEMA mixtures, a strong synergic effect was observed for $X = \text{methyl}$ and ethyl . Both high strength and energy at break values were observed with 66 wt % PVDF.

The values of energy and strength at break responses obtained for the experimental design in Figure 1 are presented in Tables 1, 2 and 3 for the PS/PEMA/PVDF, PS/PEMA/PVDF and PS/PBMA/PVDF systems. The response values are averages of duplicate or higher replicate

determinations. Standard deviations for all the response averages are also included in these tables.

Full cubic models obtained by multiple linear regression using Eq. 3 proved to be the best in fitting properties of the PS/PMMA/PVDF and PS/PBMA/PVDF mixtures (see Table 5). They were statistically significant well above the 95% confidence level for energy and strength at break responses. The PMMA models present marginally significant lack of fit values at the 95% confidence level; however almost all of the explainable variance has been described by the model. The lack of fit for the PBMA models is higher than for the PMMA ones. The high percentage variance (96%) reproduced for the energy at break response is an indication that the energy at break values predicted by the full cubic model are in good agreement with the experimental results. The percentage variance of the experimental

strength at break values obtained by the full cubic model is much less, 83%. Even though this regression model is highly significant, their predicted strength at break values are less accurate than those for the PS/PMMA/PVDF system. The model parameters for the energy and strength at break responses of the PS/PMMA/PVDF and PS/PBMA/PVDF mixture energies are presented in Tables 6 and 7.

The best results for the energy and strength at break data of the PS/PEMA/PVDF system were obtained for special cubic models for both responses; however for this system the regressions are not statistically significant presenting extremely high lack of fit. Evidently all the models are too simple to reproduce the complex behavior of the responses for this system. The reason for this lack of fit is that the models, even the full cubic one, are not capable of repro-

Table 4. Interaction parameters, B, calculated with Eq. 4 and measured energy at break, E, for PS/PEMA/PVDF blends.

| PS/PEMA/PVDF | $\phi_{\text{PEMA}} / (1 - \phi_{\text{PVDF}})$ | B (MJ/m ³) | E (J) |
|--------------|---|------------------------|---------------|
| 50/00/50 | 0 | 18 | 0.06 ± 0.01 |
| 40/20/40 | 0.31 | 7.7 | 0.08 ± 0.01 |
| 33/33/33 | 0.47 | 4.5 | 1.34 ± 0.16 |
| 60/20/20 | 0.47 | 3.8 | 3.11 ± 0.08 |
| 20/20/60 | 0.23 | 10.8 | 0.013 ± 0.001 |

Table 5. Analysis of the variance of the energy and strength at break regression results for the three ternary systems^a.

Energy at break

| | PS/PMMA/PVDF | PS/PBMA/PVDF | PS/PEMA/PVDF ^b |
|------------------------------------|-------------------------|-------------------------|---------------------------|
| MS _{reg} /MS _r | 253.3 | 92.3 | 190.7 |
| F _{v1,v2} | F _{9,31} = 2.2 | F _{9,36} = 2.1 | F _{9,26} = 2.3 |
| MS _{if} /MS _{pe} | 5.4 | 34.2 | 0.04 |
| F _{v1,v2} | F _{2,28} = 3.3 | F _{3,33} = 2.9 | F _{2,24} = 3.0 |
| % variance | 99(99) | 96(99) | 99(99) |

Strength at break

| | PS/PMMA/PVDF | PS/PBMA/PVDF | PS/PEMA/PVDF ^b |
|------------------------------------|-------------------------|-------------------------|---------------------------|
| MS _{reg} /MS _r | 51.1 | 19.0 | 153.7 |
| F _{v1, v2} | F _{9,33} = 2.2 | F _{9,34} = 2.2 | F _{9,34} = 2.2 |
| MS _{if} /MS _{pe} | 6.5 | 28.2 | 28.1 |
| F _{v1,v2} | F _{2,28} = 3.3 | F _{3,31} = 2.9 | F _{2,30} = 3.0 |
| % variance | 93(96) | 83(95) | 98(99) |

a) MS_{reg}, MS_r, MS_{if} and MS_{pe} are the mean squares (sum of squares divided by number of degrees of freedom) of regression, residuals, lack of fit and pure error respectively. The F_{v1,v2} are tabulated 95% confidence values for the F distribution with v₁ and v₂ degrees of freedom. When the calculated MS_{if}/MS_{pe} ratio is smaller than F_{v1,v2} the regression does not have significant lack of fit. In these cases the fact that the MS_{reg}/MS_r ratios are larger than their corresponding F_{v1,v2} values indicates a significant regression equation. The % variance results refer to the percentage of experimental results explained by the regression followed by the percentage explainable variance in parentheses.

b) Regression results for the PS/PEMA/PVDF data sets removing the response for 50/50 PEMA/PVDF.

ducing the low PEMA/PVDF 50/50 experimental energy at break value since it is situated between two high values for the PEMA/PVDF 66/33 and 33/66 binary mixtures. This was confirmed by removing the PEMA/PVDF 50/50 mixture values from the data set and repeating the regression analysis. The model for this reduced data set was highly significant and had no detectable lack of fit. Similar behavior is found for the strength at break values. Here also the 50/50 PEMA/PVDF binary mixture has a much lower value than the 66/33 and 33/66 mixtures for these polymers. The mixture model parameter values and their standard errors for the energy and strength at break responses of the PS/PEMA/PVDF system for the reduced data set are in-

cluded in Tables 6 and 7. The corresponding analysis of the variance values are given in Table 5. The anomalous behaviors of the 50/50 PEMA/PVDF energy and strength at break values may result from a higher crystallinity. Crystallinity was evaluated by X-Ray diffraction for PEMA/PVDF binary blends obtained in the same conditions by extrusion. Values are shown in Table 8. Crystallinity decreases from 73% for pure PVDF to 40% when 33% PEMA is added but increases again to 50% when the PEMA content in the binary blend is 50%. The models should describe better totally amorphous systems or systems for which crystallinity linearly decreases with addi-

Table 6. Complete cubic mixture model parameters and their 95% confidence interval values for the energy at break responses of the three ternary systems^a.

| X/PVDF/PS ^b | PS/PMMA/PVDF | PS/PBMA/PVDF | PS/PEMA/PVDF |
|-------------------------|-----------------|--------------|-----------------|
| b _x | 0.33 ± 0.98 | 0.44 ± 0.08 | 0.95 ± 2.50 |
| bpvdf | 4.06 ± 1.54 | 3.87 ± 0.16 | 3.88 ± 2.50 |
| bps | 0.62 ± 1.54 | 0.67 ± 0.16 | 0.63 ± 2.50 |
| b _x ,pvdf | 70.06 ± 5.14 | -7.61 ± 0.51 | 135.57 ± 10.53 |
| b _x ,ps | -1.25 ± 5 | 4.57 ± 0.55 | -0.32 ± 9.23 |
| bpvdf,ps | -10.10 ± 5.69 | -9.81 ± 0.61 | -9.71 ± 9.23 |
| b _x ,pvdf,ps | -216.38 ± 36.19 | 6.21 ± 3.87 | -393.36 ± 77.98 |
| d _x ,pvdf | -224.18 ± 12.29 | 11.50 ± 1.26 | -133.45 ± 22.15 |
| d _x ,ps | 2.20 ± 13.09 | 17.34 ± 1.43 | 1.67 ± 19.22 |
| dpvdf,ps | -7.68 ± 11.71 | -7.17 ± 1.28 | -7.25 ± 18.99 |

a) 95% confidence interval values obtained calculated using the values of Tables 2 and 3 and the appropriate t-distribution parameters.

b) Unit of Joules, J. X = PMMA, PBMA and PEMA.

Table 7. Complete cubic mixture model parameters and their 95% confidence interval values for the strength at break responses of the three ternary systems^a.

| X/PVDF/PS ^b | PS/PMMA/PVDF | PS/PBMA/PVDF | PS/PEMA/PVDF |
|-------------------------|-------------------|-----------------|-------------------|
| b _x | 24.58 ± 32.47 | 6.54 ± 6.32 | 45.71 ± 13.10 |
| bpvdf | 65.66 ± 45.74 | 63.04 ± 10.00 | 63.10 ± 18.43 |
| bps | 22.52 ± 45.74 | 22.93 ± 10.00 | 21.12 ± 18.43 |
| b _x ,pvdf | 324.55 ± 154.58 | -124.79 ± 30.80 | 709.31 ± 74.96 |
| b _x ,ps | 1.56 ± 147.64 | -3.24 ± 33.25 | -41.17 ± 59.39 |
| bpvdf,ps | -152.81 ± 170.10 | -147.93 ± 36.92 | -146.27 ± 79.67 |
| b _x ,pvdf,ps | -977.50 ± 1061.02 | 286.58 ± 229.70 | -1739.93 ± 442.16 |
| d _x ,pvdf | -1158.48 ± 351.22 | 145.48 ± 70.58 | -345.49 ± 173.28 |
| d _x ,ps | 91.52 ± 366.54 | -82.11 ± 92.62 | 53.19 ± 131.69 |
| dpvdf,ps | -66.49 ± 358.37 | -59.41 ± 77.72 | -55.25 ± 135.17 |

a) See Table 6. Units of MPa.

b) See Table 6.

tion of the amorphous component. The crystallinity may decrease the strength at break to unexpected values.

The b_{PVDF} , b_{PS} , $b_{PVDF,PS}$ and $d_{PVDF,PS}$ parameters depend only on the PVDF and PS components. For this reason their values are expected to be constant, as the third component changes among PMMA, PBMA and PEMA. This can be confirmed by examining the values of these parameters in Tables 6 and 7. The b_{PVDF} energy at break values are all statistically significant as can be seen in Table 6 with values varying from 3.87 to 4.06 J for the three ternary systems. At the 95% confidence levels this parameter is equivalent to the 3.90 J energy at break value measured for pure PVDF and given in Tables 1-3. In a similar way the measured strength at break value of 64.4 MPa in these tables are equivalent to all the b_{PVDF} parameter values in Table 7. Also the b_{PS} energy at break values in Table 6 are equivalent at the 95% confidence interval to the measured average energy at break value of 0.64 J except for the 0.67

PS/PBMA/PVDF. For strength at break values b_{PS} is significant at the 95% confidence level of the PBMA and PEMA ternary systems.

The $b_{PVDF,PS}$ energy at break parameters are all statistically significant and vary from -9.71 J for the PEMA system to -10.10 J for PMMA. These results clearly indicate the existence of an antagonistic interaction between PVDF and PS independent of whether the third component is PMMA, PBMA or PEMA. They are consistent with the fact that PVDF and PS are immiscible. An analogous observation can be made for the $b_{PVDF,PS}$ parameter for strength at break. The intensity of the antagonistic interaction between PVDF and PS does not depend on the third component present since the $b_{PVDF,PS}$ parameter values are almost the same. The remaining model parameter characterized by only PVDF and PS, $d_{PVDF,PS}$, is not evaluated to be an important model parameter and is statistically insignificant for all the strength at break and energy values

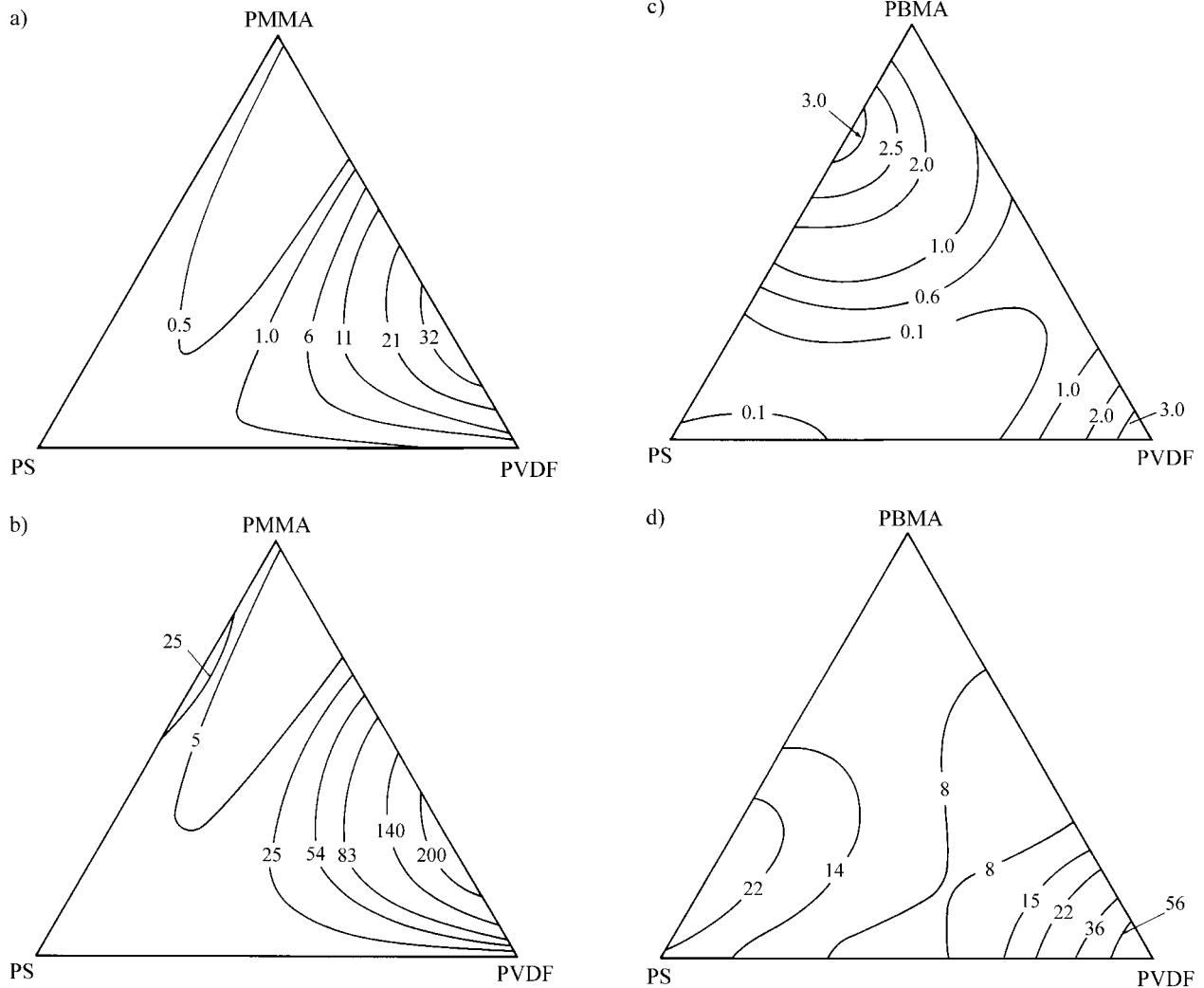


Figure 2. Response surfaces for (a) energy at break and (b) strength at break data of the PS/PMMA/PVDF mixtures and for (c) energy at break and (d) strength at break data of the PS/PBMA/PVDF mixtures.

except for the energy parameter of the PS/PBMA/PVDF system.

Large synergic effects between PVDF and both PMMA and PEMA are indicated by the positive $b_{X,PVDF}$, $X = \text{PMMA}$ and PEMA , energy and strength at break values in Tables 6 and 7. All the 66/33 and 33/66 PMMA:PVDF and PEMA:PVDF mixtures have energy and strength at break values that are much larger than those found for the three pure PMMA, PEMA and PVDF components. Even the 50/50 PEMA:PVDF strength at break value (105 MPa) is much larger than the values of this response for the pure PEMA and PVDF components, 47 and 64 MPa. This stems from the high PEMA/PVDF and PMMA/PVDF miscibilities (low B_{ij} values).

The evidence for the strong synergic interactions involving PMMA-PVDF and PEMA-PVDF contrast with those for PBMA-PVDF. The $b_{PBMA,PVDF}$ values are significant and negative, -7.61 J and -124.79 MPa. The 66/33, 50/50 and 33/66 binary PBMA-PVDF mixtures all have energy and strength at break values well below the corresponding pure PVDF values, 3.90 J and 64.4 MPa, and below or only slightly higher than the response values for pure PBMA, 0.51 J and 6.52 MPa.

The only significant binary interaction involving the PXMA components and the PS polymer occurs for the PBMA/PS interaction for the energy at break response. The $b_{PBMA,PS}$ value of 4.57 ± 0.55 J indicates a small but highly significant synergic effect between the polymeric components. However this binary effect is not significant for the PBMA/PS interaction for strength at break.

Antagonistic three component interactions for energy and strength at break values for the PS/PMMA/PVDF and PS/PEMA/PVDF systems are indicated by the negative $b_{PMMA,PVDF,PS}$ and $b_{PEMA,PVDF,PS}$ parameter values in Tables 6 and 7. These results indicate interactions affecting both response values only when all three ingredients of each system are present simultaneously in the mixture. However the effect of these ternary antagonistic interactions on the energy and strength at break values are more than compensated by contributions from the $b_{X,PVDF}$ terms. On the other hand the $b_{PBMA,PVDF,PS}$ values of 6.21 ± 3.87 J and 286.58 ± 229.50 MPa indicate synergic effects involving all three mixture ingredients that can not be explained by possible binary interactions.

The d_{ij} cubic parameters are more difficult to interpret. Negative $d_{X,PVDF}$ coefficients are found for the PS/PMMA/PVDF and PS/PEMA/PVDF ternary systems. In contrast the $d_{X,PVDF}$ values for the PS/PBMA/PVDF systems are positive and statistically significant although their absolute magnitudes are smaller than those for the other ternary systems. The $d_{X,PS}$ parameters are not statistically significant except for the PS/PBMA/PVDF energy and strength at break results. The energy at break $d_{PBMA,PS}$

parameter is negative whereas the strength at break parameter is positive. This contrasts with all other statistically significant model parameters for which identical signs are observed for both the energy or strength at break responses.

Isoresponse contour curves for the energy and strength at break properties as a function of the PS/PMMA/PVDF and PS/PBMA/PVDF component proportions are presented in Fig. 2. The response surface contour curves for the energy and strength at break responses of the PS/PMMA/PVDF system have essentially the same forms as can be seen in Figs. 2a and 2b. This indicates that these properties are highly correlated for this ternary system. Values of energies and strengths at break are predicted to be maximum for binary mixtures of about 30% PMMA and 70% PVDF. The left hand sides of both the energy and strength at break concentration triangles, representing mixtures rich in PS and/or PVDF, have response values close to zero. Table 9 shows values of tensile strength at break for PS/PMMA/PVDF which were not used to construct the models and the isoresponse contour curves. They can therefore be used to confirm the model efficiency. As can be seen all the values are in agreement with the predicted values in Fig. 2.

The energy at break values of the PS/PBMA/PVDF binary and ternary mixtures are all smaller than the energy at break of pure PVDF. All the PS/PBMA/PVDF measured energy at break values are predicted by the mixture model to be less than 4 J, much less than the energy at break values observed for the PMMA/PVDF 50/50 and 33/66 binary mixtures. This same ordering is also observed for the strength at break values of the PS/PBMA/PVDF and PS/PMMA/PVDF systems. This indicates that PMMA is a better compatibilizer than PBMA for the PVDF/PS system. As shown from the $b_{PXMA,PVDF}$ values a synergic interaction was observed between PMMA and PVDF but not between PBMA and PVDF.

Table 8. Percentage of crystallinity of PEMA/PVDF binary blends.

| Blend | Percentage of crystallinity (%) |
|-----------------|---------------------------------|
| PEMA/PVDF 33/66 | 40 ± 2% |
| PEMA/PVDF 50/50 | 49 ± 3% |
| PEMA/PVDF 66/33 | 43 ± 2% |
| PVDF | 73 ± 5% |

Table 9. Strength at break for PS/PMMA/PVDF system.

| PS/PMMA/PVDF | Strength at break (MPa) |
|--------------|-------------------------|
| 49/2/49 | 21.5 ± 1.9 |
| 47.5/5/47.5 | 23.5 ± 2.4 |
| 45/10/45 | 35.1 ± 4 |
| 40/20/40 | 33.6 ± 2.8 |

Conclusions

Full cubic statistical models describe with high significance the mechanical properties of the PS/PMMA/PVDF and PS/PBMA/PVDF ternary blends. For ternary blends with PEMA in contrast to those with PMMA or PBMA, the lack of fit was high due to exceptionally low energy and strength at break values measured for 50/50 PEMA/PVDF mixtures. At least for ternary blends containing PMMA or PBMA, isoresponse contour curves could be used to predict the mechanical properties for the whole range of mixture compositions from just a limited number of experimental points. As expected statistical models describe better totally amorphous systems or systems for which crystallinity decreases linearly with addition of the amorphous component.

Statistical b_{ij} parameters determined for these models reflect the miscibility between each polymer component pair. Results also show better performance for PEMA and PMMA as compatibilizers than for PVDF/PS blend when mixed with PBMA.

Acknowledgments

The authors thank FAPESP and CNPq for partial financial support. I.N. thanks CNPq for a graduate fellowship.

References

1. Utracki, L.A. In *Polymer Alloys and Blends: Thermodynamics and Rheology*; Carl Hanser Verlag, 1990.
2. Siqueira, D.F.; Galembeck, F.; Nunes, S.P. *Polymer* **1991**, *32*, 990.
3. Fowkes, F.M.; Tischler, D.O.; Wolfe, J.A.; Lannigan, L.A.; Ademu-John, C.M.; Halliwell, M.J. *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, *22*, 547.
4. Nishi, T.; Wang, T.T. *Macromolecules* **1975**, *8*, 909.
5. Roerdink, E.; Challa, G. *Polymer* **1978**, *19*, 173.
6. Wendorff, J.H.; *J. Polym. Sci.: Polym. Lett. Ed.* **1980**, *18*, 439.
7. DiPaola-Baranyi, G.; Fletcher, S.J.; Degré, P. *Macromolecules* **1982**, *15*, 885.
8. Roerdink, E.; Challa, G. *Polymer* **1980**, *21*, 1161.
9. Al-Saigh, Y.Z.; Chen, P. *Macromolecules* **1991**, *24*, 3788.
10. Wu, S. In *Polymer Interfaces and Adhesion*; Marcel Dekker Inc., 1982.
11. Cornell, J.A. In *Experiments with Mixtures: designs, models and the analysis of mixture data*; John Wiley & Sons, 1990.
12. Neto, B.B.; Scarminio, I.S.; Bruns, R.E. In *Planejamento e Otimização de Experimentos*; Editora da UNICAMP, 1995.
13. Siqueira, D.F.; Bruns, R.E.; Nunes, S.P. *Polymer Networks and Blends* **1993**, *3*, 63.
14. Paulo, D.R.; Barlow, J.W. In *Polymer Compatibility and Incompatibility*; K. Solc., Ed., Harwood Academic Publishers, 1982.

FAPESP helped in meeting the publication costs of this article