Factor Analysis for Dynamic Mechanical Spectroscopy of Polymer Blends

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ABSTRACT: A method for studying dynamic mechanical spectroscopy (DMS) is described. By use of factor analysis, the DMS curves of twelve polyurethane/polystyrene ionomer thermoplastic interpenetrating polymer networks were studied. The isolated tan δ−temperature curves of the interface region have been extracted and the relative amounts of interface region have been determined. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64**: 2067–2071, 1997

Key words: factor analysis; dynamic mechanical spectroscopy; morphology; interpenetrating polymer network; interface

INTRODUCTION

With the aid of computers, factor analysis,[1,2] a mathematical tool for solving multidimensional problems, has captured the attention of the chemist. This technique has been employed successfully in a variety of chemical applications including light spectroscopy, nuclear magnetic resonance, mass spectroscopy, chromatography, polarography, solution properties, and biological activity. Dynamic mechanical spectroscopy (DMS) has been widely used for characterization and studying the damping behavior of polymers.[3] In this paper, factor analysis was used to analyze DMS curves. A set of molecular motions of polymer chain segments in a certain environment is in correspondence with a dissipation peak in the DMS curve within a certain temperature range, and the size of the peak is associated with the amount of these segments.[4,5] The morphologic structure of a polymer blend system usually consists of three regions, including two phases composed mainly of the components of the blend and an interface or transition region between the two phases. Because the damping peaks corresponding to these regions are superimposed on each other to form one tan δ−temperature curve, some regions with minor contributions to the curve (such as the interface region) cannot be observed clearly. The objectives of factor analysis of DMS of polyblends are to extract pure spectra of these regions and determine the relative amounts of every region, so that it becomes possible to analyze the compatibility of polyblends in a quantitative manner.

THEORETICAL BASIS OF THE METHOD

Factor analysis is a multivariate statistical technique which consists of a series of operations. Mathematically, the analysis is done by first constructing a covariance matrix as follows:

$$[Z] = [D]^T[D] \tag{1}$$

where $[Z]$ is the covariance matrix and $[D]$ is the mixture spectra matrix. Standard eigen analysis of the covariance matrix yields eigenvalues and eigenvectors that represent the data. If the data are pure, just n ($n \leq r$) eigenvalue/eigenvectors will be found. Owing to the existence of experimental error, r eigenvalue/eigenvectors are usually obtained. The r eigenvectors construct an r

Table I   Composition of TPU/PS Ionomer Thermoplastic IPNs

No.	Composition	Neutralization
1	TPU/SMAA-Na$^+$ (75/25−0.25 mmol/g)	In THF solution
2	TPU/SMAA-K$^+$ (75/25−0.25 mmol/g)	In THF solution
3	TPU/SMAA-Na$^+$ (50/50−0.31 mmol/g)	In THF solution
4	TPU/SMAA-Na$^+$ (50/50−0.31 mmol/g)	In THF solution
5	TPU/SMAA-Na$^+$ (70/30−0.17 mmol/g)	In THF/ethyl acetate (5/3) solution)
6	TPU/SMAA-Zn^{2+} (75/25−0.12 mmol/g)	In melt
7	TPU/SMAA-Ca^{2+} (75/25−0.12 mmol/g)	In melt
8	TPU/SMAA-Na$^+$ (75/25−0.25 mmol/g)	In melt
9	TPU/SMAA-Mg^{2+} (75/25−0.12 mmol/g)	In melt
10	TPU/SMAA-Zn^{2+} (50/50−0.31 mmol/g)	In melt
11	TPU/SMAA-Zn^{2+} (50/50−0.31 mmol/g)	In melt
12	TPU/SMAA-Zn^{2+} (70/30−0.17 mmol/g)	In melt

$\times r$ matrix $[Q]$. According to $[C] = [Q]^T$ and $[D] = [R][C]$, a row matrix $[R]$ and column matrix $[C]$ can be found. A number of approaches are available to find the smallest number of eigenvalues needed to represent the data being analyzed. A plot[6] of the common logarithm of eigenvalues versus factor or component index is frequently used. A major break in the initial slope of such a curve signals the transition from significant noise eigenvalues. Noise eigenvalues will be present in all real data. An empirical *IND*, or factor indicator function, has been shown by Malinowski[7] to reach a minimum at the correct number of factors. X. He and colleagues[8] suggest that the eigenvalue ratio

$$ER_j = \frac{\lambda_j}{\lambda_{j+1}}$$

reaches a maximum at the right number of factors. Eigenvalue/eigenvectors can then be assigned as being either "real" or "noise." Abstract eigenspectra and abstract column matrices are constructed by the first n columns of $[R]$ and the first n rows of $[C]$. These matrices are called "abstract" because they constitute mathematical solutions devoid of any chemical meaning.

It is often desirable to transform these abstract matrices into "real" factor space. A testing vector C_{test} can be transformed into a prediction vector C_{pred} by the following calculation:

$$C_{\text{pred}} = C_{\text{test}}[C_{\text{abst}}]^T\{[C_{\text{abst}}][C_{\text{abst}}]^T\}^{-1}[C_{\text{abst}}] \quad (2)$$

A set of unique testing vectors, which includes every column or row of a unit matrix, must be used as follows:

Table II   Results of Abstract Factor Analysis

No.	Eigenvalue	Imbedded Error	Real Error	Factor Indicator Function	Eigenvalue Ratio
1	30.32	0.0126	0.0438	3.62×10^{-4}	49.2
2	0.615	0.00902	0.0221	2.21×10^{-4}	4.03
3	0.153	0.00490	0.00981	1.21×10^{-4}	9.02
4	0.017	0.00419	0.00725	1.13×10^{-4}	2.59
5	0.0065	0.00384	0.00596	1.21×10^{-4}	1.56
6	0.0042	0.00339	0.00480	1.33×10^{-4}	1.87
7	0.0022	0.00303	0.00398	1.59×10^{-4}	1.67
8	0.0013	0.00270	0.00331	2.07×10^{-4}	1.50
9	0.00090	0.00224	0.00259	2.88×10^{-4}	1.36
10	0.00066	0.00107	0.00118	2.95×10^{-4}	1.52
11	0.00006	0.00102	0.00107	10.7×10^{-4}	1.43
12	0.00004				

$$C_{t_1,\text{test}} = (1, 0, 0, \ldots, 0, 0)$$

$$C_{t_2,\text{test}} = (0, 1, 0, \ldots, 0, 0)$$

$$\cdots\cdots$$

$$C_{t_r,\text{test}} = (0, 0, 0, \ldots, 0, 1) \qquad (3)$$

These testing vectors represent fabricated elution profiles. When the retention time of a vector, $C_{t_j,\text{test}}$, corresponds with that of a real component, the difference between $C_{t_j,\text{test}}$ and $C_{t_j,\text{pred}}$ will reach a minimum. Because the predicting curves describe better than the "unique," n vectors with the smallest minimum are chosen. Then the iterative method is used to purify the set of approximations by setting the negative values to zero until no significant improvement in precision can be gained:

$$[C_{\text{new}}] = [C_{\text{old}}][C_{\text{abst}}]^+[C_{\text{abst}}] \qquad (4)$$

where $[C_{\text{abst}}]^+$ is the pseudoinverse matrix of $[C_{\text{abst}}]$. The result obtained from the iteration is substituted into eq. (5):

$$[R] = [D][C]^+ \qquad (5)$$

where $[C]^+$ is a pseudoinverse matrix of $[C]$. Then, on the condition that the element of $[R]$ cannot be negative, $[R]$ can also be purified further by iteration according to the following equation:

$$[R_{\text{new}}] = [R_{\text{abst}}]\{[R_{\text{abst}}]^T[R_{\text{abst}}]\}^{-1}[R_{\text{old}}] \quad (6)$$

Substitute the result into eq. (7):

$$[C] = [R]^+[D] \qquad (7)$$

Repeat the process from eqs. (4)–(7) until the results satisfy both eqs. (4) and (6).

As an example, the method described above was used for the analysis of tan $\delta - T$ (temperature) curves of TPU/PS ionomer thermoplastic interpenetrating polymer networks.

EXPERIMENTAL

Materials

Poly(ethylene adipate) glycol with hydroxyl number 56.89, obtained from the Yantai Factory of Artificial Leather (Shandong, China), was dried in vacuum at 80°C for 5 h. 1,4-butanediol, styrene,

methacrylic acid, and benzoyl peroxide (BPO) were all CP grade reagents. MDI, an industrial product, was purified by distillation before use.

Preparation of TPU/PS Ionomer Thermoplastic IPNs

PU/SMAA was synthesized simultaneously by adding poly(ethylene adipate), MDI, styrene, methacrylic acid, 1,4-butanediol, and BPO to a flask at 80°C with vigorous stirring for 3 min. The mixture was cured at 80°C for 12 h and at 120°C for another 12 h. Then the product was heated in the mixer of a Brabender Plasticorder and neutralized by the addition of $1N$ solution of divalent metal acetate or $1N$ solution of NaOH at 170 to 180°C with a shear rate of 60 rpm. The neutralized masses were compression-molded between polyester films at 130°C. Instead of neutralization in the melt, the products can also be neutralized in 10% tetrahydrofuran solution with $0.1N$ KOH or NaOH methanol solution. Films were obtained by casting and evaporating off the solvent (see Table I).

Measurement

The viscoelastic properties of the polyblends were measured with an Autovibron Dynamic Viscoelastometer (Rheovibron DDV-III-EA type; Toyo Baldwin Co. Ltd., Japan). The heating rate was 3°C/min, and the frequency was set at 35 Hz.
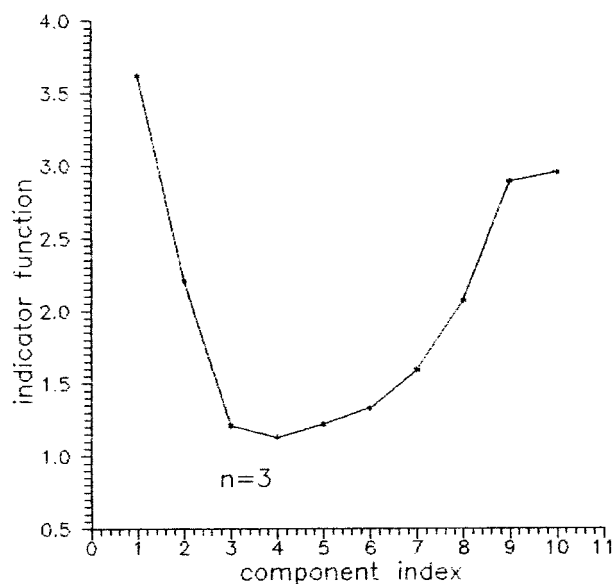

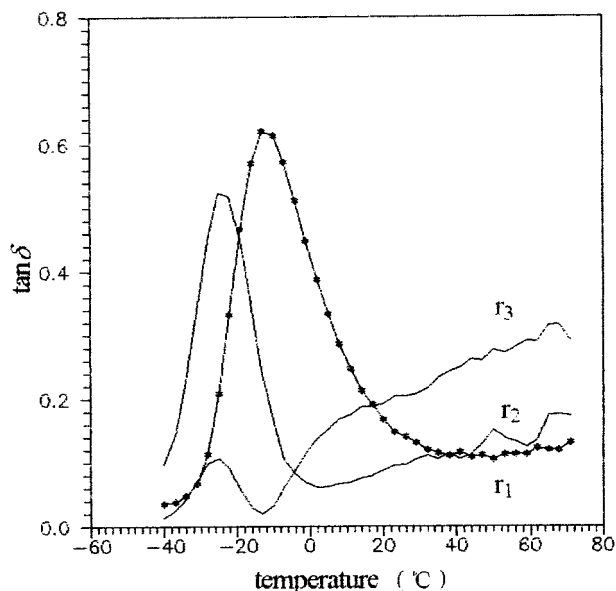**Figure 1**   The indicator function of AFA.

Figure 2 Three unconnected isolated spectra extracted from original data matrix.

All calculations were performed by the FORTRAN 77 program on an Intel 80386 personal computer. The program was designed by the first author.

RESULTS AND DISCUSSION

The tan δ–temperature curves with 38 temperature points between $-40°C$ and $71°C$ of 12 samples
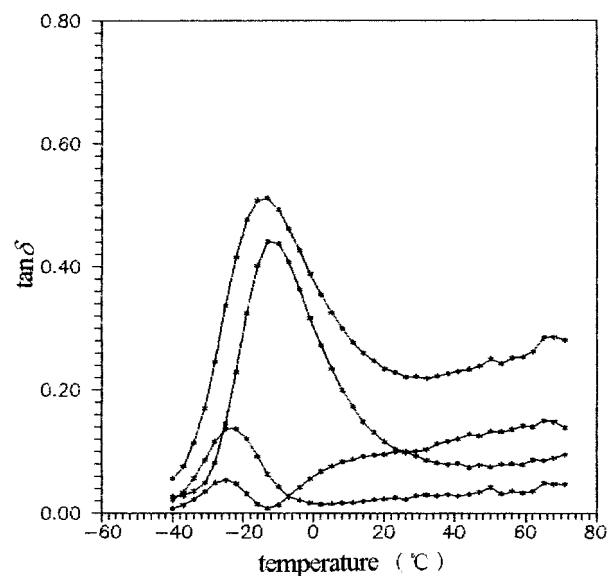

Figure 3 The tan δ–temperature curves resolution results for TPU/SMAA-Na$^+$ (75/25−0.25 mmol/g).
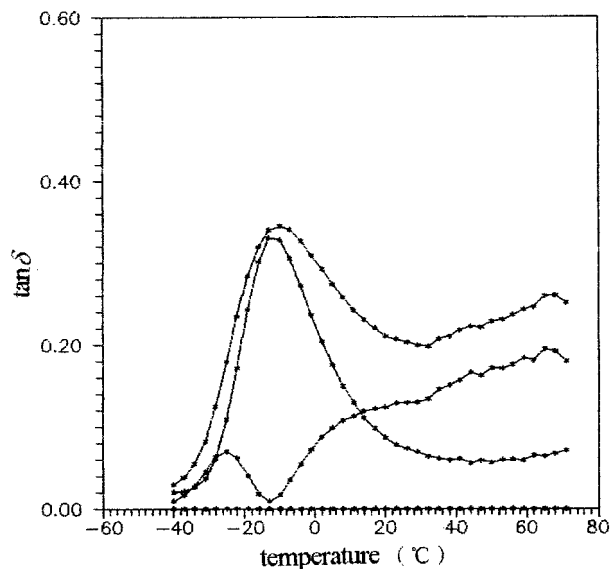

Figure 4 The tan δ–temperature curves resolution results for TPU/SMAA-Zn^{2+} (50/50−0.31 mmol/g).

of the thermoplastic IPNs were studied. The 38 $\times$ 12 data matrix was subjected to abstract factor analysis; results are summarized in Table II. The plot of IND or factor indicator function versus component index (Fig. 1) reaches nearly a minimum at component index 3. The eigenvalue ratio reaches a maximum at a component index of 3. Imbedded error and real error[7] show no significant change after factors reach 3. These facts indicate the clear presence of three factors or components.

By iterative target transform analysis, three unconnected, isolated pure spectra were extracted from the original data matrix. In Figure 2, r_1 and

Table III   Relative Amount of Components in IPNs Obtained from Factor Analysis

No.	r_1	r_2	r_3
1	0.750	0.0	0.081
2	0.786	0.074	0.100
3	0.022	0.154	0.164
4	0.036	0.136	0.023
5	0.253	0.296	0.166
6	0.870	0.156	0.164
7	0.741	0.212	0.107
8	0.555	0.212	0.381
9	0.733	0.221	0.157
10	0.361	0.0755	0.440
11	0.416	0.00	0.492
12	0.404	0.0484	0.470

r_2 damping peaks at $-16°C$ and $-25°C$, respectively, correspond to the glass transition temperature of the phases containing polyurethane. With a wide, spread transition above $-13°C$, r_3 may be caused by the interface region between the two phases. Figures 3 and 4 show tan δ–temperature curve resolution results for TPU/SMAA-Na$^+$ and TPU/SMAA-Zn^{2+}, respectively. Table III shows the relative amount of every region texture in thermoplastic IPN. From Table III, the following conclusions can be drawn: (1) the amount of transition region of the samples obtained by solution casting (No. 1–5) is less than that by naturalization in the melt state (No. 6–12); (2) in the four samples of No. 6 to No. 9 (inclusive), Na$^+$ (No. 8) has a maximum value of r_3; (3) the composition influences the relative amount of transition region: as the content of ionomer increased, the relative amount of r_3 increased, which indicates an increase in the amount of interface region.

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