Compositional Trend Analysis on Poly(phenylene ether) Based Thermoplastic Elastomers

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ABSTRACT: Detailed statistical trend analysis of thermoplastic elastomers based on poly (phenylene ether) (PPE), polystyrene (PS), ethylene vinyl acetate (EVA) and styrene-ethylene-butylene-styrene (SEBS) was done through Design Expert software by Stat-Ease. D optimal crossed design was followed to capture the interaction with the parameters. Effect of blend ratio, vinyl acetate (VA) content of EVA, molecular weight (MW) of SEBS and intrinsic viscosity (IV) of PPE on the blend performance (response) was studied in detail. Design of Experiment (DOE) analysis showed the ''optimized formulation'' of the blend. Increase in PPE-polystyrene (PS) content increased tensile strength and modulus of the blend, followed by a decrease in strain at break. However, EVA had a reverse effect on tensile strength and modulus. Strain at break increased significantly with increasing SEBS content in the blend. Graphical and numerical optimization showed that superior mechanical properties (tensile strength, strain at break and modulus) could be achieved at VA content $\sim$ 50% at a particular loading of EVA. Low MW SEBS was found to be more compatible with the other components of the blend. Mechanical properties of the quaternary blend were marginally affected with change in IV of PPE in the range of 0.33 to 0.46. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3743–3756, 2007

Key words: blends; elastomers; mechanical properties; thermoplastics; modeling

INTRODUCTION

Thermoplastic elastomer is a class of rubbery material, which can be fabricated by techniques usually associated with thermoplastic resins.[1,2] These materials have become important in recent years, especially in the automotive industry, where there is a strong need for soft thermoplastic elastomers, which retain their properties (large elastic deformations, almost complete recovery of initial shape after deformation) up to a higher temperature.[3] Use of high T_g polymers in blends to impart superior thermal resistance has been reported in the literature. For example, Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is known to be compatible with syndiotactic/atactic polystyrene (PS) over all concentration ranges[4,5] with a $T_g \sim$ 210°C, $\sim$ 100°C, and $\sim$ 150°C for PPE, PS, and PPE/PS (60 : 40), respectively. Few studies dealing with the incorporation of PPE in polystyrene based blends have been reported.[6–13] The phase behavior of mixtures of block copolymers and homopolymers has been studied.[6,9,10,14–28] Paul and coworkers[9,10,22] have published papers, which dealt with the morphology and phase behavior of mixtures of Styrene (ethylene-*co*-butylene) styrene (SEBS) and PPE. Most of the studies on blends reported in the literature[6,9,10,14–28] have dealt with samples prepared by solution casting, followed by annealing, to obtain equilibrium morphology. Commercial blends, on the other hand, are prepared by extrusion technique. In such processes, in addition to the thermodynamic miscibility between the block copolymer and the homopolymers the extent of shear applied and the viscosities of each component control the phase behavior and the resulting morphology, which, in turn, affect the final mechanical properties of the blends.[29]

The development of PPE-based novel thermoplastic elastomer with good mechanical integrity, elastic recovery, and recyclability has been recently reported by us.[30] EVA dispersed in the mainly cocontinuous matrix of SEBS/PPE-PS has led to better mechanical properties. Miscibility and phase interaction have played an important role in controlling the mechanical properties of these blends. In the developed injection molded TPE (SEBS/EVA/PPE-PS), EVA acts like a compatibilizer to improve the delamination effect of SEBS/PPE-PS (mainly with high molecular weight (MW) SEBS) and poor elongation at break. Moreover, it has helped from the perspective of cost, compatibility and performance. About 180% elongation at break, tensile strength $\sim$ 15 MPa and

TABLE Ia
Specification of Poly(phenylene ether) (PPE)

	Intrinsic viscosity (IV) in dl g^{-1}	M_w, g mol^{-1}
PPE 1	0.32	34000
PPE 2	0.41	44000
PPE 3	0.46	53000

tension set <20% with excellent recyclability have been achieved. By incorporation of the thermoplastic part (PPE-PS), the onset of degradation of the overall blend has been improved by 20°C compared to EVA/SEBS blend.[31]

Many informative studies have been published on the experimental designs[32–43] in the field of polymer blends and composites for optimizing different parameters to achieve superior properties. Krakowski and Tinker's work is one such example that has given an excellent introduction and discussion on using a response surface methodology designed experiment examining NR (natural rubber)/BR (poly butadiene rubber) blends.[42,43] When dealing with multivariable problems in polymer processing, the use of advanced statistical techniques is recommended.[44] In our present work, efforts have been put to understand the trends in the mechanical properties of SEBS/EVA/PPE-PS blends as a function of composition and molecular variables of the constituent polymers. These trends have been obtained by the analysis of statistical "Design of Experiments" using Design Expert, which is a commercial software package from Stat-Ease, USA. There are no reports of any statistically designed experiments that have been carried out to determine the effects of various factors on the physical properties of PPE based TPE blends.

EXPERIMENTAL

Materials

Poly (2,6-dimethyl-1,4-phenylene ether) was obtained from GE Plastics Bangalore, India (PPE, commercial grade). Molecular properties of PPE (PPE1, PPE2 and PPE3) are reported in Table Ia. Three different grades were selected on the basis of different intrin-

sic viscosities. General purpose PS (GPPS) with the grade name SC203EL was procured from Supreme Petrochemical Ltd., Mumbai, India. GPPS properties are reported in Table Ib.

Styrene ethylene butylene styrene (SEBS) block copolymers used in this work were commercial grade materials (KRATON®G 1650 and 1652), which were obtained from the KRATON POLYMERS, North America. Two glass transition temperatures (~ -55°C and ~ 95°C) were observed. Different properties of KRATON® are reported in Table Ic. Ethylene vinyl acetate (EVA) copolymer (LEVAPREN® 400, 500, 600, and 700), manufactured by Lanxess, Leverkusen, Germany, was obtained from the local market. Molecular properties are reported in Table Id.

Compositional trend analysis

Compositional trend analysis of SEBS/EVA/PPE-PS blends was done with the help of Design Expert, a commercial software package from Stat-Ease Inc, Minneapolis, MN 55,413-2726 (Details of the Design Expert Software are given in the Appendix). D optimal design was taken because D optimal is a statistical algorithm used to sample a design space. D optimal design is a design for categorical factors that is created based on the model. The design will be a subset of all possible combinations of the factors and is generated to minimize the error associated with the model coefficients. The algorithm allows us to sample in such a way that the coefficients of the model terms of interest are estimated with least possible number of compounding. In this design software, "Crossed D Optimal design" was selected since we have a combination of mixture and numerical (continuous/categorical) variables. A mixture variable is part of a set of continuous variables governed by a mixture additive constraint. For example, weight fraction of all ingredients in a blend mixture should add up to "1" or any specified number. If there are "n" mixture variables, only (n-1) can be independently varied. The nth mixture variable has to follow the mixture constraint. In the compositional trend analysis of SEBS/EVA/PPE-PS, the SEBS, EVA, and PPE-PS contents were defined as mixture variables. The variation limits of these components

TABLE Ib
Specifications of General-Purpose Poly Styrene (GPPS)

	Melt flow (200/5)g/ 10 min ASTM D1238	Vicat softening point (°C) ASTM D1525	HDT (°C) ASTM D648	Tensile strength MPa ASTM D638	Elongation (%) ASTM D638	Flexural modulus (MPa *1000) ASTM D790	Flexural strength (MPa) ASTM D790	Izod impact energy (J/m)D256	Specific gravity
GPPS	8	100	83	47	5	2.8	60	20	1.05

TABLE Ic
Kraton®SEBS Specifications

	Kraton®G 1650 (High MW)	Kraton®G 1652 (Low MW)
Styrene/Rubber (wt %)	30/70	30/70
M_w, g mol^{-1}	101,827	78,549
M_n, g mol^{-1}	99,895	77,001
PDI	1.02	1.02
Specific gravity	0.91	0.91
Shore A hardness	72	69
Ultimate tensile strength (MPa)	34.47	31.03
Elongation at break (%)	500	500

are shown in Table II. The total content of SEBS/EVA/PPE-PS always adds up to 100.

Another set of variables was incorporated in the design known as categorical variables. These are discrete variables, like type of polymers, which can only take specified values (levels) but cannot take intermediate values. In the compositional trend analysis of SEBS/EVA/PPE-PS, molecular weight (MW) of SEBS, vinyl acetate (VA) content of EVA and intrinsic viscosities (IV) of PPE were defined as the categorical variables. Different levels of categorical variables are mentioned in Table III.

In "Crossed D optimal design," minimum numbers of experiments required were equal to the number of model terms chosen in the design. To make the model robust we took replication into account to estimate error, if any. The model terms of interest were 39. In addition to that we chose four levels of VA content, three levels for PPE IV, and two levels of SEBS molecular weight. Total 24 (3 × 2 × 4) experiments were derived from categorical points. Based on these requirements, the D-optimal algorithm had chosen 39 sampling points within the design space as being adequate to estimate the 39 numbers of model terms. In general, main effects were regressed from the vertex or corner data points etc. Five replicates were done to make the model robust. Total 44 (39 + 5) experiments were carried out.

TABLE Id
Specifications of Ethylene Vinyl Acetate (EVA)

	Vinyl acetate (VA) content [%]	M_w, g mol^{-1}	M_n, g mol^{-1}	PDI
LEVAPREN®400	40	231,011	108,810	2.1
LEVAPREN®500	50	231,011	109,810	2.1
LEVAPREN®600	60	273,915	110,329	2.5
LEVAPREN®700	70	268,019	103,826	2.6

Six responses were incorporated in the Design Expert (shown in Table IV). These responses were defined considering the overall performance of the TPE. Through this statistical software the dependence of the defined responses on the mixture/categorical factors were evaluated. Based on the design, the 44 experimental compositions with three mixture variables and three categorical variables were divided into different sectors (a–j) based on fixed combination of mixture variables, as shown in Table V. The PPE-PS ratio was always taken to be 60 : 40 in all these experiments. The categorical factors were varied considering PPE intrinsic viscosity (IV), SEBS molecular weight and the VA content of EVA. Similarly by varying the respective mixture variables and categorical variables for 44 runs the best sampling points in the whole design space were statistically derived. Effects of each of these variables on the defined responses were analyzed.

Preparation of samples

PPE/PS were mixed in the ratio of 60/40 by weight. After mixing in a dry mixer the material was fed into a twin-screw extruder (ZSK 25 from Krupp Werner and Pfleiderer, Stuttgart, Germany). The temperature was maintained at 260–270°C. Extruded PPE/PS granules were again mixed with SEBS and EVA in different proportions and fed into the 10-barrel twin-screw extruder system with a $L/D = 40$; the temperature at different zones was set as follows: 100°C (Zone 1) to 270°C (Zone 10) and the Die at 275°C. Screw speed was set at 300 rpm with a throughput rate of 15 kg/h. To avoid moisture induced thermal degradation, the granules were dried at 70°C prior to feed into the injection-molding machine (De-Tech100 LNC4-E (L and T-100T); $L/D \sim 20$; screw diameter of 32 mm) Chennai, India. Temperature at different zones were as follows 270°C (NOZ); 275°C (MH3); 260°C (MH2); 240°C (MH1); 60°C (Feed); 60°C (Mold). Injection pressure was 50 bar and injection speed 18 mm/s. Backpressure was 7 bar and total cycle time was kept as 32 s. The samples were molded according to specimen size mentioned in ASTM D 412-98a. The samples were conditioned at 50% humidity and 25°C for 48 h.

TABLE II
Mixture Variables Assigned in the Design of Experiments

	Type of variables	Low	High
EVA content [%]	Mixture	10.0	30.0
SEBS content [%]	Mixture	35.0	60.0
PPE-PS content [%]	Mixture	25.0	35.0

	Type of variables	Level 1	Level 2	Level 3	Level 4
PPE IV (intrinsic viscosity)	Categorical	0.33	0.41	0.46	–
SEBS MW (molecular weight)	Categorical	Low	High	–	–
VA (vinyl acetate) content of EVA [%]	Categorical	40	50	60	70

Testing procedures

Mechanical tests

Tensile test was carried out in an Instron 3365, Norwood, USA. The samples were prepared following ASTM D412-98a specimen specification. The strain rate was maintained at ~ 200 mm/min. Pneumatic grips were used for better gripping and controlled studies. Long arm extensometer was used to measure modulus at 50, 100, and 200% elongation.

Hardness was reported in Shore A scale measured in Rex Durometers (following ASTM D2240 method) Type A Model 2000, Buffalo Grove, USA.

Tension set was performed in an Instron 3365. One-inch initial mark on the sample was extended up to 100% in the tensile direction and kept for 10 min. The change in dimension in tensile direction was measured after 48 h and reported as tension set.

Transmission electron microscopy

The internal microstructure of all samples mentioned in this work was studied with a FEI Tecnai G2 TEM, Eindhoven. Transmission electron microscopy (TEM) specimen blocks were prepared from the parent sample to section TEM specimen in flow direction. About 100 nm thick sections required for TEM studies were microtomed at $-140°C$ using a Leica FCS ultramicrcotome with a diamond knife procured from Microstar Technologies Inc Huntsville, USA. These sections were then vapor stained with RuO_4 (Ruthenium Tetroxide) for 30 s at 23°C to differentiate different components in the formulation. Digital images were acquired with a Gatan 971 camera coupled with acquisition and image processing software, Digital Micrograph.

TABLE IV
Responses Assigned in the Design of Experiments

	Units
Tensile strength	MPa
Strain at break	%
Modulus @ 50% elongation	MPa
Modulus @ 100% elongation	MPa
Hardness	Shore A
Tension set	%

RESULTS AND DISCUSSION

Trend analysis was done through Design Expert software in EVA/SEBS/PPE-PS blend to understand the dependency of different factors on responses. Based on the virtual center of gravity of the design space, the reference point of the blend was chosen. This need not be an actual blend composition. However, by incorporating all the data the desired effects at the reference point can be computed through significant model equation. In other words, once the significant model was frozen, the equation was used to compute the response at the reference point. Deviation from the reference point was derived depending on the variation of the response by changing one particular factor at a time from its reference point while keeping all other factors constant at their respective reference points. Different model graphs were generated through trace plotting option by Design Expert software for different mechanical responses. Trace plots (also called perturbation plots in response surface and factorial design) helped us to compare the effects of all the components in the design space. The lines in the trace plots represented the effect of changing each mixture component while holding all others at a constant ratio. The response was plotted while moving along an imaginary line from a reference blend to the vertex of the component being incremented. The default reference blend was the centroid of the design. The trace plots can be created using either Piepel's direction (using a trace in pseudo units) or Cox's direction (using a trace in real units). For Piepel's direction, anywhere along the line the ratios of the changeable amounts of all other components are held constant. Trace (Pieple) option has been used for plotting different responses in the EVA/SEBS/PPE-PS trend analysis. The intersection point corresponds to the response value (Y axis) for the reference blend composition.

The dependency of mechanical properties of 44 SEBS/EVA/PPE-PS compositions on various factors is reported in Table VI. Overall data indicated that EVA/SEBS/PPE-PS (10/60/30) quaternary blend (Table VIb) achieved a tensile strength ~ 23.75 MPa with a strain at break $\sim 184\%$, modulus ~ 15.14 MPa (at 50% elongation), hardness ~ 87 Shore A and a tension set <20% (Run 38). Depending on the mixture and categorical variables there was a need

TABLE V
Blend Compositions Through Design of Experiments (In Each Sector Mixture Variables Constant; Catagorical Variables Vary)

Run no	EVA content mixture variable	SEBS content mixture variable	PPE-PS content mixture variable	PPE IV categorical	SEBS MW categorical	VA content (%) categorical
(a) EVA/SEBS/PPE-PS = 10/55/35						
5	10	55	35	0.33	high	40
6	10	55	35	0.33	high	60
22	10	55	35	0.46	low	70
24	10	55	35	0.41	high	70
29	10	55	35	0.41	low	60
31	10	55	35	0.46	high	50
35	10	55	35	0.33	low	50
(b) EVA/SEBS/PPE-PS = 10/60/30						
2	10	60	30	0.46	low	40
7	10	60	30	0.46	low	70
11	10	60	30	0.41	low	60
37	10	60	30	0.46	low	70
38	10	60	30	0.33	low	50
(c) EVA/SEBS/PPE-PS = 15/60/25						
1	15	60	25	0.46	low	50
3	15	60	25	0.33	high	70
19	15	60	25	0.33	high	70
21	15	60	25	0.33	high	60
32	15	60	25	0.41	low	40
33	15	60	25	0.41	high	50
(d) EVA/SEBS/PPE-PS = 19/51/30						
4	19	51	30	0.33	high	40
16	19	51	30	0.46	high	50
34	19	51	30	0.41	high	70
(e) EVA/SEBS/PPE-PS = 19.5/48/32.5						
14	19.5	48	32.5	0.46	low	70
(f) EVA/SEBS/PPE-PS = 20/45/35						
36	20	45	35	0.33	high	60
41	20	45	35	0.41	high	40
(g) EVA/SEBS/PPE-PS = 22.5/52.5/25						
9	22.5	52.5	25	0.33	low	40
27	22.5	52.5	25	0.41	low	60
43	22.5	52.5	25	0.46	high	40
(h) EVA/SEBS/PPE-PS = 30/35/35						
8	30	35	35	0.33	low	70
10	30	35	35	0.46	high	70
12	30	35	35	0.46	low	60
15	30	35	35	0.41	low	50
17	30	35	35	0.33	high	50
18	30	35	35	0.46	high	70
26	30	35	35	0.33	low	70
39	30	35	35	0.33	high	40
42	30	35	35	0.46	low	60
44	30	35	35	0.41	high	60
(i) EVA/SEBS/PPE-PS = 30/40/30						
13	30	40	30	0.46	high	60
28	30	40	30	0.41	low	40
(j) EVA/SEBS/PPE-PS = 30/45/25						
20	30	45	25	0.33	low	60
23	30	45	25	0.41	high	70
25	30	45	25	0.46	low	70
30	30	45	25	0.41	low	50
40	30	45	25	0.46	high	50

to understand the effect of blend ratio of EVA/ SEBS/PPE-PS, VA content of EVA, SEBS molecular weight and finally the IV of PPE on the mechanical properties of the quaternary blend. However, all these mechanical properties of SEBS/PPE-PS (70/30) were found to be inferior as compared to that of

TABLE VI
Mechanical Responses of EVA/SEBS/PPE-PS Blends (Standard Deviation Reported in Brackets)

Run no	Tensile strength (MPa)	Strain at break (%)	Modulus at 50% (MPa)	Modulus at 100% (MPa)	Hardness shore A	Tension set (%)
(a) EVA/SEBS/PPE-PS = 10/55/35						
5	22.74 (0.3)	147 (7.0)	17.11 (0.3)	20.45 (0.3)	94 (1.0)	26
6	15.85 (0.5)	108 (4.0)	13.06 (0.5)	15.65 (0.5)	92 (1.5)	–
22	21.99 (0.7)	129 (8.2)	15.08 (0.3)	20.03 (0.3)	85 (2.0)	12
24	15.70 (0.2)	107 (4.2)	12.59 (0.2)	15.37 (0.2)	93 (1.0)	–
29	23.20 (0.1)	154 (6.0)	15.42 (0.2)	20.19 (0.2)	88 (1.7)	18
31	20.48 (0.4)	150 (6.0)	14.15 (0.6)	17.8 (0.6)	95 (0.6)	20
35	23.16 (1.8)	139 (15.0)	17.52 (0.5)	–	92 (0.6)	15
(b) EVA/SEBS/PPE-PS = 10/60/30						
2	20.99 (0.5)	131 (11.0)	13.89 (0.6)	18.74 (0.5)	88 (1.0)	9
7	21.30 (0.8)	157 (10.0)	12.5 (0.4)	16.70 (0.4)	88 (0.6)	19
11	20.34 (1.6)	182 (12.0)	12.40 (0.4)	16.58 (0.4)	87 (0.6)	14
37	20.74 (0.5)	166 (9.0)	12.38 (0.3)	16.50 (0.3)	88 (1.0)	17
38	23.75 (0.8)	184 (12.0)	15.14 (0.3)	18.98 (0.3)	87 (0.6)	19
(c) EVA/SEBS/PPE-PS = 15/60/25						
1	20.98 (1.4)	184 (18.0)	11.77 (0.1)	16.02 (0.1)	85 (0.6)	8
3	13.35 (0.5)	171 (13.0)	8.97 (0.1)	11.18 (0.1)	90 (0.6)	12
19	12.83 (0.4)	142 (5.2)	9.41 (0.2)	11.67 (0.3)	90 (1.7)	12
21	12.97 (0.4)	193 (2.3)	7.97 (0.2)	10.1 (0.3)	88 (1.0)	14
32	20.72 (0.6)	198 (6.1)	11.59 (0.5)	15.65 (0.6)	84 (1.0)	17
33	18.32 (0.5)	231 (25.0)	9.85 (0.3)	12.53 (0.4)	88 (1.7)	18
(d) EVA/SEBS/PPE-PS = 19/51/30						
4	17.14 (0.6)	145 (7.4)	12.27 (0.2)	15.26 (0.3)	91 (1)	13
16	17.29 (0.3)	155 (9.3)	11.98 (0.4)	15.04 (0.4)	89 (1.5)	20
34	16.50 (0.3)	125 (2.0)	13 (0.1)	15.00 (0.2)	91 (1.0)	16
(e) EVA/SEBS/PPE-PS = 19.5/48/32.5						
14	18.76 (0.2)	136 (2.1)	12.24 (0.1)	16.99 (0.1)	86 (1.0)	14
(f) EVA/SEBS/PPE-PS = 20/45/35						
36	14.04 (0.2)	94 (2.6)	12.3 (0.2)	–	90 (1.5)	–
41	16.31 (0.3)	120 (4.5)	12.78 (0.1)	15.68 (0.2)	91 (1)	14
(g) EVA/SEBS/PPE-PS = 22.5/52.5/25						
9	19.15 (0.6)	192 (7.0)	11.13 (0.2)	14.93 (0.2)	83 (0.6)	12
27	17.04 (0.2)	188 (3.2)	9.14 (0.2)	12.92 (0.2)	81 (0.6)	13
43	15.07 (15.1)	176 (13.0)	9.45 (0.1)	12.19 (0.2)	91 (1.0)	13
(h) EVA/SEBS/PPE-PS = 30/35/35						
8	18.79 (0.8)	90 (8.0)	15.08 (0.6)	18.63 (0.8)	87 (1.1)	–
10	13.45 (0.2)	76 (2.4)	12.74 (0.3)		91 (0.6)	–
12	18.60 (0.6)	107 (4.3)	14.04 (0.3)	18.42 (0.6)	86 (1.2)	–
15	20.66 (0.2)	116 (6.0)	15.40 (0.3)	20.06 (0.3)	87 (0.6)	–
17	16.70 (0.5)	102 (4.0)	14.30 (0.3)	15.63 (2.0)	92 (1.0)	–
18	13.57 (0.5)	91 (6.4)	12.13 (0.2)	–	91 (0.6)	–
26	18.76 (0.1)	88 (4.0)	14.32 (0.2)	18.43 (0.1)	88 (1.0)	–
39	16.06 (0.3)	93 (3.0)	14.12 (0.2)	–	92 (1.0)	–
42	16.45 (0.5)	106 (4.3)	12.80 (0.1)	16.34 (0.3)	87 (2.5)	–
44	12.32 (0.5)	89 (4.0)	11.26 (0.6)	–	93 (1.0)	–
(i) EVA/SEBS/PPE-PS = 30/40/30						
13	11.67 (0.3)	102 (4.7)	10.00 (0.05)	11.65 (0.3)	88 (1.0)	–
28	18.14 (0.9)	144 (10.00)	12.26 (0.3)	16.39 (0.5)	83 (1.5)	14
(j) EVA/SEBS/PPE-PS = 30/45/25						
20	14.33 (0.7)	176 (8.3)	8.78 (0.2)	11.8 (0.3)	83 (1.5)	11
23	12.18 (0.7)	146 (8.0)	8.99 (0.2)	11.23 (0.4)	86 (1.5)	14
25	15.85 (0.2)	163 (7.0)	9.48 (0.2)	13.29 (0.2)	83 (1.7)	15
30	19.64 (0.5)	191 (13.2)	11.02 (0.2)	15.18 (0.1)	82 (1.0)	15
40	14.59 (0.8)	176 (5.0)	9.61 (0.2)	12.27 (0.3)	90 (1.5)	16

Values in the parenthesis indicate the standard deviations.

SEBS/EVA/PPE-PS.[31] This increase in mechanical properties of the quaternary blend in presence of EVA is due to the physical compatibilization effect of EVA in the blend. EVA is compatible with the ethylene-butylene block of SEBS and having a close surface tension with PPE and PS.
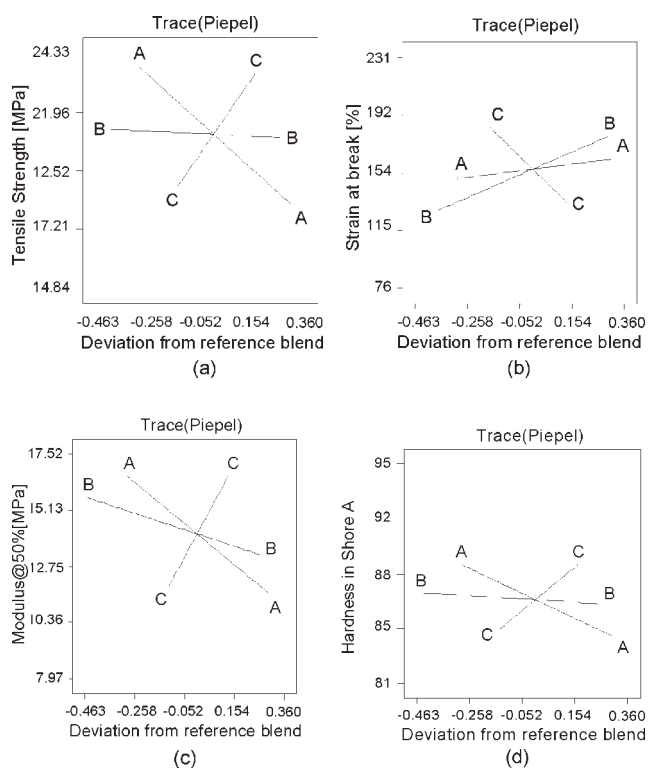
Figure 1 Trace plots of different mechanical responses: Actual Components: A: EVA = 19.00; B: SEBS = 51.00; C: PPE-PS = 30.00 (a) Tensile strength in MPa for PPE IV (intrinsic viscosity) = 0.33, SEBS MW = Low and VA content = 40 (b) Strain at break in % for PPE IV = 0.33, SEBS MW = Low and VA content = 40 (c) Modulus @ 50% in MPa for PPE IV = 0.33, SEBS MW = Low and VA content = 40 (d) Hardness in Shore A for PPE IV = 0.33, SEBS MW = Low and VA content = 40.

Effect of blend ratio

In the design space, blend ratios were varied through the mixture variables (EVA, SEBS, and PPE-PS contents). The contents of EVA, SEBS, and PPE/PS were varied from 10–30 wt %, 35–60 wt %, and 25–35 wt % respectively, in the blend compositions (Table V; Run 1–44). The total weight of the blend was kept at 100. The PPE-PS ratio was kept at 60:40 for all the compositions due to ease of processibility of PPE. The effect of blend ratio with different mechanical properties as response is shown in Figure 1. In all the trace plots, the intersection point of the plots A, B, and C is referred to the composition of the reference blend (EVA = 19; SEBS = 51; PPE-PS = 30).

The variation of tensile strength with EVA content (line A), SEBS content (line B) and PPE-PS content (line C) is shown in Figure 1(a). From line A, it was found that with increase in EVA content the tensile strength of the quaternary blend decreased significantly. Lowering of the tensile strength of the quaternary blend was due to the low tensile strength

(<8 MPa) of the pure EVA component with a VA content ~ 40%. Line B indicated a flat behavior in tensile strength with increasing SEBS content. One would expect an increase in tensile strength by replacing EVA by SEBS. However, in this case the increased tensile strength with increase in SEBS is compensated by the decrease in PPE-PS content. An increase in overall tensile strength of the quaternary blend was observed with increase in PPE/PS quantity (Line C) as the plastic phase (PPE-PS) has a higher tensile strength having cocontinuous morphology. In Figure 1(b), the strain at break increased significantly with the content of SEBS (Line B), marginally increased with content of EVA (Line A) and decreased significantly with the content of PPE-PS (Line C). SEBS had a greater influence than EVA due to the fact that SEBS forms the cocontinuous phase in the quaternary blend.[30] In Figure 1(c), the modulus at 50% elongation was monitored. With increase in EVA having the lowest modulus in the composition (Line A), the overall modulus of the blend decreased significantly. On the other hand with high modulus thermoplastic component i.e., PPE-PS (Line C) the modulus of the blend increased significantly. SEBS content (Line B) had a less significant effect on modulus. Figure 1(d) indicates the positive effect of thermoplastic component (Line C) on hardness and negative effect of both the rubber components (Line A and Line B) on hardness, which are easily explained. Tension set is a measure to account for the elastic nature of the material. With increase in the thermoplastic part, the permanent deformation became more prominent leading to higher values of tension set (not desirable), whereas with the content of rubbers (SEBS and EVA content) the recovery was more, leading to lower tension set (Table VI).

In general, it was understood that the thermoplastic component (PPE-PS) should be increased to increase the tensile strength, modulus, and hardness. At the same time, we also need to understand the effect on strain at break. Optimization of strain at break and tensile strength with low tension set were the key factors behind the selection of a correct blend ratio in TPEs.

Effect of VA content of EVA

The trend analysis was done taking one response at a time. The first trend analysis was done on tensile strength. Figure 2 shows the variation of tensile strength with different mixture variables at a fixed combination of categorical factors. The software based on the overall compositions has selected a reference point. For a fixed PPE IV = 0.33, SEBS MW = Low and VA content = 40, 50, 60, and 70, respectively, the variation of the mixture variables is
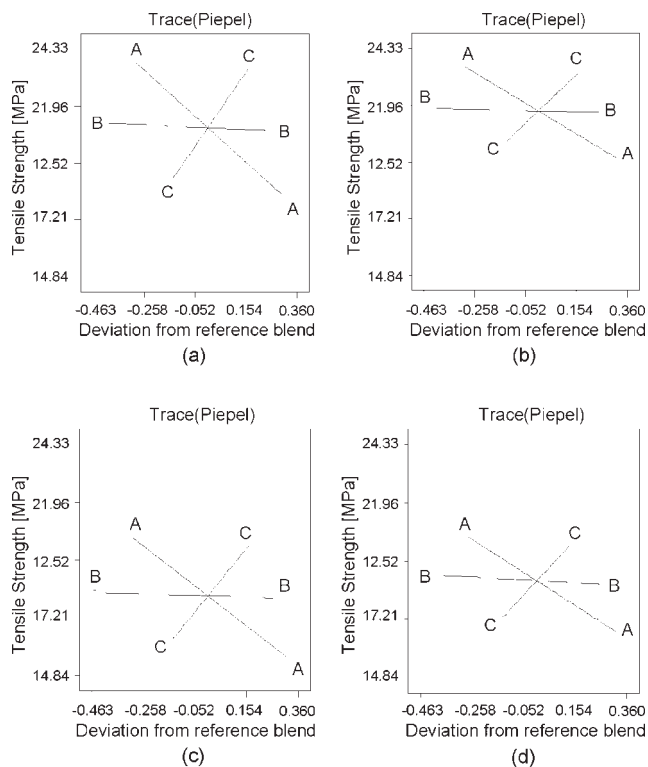
Figure 2 Trace plots on tensile strength with vinyl acetate (VA) content variation: Actual Components: A: EVA = 19.00; B: SEBS = 51.00; C: PPE-PS = 30.00 (a) Tensile strength change at PPE IV = 0.33, SEBS MW = Low and VA content = 40 (b) Tensile strength change at PPE IV = 0.33, SEBS MW = Low and VA content = 50 (c) Tensile strength change at PPE IV = 0.33, SEBS MW = Low and VA content = 60 (d) Tensile strength change at PPE IV = 0.33, SEBS MW = Low and VA content = 70.

Figure 3 Variation of tensile strength with different VA content for 60/10/30 (SEBS/EVA/PPE-PS) composition with low molecular weight of SEBS.

shown in Figure 2(a–d). The maximum tensile strength of the reference blend was found to be ~ 21 MPa. Actual components of the quaternary blend are described as A, B, and C for EVA, SEBS, and PPE-PS, respectively. Based on the reference point (intersection point) in Figure 2(a–d), it is observed that the tensile strength changes with VA content of EVA. At VA = 50, maximum tensile strength was observed at the intersection point [Fig. 2(b)]. Beyond this value of VA = 50, the tensile strength decreased [Fig. 2(c,d)]. In Figure 3, the variation of tensile strength is shown as a function of VA content for a 60/10/30 (SEBS/EVA/PPE-PS) combination with low molecular weight of SEBS. All the mixture variables and the categorical variables except the VA content of EVA were kept constant. Thus, the effect of VA content of EVA was clearly understood. It is now important to understand the scientific reason behind the effect of VA content on mechanical properties. Change in VA content of EVA changed the polarity of the rubber, which affected the compatibility of the blend. VA content in between 40 and 50% showed promising properties. Increasing VA content (>50%) increases

the softness of EVA along with a reduction in crystallinity. Thus, higher VA content of EVA affects the compatibility as well as mechanical properties (tensile strength, elongation at break, modulus) of the blend.

In the quaternary blend of SEBS/EVA/PPE-PS, EVA acted as a physical compatibilizer. A change in solubility and crystallinity of EVA affected the physical interaction. Additive method of Small[45] was applied to calculate the change in solubility parameter (δ) with the VA content of EVA. By considering a number of simple molecules, Small was able to compile a list of molar attraction constants (G), for the various parts of a molecule. By adding the molar attraction constants it is possible to calculate the δ by the relationship

$$\delta = D \sum G/M \qquad (1)$$

where D is the density and M is the molecular weight.

This method is not suitable for compounds with strong hydrogen-bonding. From the molar attraction constant (G) at 25°C the poly(vinyl acetate) showed a solubility parameter (δ) value 17.07 MPa$^{1/2}$. Similarly, poly (ethylene) showed a solubility parameter (δ) value 17.80 MPa$^{1/2}$. Considering VA content to be 10, 30, 50, and 70%, the overall solubility parameter (δ) of EVA is given in Table VII.

As solubility parameter is changed with the VA content of EVA, the blend became more compatible

TABLE VII
Solubility Parameter from Small's Method for EVA with Different VA Content

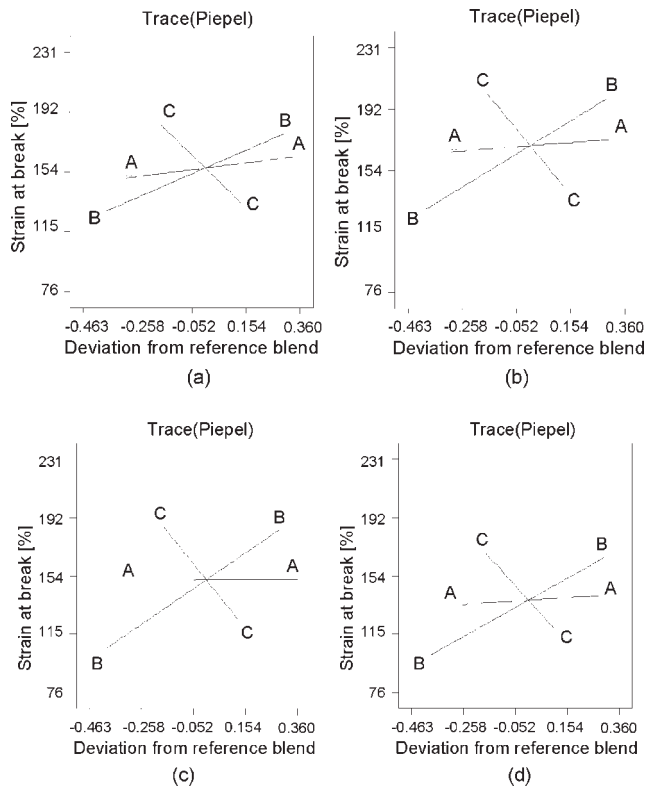| VA content in EVA [%]	δ (MPa$^{1/2}$)
10	17.75
30	17.60
50	17.45
70	17.30

Figure 4 Trace plots on strain at break with vinyl acetate (VA) content variation: Actual Components: A: EVA = 19.00; B: SEBS = 51.00; C: PPE-PS = 30.00 (a) Strain at break change at PPE IV = 0.33, SEBS MW = Low and VA content = 40 (b) Strain at break change at PPE IV = 0.33, SEBS MW = Low and VA content = 50 (c) Strain at break change at PPE IV = 0.33, SEBS MW = Low and VA content = 60 (d) Strain at break change at PPE IV = 0.33, SEBS MW = Low and VA content = 70.

with SEBS and PPE-PS at certain VA (~ 50%) content and showed superior mechanical properties.

Moving to the next response "strain at break," it was observed that strain at break varied with VA content of EVA. Figure 4 shows the effect of VA content on strain at break. In Figure 4(a–d), "strain at

break" was found to increase with EVA (Line A) and SEBS content (Line B), decreased with increase in PPE-PS content (Line C). At VA = 50 the highest value of strain at break (following the intersection point; SEBS/EVA/PPE-PS = 51/19/30) was observed. The effect of VA content on strain at break is shown in Figure 5 with the composition of 60/10/30 (SEBS/EVA/PPE-PS) with low molecular weight SEBS. Thus, in both set of combinations of SEBS/EVA/PPE-PS, VA content ~ 50% was found to be optimum for "strain at break." In Figure 6(a,b), strain at break is analyzed as a function of VA content for different blend compositions (SEBS/EVA/PPE-PS = 55/10/35 and 35/30/35, respectively). In all the blend compositions it was observed that VA content of EVA = 50% gave maximum elongation at break.

In Figure 7(a–d), "modulus at 50% strain" was found to decrease with an increase in rubber component (EVA or SEBS), whereas an increasing trend was found with PPE-PS content. Variation of modulus (at the intersection point) is shown as a function of VA content of EVA. It was found that the "modulus at 50%" for SEBS/EVA/PPE-PS was maximum with VA content ~ 40 and 50%. Further increase in VA content led to a decrement in modulus.

In Figure 8 the variation of modulus is shown as a function of VA content for a 60/10/30 (SEBS/EVA/
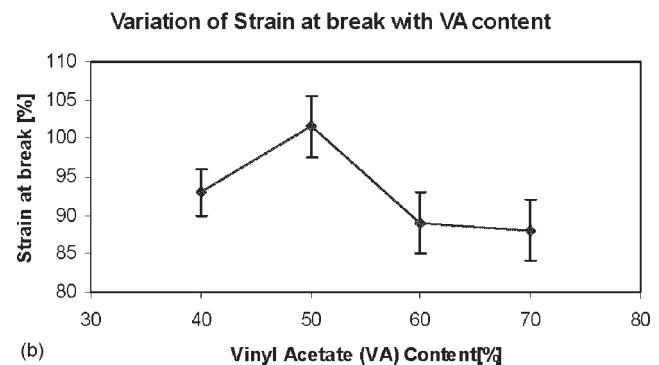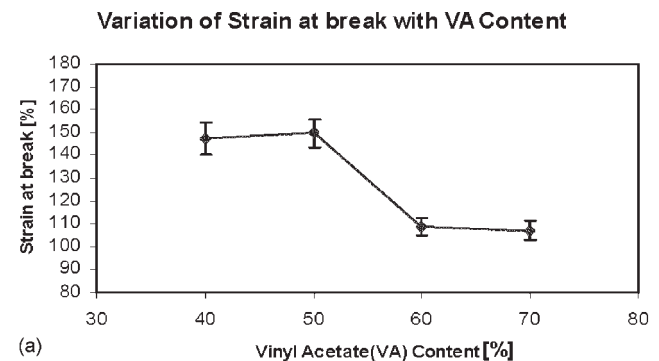

Figure 5 Variation in strain at break with VA content EVA/SEBS/PPE-PS: 10/60/30 low molecular weight (MW) SEBS.

Figure 6 The variation of strain at break with VA content for different set of SEBS/EVA/PPE-PS combination (a) EVA/SEBS/PPE-PS: 10/55/35 in high MW SEBS (b) EVA/SEBS/PPE-PS: 30/35/35 in high MW SEBS.
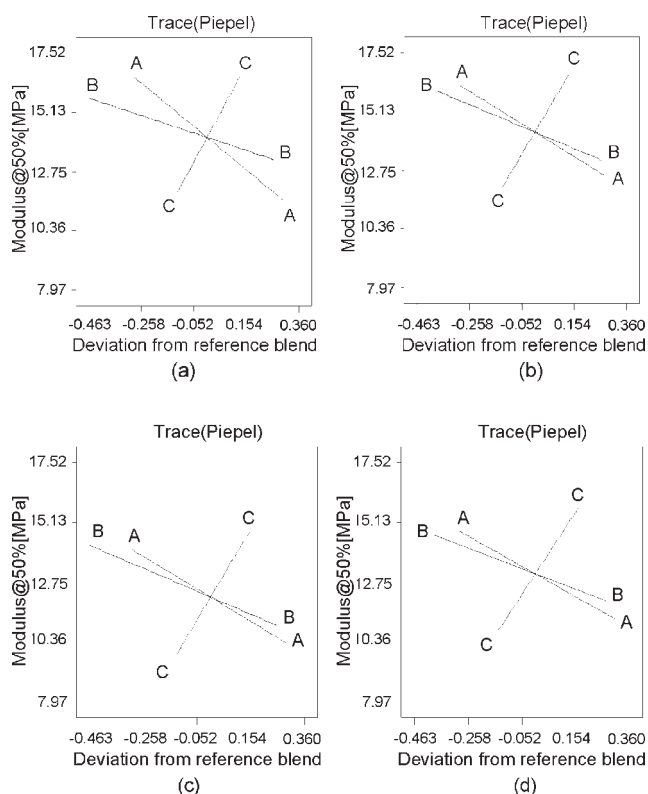
Figure 7 Trace plots on modulus at 50% elongation with vinyl acetate (VA) content variation: Actual Components: A: EVA = 19.00; B: SEBS = 51.00; C: PPE-PS = 30.00 (a) Modulus change at PPE IV = 0.33, SEBS MW = Low and VA content = 40 (b) Modulus change at PPE IV = 0.33, SEBS MW = Low and VA content = 50 (c) Modulus change at PPE IV = 0.33, SEBS MW = Low and VA content = 60 (d) Modulus change at PPE IV = 0.33, SEBS MW = Low and VA content = 70.

PPE-PS) combination with low molecular weight of SEBS. It was observed that at VA content $\sim$ 50%, maximum modulus was achieved.

Hardness and tension set of the blend had a marginal effect by changing the VA content of EVA (not shown here).
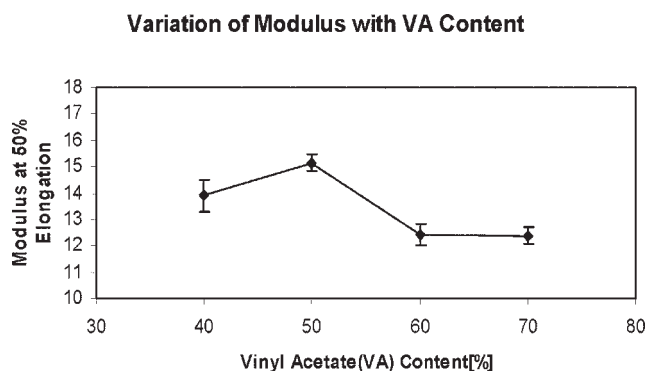
Effect of SEBS MW

Figure 9 shows the effect of SEBS molecular weight (MW) on the tensile strength. It was observed that tensile strength was higher with lower molecular weight SEBS in SEBS/EVA/PPE-PS quaternary blends. We have reported a significant amount of delamination in PPE-PS/SEBS blend with high molecular weight SEBS.[30] Mechanical properties of the PPE-PS/SEBS (high MW) blend, mainly the elongation at break, were very inferior with reference to the quaternary blend (SEBS/EVA/PPE-PS). This indicated a compatibility issue with the high molecular weight SEBS. Molecular weight was related to the viscosity of the system. Viscosity difference between the two components could take up a major role in delamination under high shear. Wetting with the low molecular weight (MW) SEBS should be higher compared to high MW. In quaternary blends of SEBS/EVA/PPE-PS the mechanical properties (tensile strength and elongation at break) improved significantly by using low MW SEBS. As the low molecular weight SEBS had a better compatibility with PPE-PS, it was reflected in the overall mechanical response (like tensile strength) in the quaternary blend. The effect of MW of SEBS on morphology of the quaternary blends is shown in Figure 10. EVA copolymer (white domains) was found in mainly cocontinuous morphology of SEBS/PPE-PS. With high MW SEBS, the EVA domains were found to be more lamellar and cocontinuous [Fig. 10(a)], whereas with low MW SEBS the quaternary blend showed dispersed EVA domains with less lamellar morphology [Fig. 10(b)]. However, at higher magnification, no significant change in EVA interface was visible with SEBS MW, as shown in Figure 10(c,d). Thus, the lamellar to dispersed morphology transformation of EVA domains, as affected by the molecular weight of SEBS, contributed significantly to the improvement in mechanical properties (tensile strength and elongation at break). Improvement in
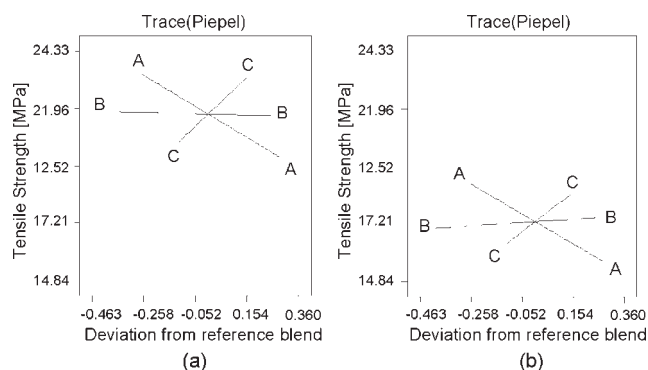

Figure 8 Change in modulus with VA content for a 60/10/30 (SEBS/EVA/PPE-PS) combination with low molecular weight SEBS.

Figure 9 Change in tensile strength with different SEBS MW (a) Low MW SEBS (b) High MW SEBS.
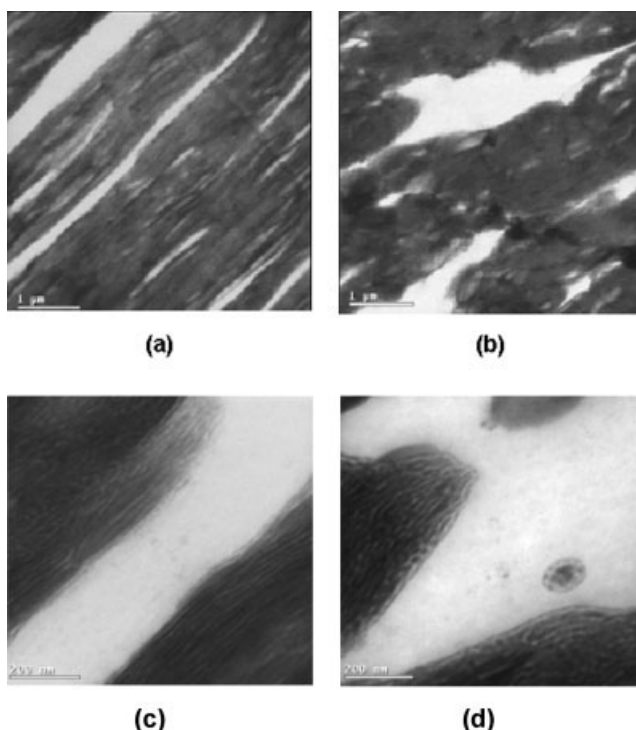
Figure 10 Effect of SEBS molecular weight on overall compatibility of the blend. (a) SEBS (high MW)/EVA (VA: 50)/PPE-PS: 60/15/25 [in low magnification] (b) SEBS (low MW)/EVA (VA: 50)/PPE-PS: 60/15/25 [in low magnification] (c) EVA Interface in SEBS (high MW)/EVA (VA: 50)/PPE-PS: 60/15/25 [in high magnification] (d) EVA Interface in SEBS (low MW)/EVA (VA: 50)/PPE-PS: 60/15/25 [in high magnification].

compatibility with low molecular weight SEBS was also reflected in the modulus data. ''Modulus at 50% strain'' of the quaternary blend was found to be higher with low MW SEBS. Figure 11 shows that ''elongation at break'' was also dependent on molecular weight of SEBS. Monitoring the intersection
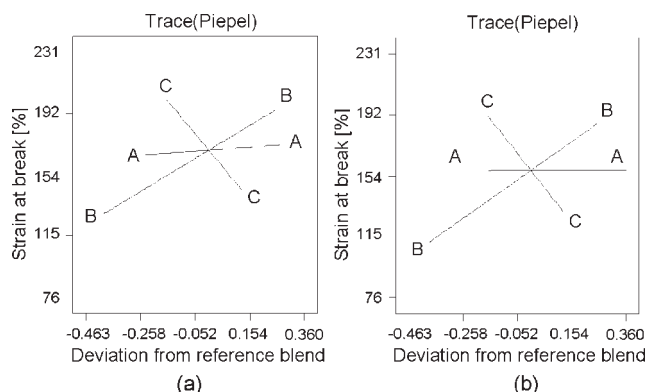

Figure 11 Effect of SEBS molecular weight on strain at break of SEBS/EVA/PPE-PS blend (a) with low molecular weight SEBS (b) with high molecular weight SEBS.
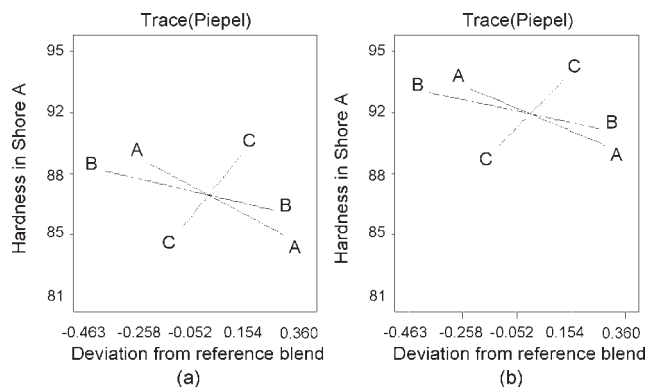

Figure 12 Effect of SEBS molecular weight on Hardness in Shore A of SEBS/EVA/PPE-PS blend (a) with low molecular weight SEBS (b) with high molecular weight SEBS.

point and corresponding y-axis value it was evident that low molecular weight SEBS had an edge over high molecular weight as far as elongation at break was concerned. In Figure 12 the hardness of the quaternary blend was found to increase with molecular weight of the SEBS.

Tension set was independent of the molecular weight of SEBS in the blend of SEBS/EVA/PPE-PS. The key finding on the effect of molecular weight of SEBS on the mechanical performance of the blend was driven by the compatibility. Overall study indicates that low molecular weight SEBS shows better compatibility to achieve superior mechanical properties in PPE based TPE. Structural development, better wetability of the blend along with the required viscosity match with the low molecular weight SEBS drove better performance.

Effect of IV of PPE

IV of the PPE was varied in three levels (0.33, 0.41, and 0.46). It was found that PPE-PS intrinsic viscosity (PPE IV) had a marginal effect on tensile strength of the quaternary blend. From Figure 13, it was observed that the intersection point of the mixture variables (A, B, and C) did not change significantly with three intrinsic viscosities of PPE (0.33, 0.41, and 0.46). In addition to this, no significant change in modulus and hardness of the material were observed with change in IV of PPE.

DOE optimization

The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. To use optimization, responses should be analyzed to establish the appropriate model. Optimization of one response or the
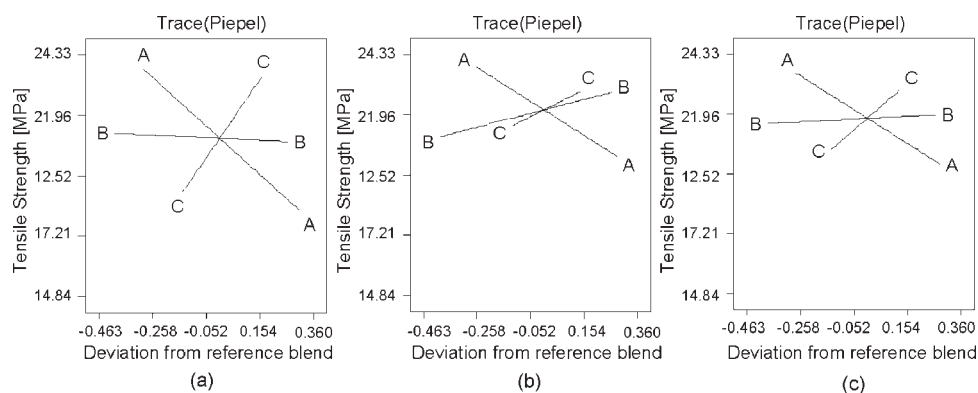
Figure 13 Variation in tensile strength with intrinsic viscosity (IV) of PPE (a) 0.33 IV PPE (b) 0.41 IV PPE (c) 0.46 IV PPE.

simultaneous optimization of multiple responses can be performed graphically or numerically.

Numerical optimization

Numerical optimization will optimize any combination of one or more goals. The goals may apply to either factors or responses. Optimization can be done based on the maximum/minimum value of the response, or a specific range of response values.

Our current design criteria were based on a range of values with respect to tensile strength; strain at break and tension set. Numerical optimization was desired keeping tensile strength in the range of 20–23 MPa, strain at break 200–231% and finally the tension set in the limit of 8–14%. Running the optimization process, eight formulations were recommended by the software (listed in Table VIII). It is important to note that only one set of categorical factors (low SEBS MW; VA content 50 and PPE IV 0.41) comes out in the first six formulations with the range of compositions of mixture variables like EVA, SEBS, and PPE-PS content. To confirm the hypothesis, the best formulation (EVA, 19.12%; SEBS, 55.16%; PPE-PS, 25.73%) was prepared and the properties were determined. It is interesting to note that experimen-

tal values of tensile strength and strain at break are in good accord (within 2%) with the statistical prediction.

Graphical optimization

The main intention of graphical optimization with multiple responses is to find the optimized area in the quaternary blend compositions, which reflects the optimum properties. The "optimized area" determined in the current DOE was based on the same set of criteria as followed in numeric optimization (tensile strength: 20–23 MPa, strain at break 200–231% and finally the tension set in the limit of 8–14%). The results are graphically represented in Figure 14. Any "window" that is not shaded (white zone) satisfies the multiple constraints on the responses. Unless the default color settings are changed, the area that satisfies the constraints will be yellow in color or white in B/W photograph. The area that does not meet the criteria is gray. In Figure 14 the "white" zone corresponds to the "optimized area" with one of the formulations as EVA content ~ 15.48%, SEBS content ~ 57.82%, and PPE-PS content ~ 26.69%. The responses corresponding to this composition were tensile strength ~ 22.49 MPa,

TABLE VIII
Numerical Optimization Results

| Number	EVA	SEBS	PPE-PS	PPE IV	SEBS MW	VA content [%]	Tensile strength [MPa]	Strain at break [%]	Tension set [%]	
1	19.12	55.16	25.73	0.41	Low	50	21.68	203	13	Selected
2	20.45	53.29	26.26	0.41	Low	50	21.48	203	13	
3	26.24	48.7	25.05	0.41	Low	50	20.25	200	13	
4	20.61	53.93	25.46	0.41	Low	50	21.37	208	13	
5	18.47	55.58	25.95	0.41	Low	50	21.83	209	13	
6	24.99	49.78	25.23	0.41	Low	50	20.51	201	13	
7	15.92	59.04	25.04	0.46	Low	50	21.08	200	10	
8	14.86	59.91	25.22	0.46	Low	50	21.29	200	10	
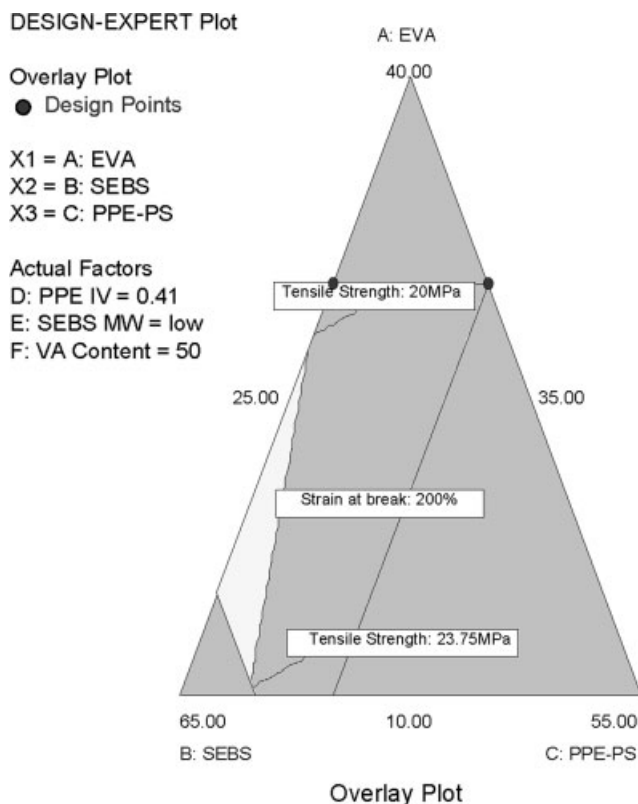
Figure 14 Graphical optimization of the quaternary blend of EVA/SEBS/PPE-PS.

strain at break ~ 210% and tension set ~ 13%. This composition had the following three categorical variable components: VA content of EVA = 50; SEBS molecular weight = Low, and PPE IV = 0.41. No "optimized area" was generated with other combinations of these three categorical variables (VA content of EVA; SEBS molecular weight and IV of PPE). So from graphical optimization, preferred categorical factors along with the right combinations of mixture variables were identified.

CONCLUSIONS

Through design expert software the effect of the mixture and categorical variables on different responses were analyzed in details. This statistical method efficiently sampled minimum number of experimental points to generate useful property trend analysis of the quaternary blend. Replicates were done to make the model more robust. PPE-PS had a strong effect on the tensile strength; strain at break, modulus, hardness and tension set. With increase in PPE-PS content, tensile strength, modulus and hardness increased whereas strain at break and tension set decreased. The slope of change in properties with PPE-PS content indicated the

strong effect on the blend. Increasing the amount of EVA reduced the tensile strength significantly, whereas amount of SEBS played the major role in increasing the strain at break of the quaternary blend. Tensile strength, strain at break and modulus were varied at different VA contents. VA ~ 50 seems to be the optimized quantity of VA to be used in the system. VA content of EVA had marginal effect on hardness and tension set of the blend. With the variation of SEBS molecular weight (MW), significant effect was found on the responses. Low MW SEBS was found to be more compatible with PPE-PS and EVA rather than high MW SEBS. Better compatibility led to achieve superior mechanical properties (tensile strength, elongation at break etc). PPE IV had a very insignificant effect on the responses. This statistical analysis led to develop a compositional concept for optimization of the required mechanical properties for the novel PPE based thermoplastic elastomer. Numerical and graphical optimization of the "Design of experiment (DOE)" identified the optimized composition range leading to superior properties.

APPENDIX

About design expert (http://www.statease.com)

Stat-Ease offers Design of Experiments (DOE) software, books, training, and consulting services. You can improve the quality of your products, develop efficient processes, quickly solve manufacturing problems, and make breakthrough discoveries by applying powerful statistical methods. A must for Six Sigma, DOE helps you find that elusive sweet spot where all of your requirements are met at minimal cost.

Stat-Ease version 6 of DESIGN-EXPERT software helps to optimize the product or process. This Windows-compatible software provides highly efficient design of experiments (DOE) for:

- Factorial Designs—Identify the vital factors that affect your process or product. Then you can make breakthrough improvements.
- Response Surface Methods (RSM)—Find the ideal process settings. Achieve optimal performance.

GUPTA ET AL.

- Mixture design techniques—Discover the optimal formulation.

DESIGN-EXPERT program offers rotatable 3D plots for visualization of response surfaces. Use mouse to explore the contours on interactive 2D graphics. Click the graph to set flags that display coordinates and the predicted response. Check out the numerical optimization function: It finds maximum desirability for up to dozens of responses simultaneously.

What's new in version 6 (the highlights) additional experimental designs (and associated capability for analysis)?

- General (multilevel) factorials with numeric and/or categorical factors.
- D-optimal design selection for multilevel factorial designs.
- Crossed mixture and process designs.
- Taguchi orthogonal arrays (19 designs from L4 to L64).
- Minimum aberration fractional factorial designs
- Historical data.

D-optimal factorial design

The D-optimal factorial design is designed for use with categorical factors as an alternative to the general factorial design option. The general factorial design builder may produce designs with more runs than you are willing to run. The D-optimal design will choose an ideal subset of all possible combinations, based on the model that you specify.

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