# Enhancement of the Tensile Retraction Properties of a Styrenic Block Copolymer by Melt Blending with PA6

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**ABSTRACT:** Styrene–ethylene-propylene–styrene triblock copolymer (SEPS), a thermoplastic elastomer (TPE) was blended with polyamide-6 (PA6) in an attempt to improve the retraction properties of the TPE. A maximum loading of 30 wt % of polyamide was incorporated into SEPS using twin-screw compounding. Various reactive compatibilisers were also incorporated at a maximum loading of 10 wt %. The blends were evaluated in terms of their tensile, dynamic mechanical, and rheological behavior. Design of experiments (DOE) was used to study the effect of blending variables on the tensile properties of the blends. Complex interactions between these variables were identified using this approach. It was shown that by incorporating PA6 into SEPS, in conjunction with a compatibilizer, blends with superior retraction properties and increased tensile strength could be obtained. A mean hysteresis of $54.2 \pm 0.7\%$ was recorded for a blend containing 5 wt % PA6 and 4 wt % compatibilizer compared to $58.5 \pm 0.5\%$ for virgin SEPS. The tensile strength of this blend was almost 75% higher than virgin SEPS. Further evidence of the benefit of incorporating a reactive compatibilizer was the absence of a distinct polyamide relaxation in the dynamic mechanical thermograms for the compatibilized blends. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2024–2033, 2010

**Key words:** blends; compatibilization; mechanical properties; modeling

## INTRODUCTION

TPEs are widely used as the jacketing material in retractable coil-cord cables due to their melt processability and retraction properties. Ideally, for such applications, the selected TPE should be melt processable at high shear rates, have a high level of tensile retractability and be low in cost.

TPEs based on styrenic block copolymers were amongst the earliest to be investigated[1] and are now the most widely used TPEs. Their relatively simple, uniform, and reproducible molecular structure has led to styrenic block copolymers being used as model polymers for the development of new TPE grades. Many styrenic TPEs have the structure poly(styrene-*block*-butadiene–styrene) or poly(styrene-*block*-isoprene–styrene). These are generally abbreviated as SBS and SIS, respectively. The phase structure of SBS, SIS, and similar polymers has given rise to what is known as the 'domain theory'. This theory postulates that the polystyrene segments exist as separate spherical regions or domains within an elastomeric network.[2] The unsaturation in the polybutadiene or polyisoprene blocks in SBS and SIS limits the resistance of these copolymers to oxidation and ozone, and can therefore affect their mechanical performance. However, styrenic block copolymers can be chemically modified to improve certain properties. The most effective modification is by a process whereby the butadiene or isoprene midblocks of the styrenic copolymer are hydrogenated during polymerization to form ethylene–butylene or ethylene–propylene midblocks respectively. The resultant block copolymers—SEBS or SEPS, respectively—have fully saturated midblocks and improved resistance to degradation.

While styrenic TPEs such as SEPS have excellent process flexibility and are low in cost relative to many readily available TPEs, their tensile retraction characteristics are only average compared to, for example, polyamide TPEs. This is due to irreversible damage in the internal structure of the polystyrene domains due to their glassy nature.[3] This limits their potential for use as a jacketing material for retractable coil-cords. However, through modification of SEPS, it may be possible to obtain a material with improved tensile retraction properties compared to virgin SEPS. Modification via chemical synthesis is an option but is highly specialized and expensive. A more economical and potentially more effective route is through blending with a second component.[4]

Incorporation of a rigid component into a TPE such as SEPS will generally restrict the chain

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mobility and plastic deformation of the thermoplastic and elastomeric phases as observed by Ganss et al.[5] when a silicate filler was incorporated into SEBS block copolymers. While this led to a reduction in stress softening of the SEBS copolymer at low strains, it was observed that the hysteresis of the SEBS- sillicate composites was higher than the virgin SEBS due to the induced changes in the morphology at the interface between the polymer and the inorganic/organic hybrid material. Lai et al.[6,7] also encountered complex interphase interactions with blends of SEBS and silicate fillers.

In the present study, a rigid thermoplastic (polyamide) was incorporated into SEPS rather than an inorganic filler, thus avoiding the complex interface between the polymer and the inorganic/organic hybrid material. Instead, the polyamide should form an additional phase within the styrenic copolymer that may behave in a manner similar to physical crosslinks in a conventional TPE. These high modulus physical crosslinks will lead to improved resistance to plastic deformation during tensile extension therefore improving the tensile retractability.

As the cost of producing a blend is usually fixed by the material and compounding costs, the economical value, and potential of the product is effectively dependent upon the blend's morphology. Thus, it is critical that the chosen blend components combine together to form a mechanically stable and improved material. In most polymer blend systems, it is necessary to modify the components through the process of compatibilization to ensure that they combine effectively. Compatibilization attempts to maximize the interfacial interaction during melt blending—thus improving the ultimate tensile and tensile retraction properties—and can be either reactive or non-reactive. The former generally results in the formation of covalent bonds between blend components whereas latter generally improves compatibility primarily by generating physical interactions between blend components.

The process of blending therefore involves many variables, each of which can significantly contribute to the properties of the resulting blend. To enable an objective and controlled study of the factors affecting the mechanical properties of the blends design of experiments (DOE) can be an extremely effective tool. Fundamentally, DOE involves designing a set of experiments in which all input variables, known as factors, are varied in a controlled manner. This set generally consists of no more than 20 experimental runs. Following measurement of selected process or output characteristics, known as responses, statistical analysis is carried out, which can subsequently be used to determine the key factors, investigate interactions between factors and identify the optimal combination of factors. DOE has been used exten-

sively in the past to study effect of polymer blending variables on the mechanical properties.[8–14]

## EXPERIMENTAL

### Materials

Polymer blending was carried out using a styrene–ethylene-propylene–styrene (SEPS) block copolymer as the major blend component. A PA6 semicrystalline thermoplastic was blended with SEPS together with a compatibilizer. The blends were prepared using twin-screw compounding in an attempt to develop a novel material with enhanced retraction properties relative to those of virgin SEPS. Three commercially available compatibilizers were selected, each of which contained grafted maleic anhydride. Maleic anhydride reacts chemically with polyamide thus forming a covalent link between the compatibilizer and the PA6 component of the blend. The polymeric components of these three reactive compatibilizers, namely Kraton FG-1901X, Vinbond P100, and Exxelor VA 1803, were SEBS, polypropylene, and ethylene–propylene rubber, respectively. Selected details, specified by the material suppliers, for the materials used for blending are given in Table I.

### Design of experiments

DOE was used principally to carry out a detailed and controlled study of the effect that blend variables and compounding parameters had on the mechanical properties of the blend materials, thus providing an invaluable insight into the effectiveness of the blending process. In the attempt to optimize the retraction properties of these blends, it was also desirable that the optimum level of each blend variable and compounding parameter be identified. Design Expert®, a DOE software package, was utilized as part of this study to design the experiments and to carry out statistical analysis on the experimental test data.

Selection of factors and factor levels is a critical stage of DOE and a comprehensive knowledge of the systems being studied is highly desirable before designing an experiment. A trial blend study was thus carried out[15] on the SEPS/PA6 blends to provide specific conclusions that enabled the selection of the factors that should be included in the DOE blend study. It was found that the following factors were likely to be the most critical in determining the tensile retraction properties of the SEPS/PA6 blend:

- Compatibilizer type
- Blend component loading ratio
- Compounding temperature

**TABLE I**
**Details of Polymers and Compatibilizers Selected for Blending in this Study**

| Trade name | Polymer type | Composition | Designated name | Supplier |
|---|---|---|---|---|
| Polymers | | | | |
| Monprene 1473MP | Styrenic TPE | – | SEPS | QST |
| Sniamid C548B | PA6 | – | PA6 | Nyltech |
| Compatibilizers | | | | |
| Kraton FG-1901X | SEBS-*g*-MA | 28 wt % styrene, 2 wt % MA and 70 wt % EB | Kraton | Shell chemical |
| Vinbond P100 | MA modified PP | 69 wt % PP (with 1 wt % MA) and 31 wt % other[a] | Vinbond | Bennet |
| Exxelor VA 1803 | MA functionalized elastomeric EP copolymer | 97.7 wt % polymer, 0.8 wt % MA and 1.5 wt % other[b] | Exxelor | Exxon chemical |

EP = Ethylene–Propylene, MA = Maleic Anhydride, PP = Polypropylene.
[a] Olefin polymers and copolymers, pigments, stabilizers, fillers, and additives.
[b] High density polyethylene (HDPE) dust.

Initially a first-order (linear) DOE model was designed. A linear model is only capable of detecting first-order main effects that are linear in nature and therefore cannot be used to fit models that contain curvature in a single factor. The purpose here was to analyze basic trends and to eliminate the less important factors for any subsequent experiments on the blend system. Table II outlines the factors and corresponding factor levels that were used for the first-order model. Using a Response Surface Methodology, D-Optimal design model, a series of experimental runs were then designed using the Design Expert® software. The first-order DOE included three sets of 'replicate' blends, which were incorporated to measure the lack-of-fit and the reproducibility of blend preparation and testing.

Analysis of the first-order experiment showed that DOE was successfully applied to the twin-screw compounding process and the response measurements were accurate and sensitive to the changes made to each of the blends. Moreover, the factors critical in determining the properties of the blends were identified. However, this experiment was limited in that it did not allow a study of either interactions between factors or of curvature of factor

effects. Curvature is a second or higher order main effect and can usually be represented by quadratic (second order) or cubic (third order) models. Therefore a second-order experiment was carried out, which enabled a more thorough investigation of the compounding process and the blend properties. A second-order experiment measures the first-order main effects, the second-order main effects and the interaction effects. To limit the number of experimental runs to a reasonable level for this experiment it was necessary to refine the factors and factor levels using the output from the first-order DOE. As with the first-order DOE, a Response Surface Methodology, D-Optimal design model was used to design the second-order model. The complete set of factors and factor levels that were used for the second-order DOE are given in Table III.

**Blend preparation**

The blends were compounded on an APV MP19 co-rotating twin-screw extruder. The extruder was fitted with 19 mm screws with a length to diameter ratio of 25 : 1. A Brabender volumetric twin-screw feeder was used to convey the granular polymers into the extruder hopper. The extruder was fitted with a slot die, which produced extrudate in tape

**TABLE II**
**Factors and Factor Levels for the First Order DOE**

| Factor | DOE Code | Factor level | |
|---|---|---|---|
| | | Minimum | Maximum |
| Maximum barrel temperature | A | 220°C | 230°C |
| PA6 loading level | B | 10 wt % | 30 wt % |
| Compatibilizer loading level | C | 2 wt % | 6 wt % |
| Compatibilizer type | D | Kraton, Exxelor, or Vinbond | |

**TABLE III**
**Factors and Factor Levels for the Second Order DOE**

| Factor | DOE Code | Factor level | |
|---|---|---|---|
| | | Minimum | Maximum |
| Compatibilizer loading level | A | 4 wt % | 10 wt % |
| PA6 loading level | B | 5 wt % | 15 wt % |
| Compatibilizers | C | Kraton or Exxelor | |

### TABLE IV
### Selected APV Twin-Screw Extrusion Parameters the First Order DOE

| Blend ID | Compounding temp. range (°C) | Torque (%) | Melt temp. (°C) |
|---|---|---|---|
| 64/30/6E 220 | 215–220 | 43 | 227 |
| 64/30/6K 230 | 220–230 | 37 | 237 |
| 88/10/2K 220 | 215–220 | 35 | 226 |
| 76/20/4K 225 | 220–225 | 35 | 232 |
| 88/10/2E 230 | 220–230 | 35 | 237 |
| 68/30/2V 230 | 220–230 | 35 | 238 |
| 84/10/6V 220 | 215–220 | 35 | 227 |
| 68/30/2V 230 | 220–230 | 35 | 237 |
| 84/10/6V 220 | 215–220 | 35 | 227 |
| 88/10/2E 230 | 220–230 | 35 | 237 |
| 84/10/6K 230 | 220–230 | 34 | 238 |
| 68/30/2K 220 | 215–220 | 37 | 227 |

form (approximately 50 mm in width and 800 ± 20 µm in thickness). The tape was hauled off using a 3-roll water-cooled stack. Specimens of dimensions suitable for tensile testing and dynamic mechanical testing were cut from the tape. Selected processing parameters recorded during compounding are presented in Tables IV and V for first-order and second-order DOE, respectively.

Before compounding the PA6 was dried for 30 h at 80°C in a vacuum oven. Moisture analysis confirmed that these drying conditions resulted in a moisture content of <0.15 wt % (this is the maximum moisture level recommended by the supplier for processing of this grade).

### Preconditioning of test specimens

Before mechanical and thermal testing, all specimens were dried using the drying conditions for the PA6 virgin material (30 h at 80°C in a vacuum oven). After drying, all specimens were cooled to room temperature under vacuum and then preconditioned for a minimum of 1 h at 23 ± 2°C in a dessicator before testing.

### Mechanical testing

Tensile testing of all blend materials was carried out on the extruded tape samples and in accordance with ISO 527-3:1995 (Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets). Dumbbell-shaped tensile specimens (Type 5), having a minimum length of 115 mm, a width of 6 ± 0.4 mm and a maximum thickness of 0.9 mm, were cut from the tape samples. All tensile testing was carried out in the longitudinal direction and ten specimens were tested for each material.

Both tensile retraction and tensile to break testing were carried out on the blends. Tensile retraction testing involved stretching the sample at a speed of 100 mm min$^{-1}$ to an extension of 50 mm and then retracting it immediately at the same speed until the level of stress in the sample reached zero. The tensile hysteresis was calculated as follows:

$$\% \text{ Hysteresis} = \frac{\text{Energy lost during retraction}}{\text{Energy absorbed during extension}} \times 100 \quad (1)$$

The residual extension in the sample at the point where zero stress level was reached was taken as the 'permanent set' of the sample.

### Dynamic mechanical thermal analysis

Dynamic mechanical properties of selected blends were evaluated in tensile mode using a Rheometric Scientific MkIII instrument. Dynamic mechanical thermal analysis (DMTA) specimens were cut from the extruded tape samples using a dumbbell-shaped punch die that produced Type 5 standard-sized tensile specimens. The vibrating frequency was set at 1 Hz at a strain level of 16 µm peak to peak. Dynamic measurements were carried out over the temperature range of −100°C to 150°C and using a heating at a rate of 2°C min$^{-1}$.

### Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) studies were carried out on the selected samples using a PerkinElmer 6 Series DSC unit. The sample size was maintained at 10 mg. Enthalpy versus

### TABLE V
### Selected APV Twin-Screw Extrusion Parameters the Second Order DOE

| Blend ID | Compounding temp. range (°C) | Torque (%) | Melt temp. (°C) |
|---|---|---|---|
| 83/10/7E | 220–230 | 39 | 239 |
| 88/5/7K | 220–230 | 34 | 237 |
| 86/10/4K | 220–230 | 35 | 238 |
| 91/5/4K | 220–230 | 44 | 238 |
| 91/5/4E | 220–230 | 36 | 237 |
| 91/5/4E | 220–230 | 36 | 237 |
| 85/5/10E | 220–230 | 39 | 238 |
| 85/5/10K | 220–230 | 35 | 238 |
| 75/15/10E | 220–230 | 44 | 237 |
| 81/15/4E | 220–230 | 38 | 237 |
| 75/15/10K | 220–230 | 27 | 236 |
| 85/5/10E | 220–230 | 39 | 236 |
| 81.5/10/8.5K | 220–230 | 34 | 237 |
| 81/15/4K | 220–230 | 34 | 237 |

**TABLE VI**
**Tensile Results for Blends Prepared for the First Order DOE**

| Blend ID | Tensile strength (MPa) | Strain at break (%) | Hysteresis (%) | Permanent set (mm) |
|---|---|---|---|---|
| 64/30/6E 220 | 13.0 ± 1.3 | 239 ± 27 | 79.8 ± 1.3 | 22.9 ± 2.8 |
| 64/30/6K 230 | 16.5 ± 0.7 | 480 ± 62 | 66.8 ± 2.1 | 11.6 ± 1.4 |
| 88/10/2K 220 | 23.6 ± 0.4 | 793 ± 10 | 59.4 ± 2.0 | 8.3 ± 0.8 |
| 76/20/4K 225 | 21.6 ± 0.6 | 723 ± 13 | 62.3 ± 2.5 | 9.9 ± 1.0 |
| 88/10/2E 230 | 22.9 ± 0.7 | 781 ± 14 | 66.2 ± 2.2 | 10.4 ± 1.0 |
| 68/30/2V 230 | 17.2 ± 0.9 | 624 ± 39 | 78.5 ± 1.7 | 19.5 ± 2.4 |
| 84/10/6V 220 | 23.1 ± 0.6 | 750 ± 18 | 69.4 ± 1.5 | 13.2 ± 1.4 |
| 68/30/2V 230 | 16.9 ± 0.8 | 592 ± 29 | 78.9 ± 1.2 | 20.7 ± 1.7 |
| 84/10/6V 220 | 24.2 ± 0.5 | 783 ± 14 | 67.2 ± 0.9 | 11.9 ± 0.9 |
| 88/10/2E 230 | 21.5 ± 1.3 | 769 ± 16 | 66.7 ± 1.5 | 11.4 ± 1.0 |
| 84/10/6K 230 | 24.6 ± 0.6 | 803 ± 12 | 57.9 ± 0.7 | 8.5 ± 0.9 |
| 68/30/2K 220 | 15.8 ± 1.3 | 547 ± 63 | 78.8 ± 0.7 | 18.8 ± 1.3 |

temperature responses were recorded for each sample over the temperature range 30 to 200°C.

## Torque rheometry

The rheological properties were measured using a Brabender Plasticorder PL2000 fitted with a W50 measuring mixer head into which the granular polymers were fed. This measuring mixer had a capacity of 55 cm$^{-3}$ and was fitted with two counter-rotating mixing blades. The blend was then mixed in the heated chamber by a variable-speed mixing rotor. The variation in torque exerted on the rotor during the melt blending was measured and recorded. The blends were tested at a rotor speed of 75 rpm and a mixing chamber temperature of 230°C. Before testing the PA6 component was dried for 30 h at 80°C in a vacuum oven.

## RESULTS AND DISCUSSION

Blend composition and tensile test results for the first-order DOE are given in Table VI. The following

is an example of the blend notation used in this table: 64/30/6E 220 signifies the blend contained 64 wt % SEPS, 30 wt % PA6, 6 wt % Exxelor and was melt compounded using a maximum barrel temperature of 220°C. Similarly K represents Kraton and V represents Vinbond. Blend composition and tensile test results for the second-order DOE are given in Table VII. For comparison, the tensile properties of virgin SEPS and a SEPS/PA6 blend without a compatibilizer were also determined and are presented in Table VIII.

## General mechanical behavior

It was found that a number of blends produced in this study had improved retraction properties compared to virgin SEPS. For example, the mean hysteresis value recorded for 88/5/7K from the second-order DOE was more than 5% lower than that of virgin SEPS. This is illustrated graphically in Figure 1, which shows tensile retraction curves for the virgin grade and the blend. Similarly, the difference in permanent set between the blend and the virgin

**TABLE VII**
**Tensile Results for Blends Prepared for the Second Order DOE**

| Blend ID | Tensile strength (MPa) | Strain at break (%) | Hysteresis (%) | Permanent set (mm) |
|---|---|---|---|---|
| 83/10/7E | 15.9 ± 1.0 | 763 ± 17 | 60.2 ± 1.8 | 8.3 ± 0.2 |
| 88/5/7K | 24.1 ± 0.9 | 822 ± 11 | 53.1 ± 0.52 | 7.1 ± 0.2 |
| 86/10/4K | 24.3 ± 0.6 | 817 ± 11 | 55.5 ± 1.2 | 7.4 ± 0.3 |
| 91/5/4K | 24.0 ± 0.5 | 824 ± 9 | 54.2 ± 0.7 | 7.2 ± 0.2 |
| 91/5/4E | 20.2 ± 1.5 | 815 ± 18 | 58.7 ± 0.9 | 7.7 ± 0.3 |
| 91/5/4E | 20.1 ± 0.8 | 815 ± 8 | 58.2 ± 0.8 | 7.6 ± 0.1 |
| 85/5/10E | 14.1 ± 1.3 | 782 ± 12 | 55.7 ± 0.4 | 7.8 ± 0.3 |
| 85/5/10K | 22.6 ± 0.7 | 800 ± 14 | 53.7 ± 0.3 | 7.1 ± 0.2 |
| 75/15/10E | 11.9 ± 1.6 | 706 ± 36 | 58.4 ± 0.7 | 8.4 ± 0.2 |
| 81/15/4E | 16.9 ± 0.5 | 730 ± 8 | 70.9 ± 2.8 | 11.3 ± 1.2 |
| 75/15/10K | 21.2 ± 1.0 | 748 ± 21 | 55.7 ± 0.6 | 7.2 ± 0.2 |
| 85/5/10E | 15.1 ± 2.0 | 778 ± 21 | 55.1 ± 0.6 | 7.7 ± 0.3 |
| 81.5/10/8.5K | 23.3 ± 0.6 | 779 ± 15 | 54.1 ± 0.6 | 6.9 ± 0.2 |
| 81/15/4K | 21.5 ± 0.9 | 757 ± 25 | 58.5 ± 1.2 | 7.7 ± 0.3 |

TABLE VIII
Tensile Properties Measure for Virgin SEPS and a SEPS/PA6 Blend Without
Compatibilizer

|  | Tensile strength (MPa) | Strain at break (%) | Hysteresis (%) | Permanent set (mm) |
|---|---|---|---|---|
| Virgin SEPS | 16.9 ± 1.2 | 1006 ± 37 | 58.5 ± 0.5 | 7.9 ± 0.3 |
| 90/10/0 | 19.2 ± 1.2 | 704 ± 11 | 73.3 ± 1.5 | 12.3 ± 1.2 |

material was 0.8 mm. These changes represent a percentage reduction of 9 and 10% for hysteresis and permanent set, respectively, which can be considered quite significant. Thus, it is probable that incorporation of the thermoplastic PA6 phase into the virgin SEPS improved the resistance to irreversible deformation in the SEPS material during extension. This is consistent with observations by Okada et al.[16,17] in studies carried out on ethylene–propylene/PA6 blends.

However, it is clear from the present study that the incorporation of PA6 alone into the SEPS matrix was not sufficient for improving the retraction properties—the addition of a suitable compatibilizer to the blend was also essential. Figure 2 shows the stress–strain responses recorded for two blends containing 10 wt % PA6, with and without the Kraton compatibilizer. Clearly the blend prepared using 4 wt % Kraton had improved tensile strength and strain at break compared to the blend prepared without a compatibilizer. Moreover, it was observed that incorporation of any of the three compatibilizers improved the ultimate tensile and retraction properties of the SEPS/PA6 blends, albeit marginally in some cases. This suggests that these compatibilizers were effective at improving intermolecular interaction between the SEPS and PA6. Majumdar et al.[18] and Huang et al.[19] also observed improvements in ultimate mechanical properties when using a MA-grafted polymer as a compatibilizer in similar blends (PA6 and SEBS).

Vinbond, Exxelor, and Kraton primarily comprise PP, elastomeric EP copolymer and SEBS, respectively, and are each functionalized with MA. Two possible compatibilizing mechanisms for these types of compatibilizers with SEPS are as follows:

Mechanism (a): The PA6 amide group reacts with the MA group of the compatibilizer causing chain scission in the PA6 main chain.

Mechanism (b): The PA6 amine end-group reacting with the MA group of the compatibilizer resulting in water as a reaction biproduct.

A consequence of mechanisms (a) and (b) is that the molecular weight of the PA6 may be reduced—through chain scission in mechanism (a) and, indirectly, through hydrolysis in mechanism (b)—as observed previously by Park et al.[20] and Majumdar et al.[21] In both (a) and (b) the polymeric component of the compatibilizer interacts physically with SEPS. The compatibilizer therefore interacts with both PA6 and SEPS and thus effectively forms a bond between the blend components. Somewhat similar compatibilizing mechanisms have been proposed previously[20,22] for comparable blend systems.

Further analysis of the stress–strain curves presented in Figure 2 can provide some more insight into the deformation mechanism of these materials. It is evident from Figure 2 that the stress–strain
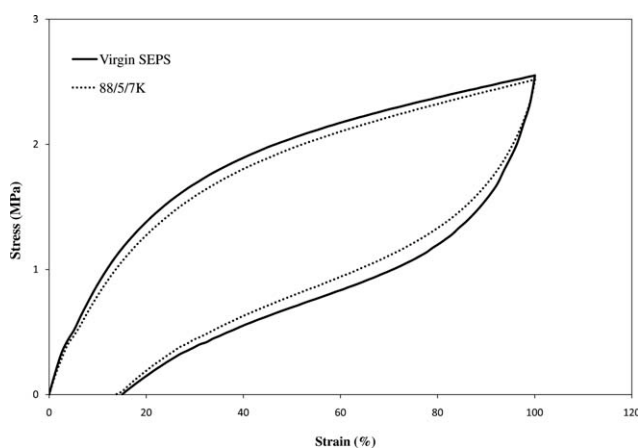


Figure 1 Tensile retraction curves for virgin SEPS and for a blend containing 5 wt % PA6 and Kraton compatibilizer.
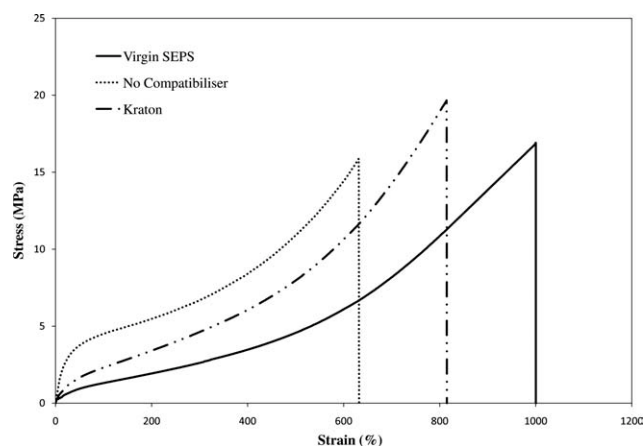


Figure 2 Tensile stress–strain curves for virgin SEPS and for blends containing 10 wt % PA6 with and without a compatibilizer.

responses recorded for virgin SEPS and the compatibilized blend are quite similar in shape at all strain levels, suggesting that the deformation mechanisms may have been comparable – although, not unexpectedly, higher stress levels are developed in the compatibilized blend due to the presence of 10 wt % PA6 component. In contrast, the stress–strain response recorded at low strains for the blend prepared without a compatibilizer is considerably different in shape than SEPS. This difference is most prominent at strain levels in the range of 0% to 100%, within which the blend showed some evidence of yielding, indicating the onset of large-scale plastic deformation, almost certainly in the PA6 phase.

It is also noteworthy that the compatibilized blend had a lower modulus at all strains and a higher strain at break than the blend prepared without a compatibilizer. This is probably due to a reduction in stress concentration within the blend due to improved compatibility. Similar reductions in modulus and improvements in strain at break were observed by Barlow and Paul[23] when a rubbery compatibilizer was incorporated into binary blends.

The absence of yielding in the blend prepared using Kraton compatibilizer is probably a reflection of a greater degree of compatibility in this blend in comparison to the blend prepared without a compatibilizer. Greater phase separation and thus poor interfacial adhesion would account for the poor ultimate tensile properties of the latter. Furthermore, the evidence of yielding-type behavior at low strains most likely accounts for the poor retraction properties observed in the blend prepared without a compatibilizer. Yielding involves significant plastic deformation, which is largely irrecoverable and is accompanied by a high absorption of mechanical energy.

Dynamic mechanical properties were evaluated in an attempt to further establish differences in blend compatibility. The loss tangent thermograms recorded are shown in Figure 3. The presence of a small but distinct relaxation in the loss tangent spectra for the blend prepared without a compatibilizer centered at approximately 65°C provides strong evidence of phase separation in this blend. The relaxation corresponds to the $T_g$ of the PA6 component, which occurred in the same temperature region. There was no clear evidence of a PA6 relaxation in the blend prepared using Kraton compatibilizer suggesting improved miscibility between the PA6 and SEPS phases in this blend.

Another notable feature of the loss tangent spectra in Figure 3 is the differences in the intensity of the glass transition peak of the elastomeric phase centered at approximately −50°C. As expected, the loss tangent peak magnitude for virgin SEPS, 0.472, was
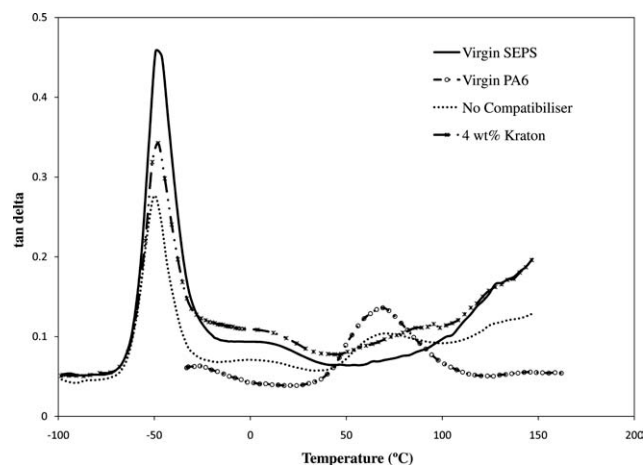


**Figure 3** Loss tangent curves for virgin SEPS, virgin PA6 and for blends containing 10 wt % PA6 with and without a compatibilizer.

greater than that recorded for either blend as the elastomer concentration was highest in the virgin material. The theoretical peak height of these two blends, using the rule of mixtures, is 0.406. It is clear, however, that the measured damping values are considerably lower than this theoretical value, indicating that the mobility of the elastomeric EP phase in the two blends was restricted as a consequence of the presence of the PA6 component. Leyva et al.[24] observed a similar effect on the damping behavior of the elastomeric phase of SBS when a rigid polyaniline phase was blended with the copolymer.

To establish if the restricted mobility in the EP elastomeric phase of the blends might simply reflect a change in the crystallinity, DSC studies were carried out on virgin SEPS and on a blend prepared using 4 wt % Kraton compatibilizer. Measurement of the ethylene–propylene (EP) melting peak area for virgin SEPS gave an enthalpy of fusion, $\Delta H_f$, value of 13.49 Jg$^{-1}$. The expected $\Delta H_f$ for the blend is 11.60 Jg$^{-1}$, taking into account the reduced weight fraction of SEPS in the blend. The measured value of $\Delta H_f$ for the blend was 12.23 Jg$^{-1}$, which is quite close to the expected value, suggesting that the degree of crystallinity of the EP phase was not significantly affected in the blend.

Therefore, it can be suggested that the reduced mobility in the elastomeric phase of the blends, compared to virgin SEPS, was probably due to the presence of the PA6 component in the blend forming additional hard segment domains within in the elastomeric phase of SEPS.

## Design of experiments

To analyze the results of a designed experiment the significant factor effects must firstly be identified.
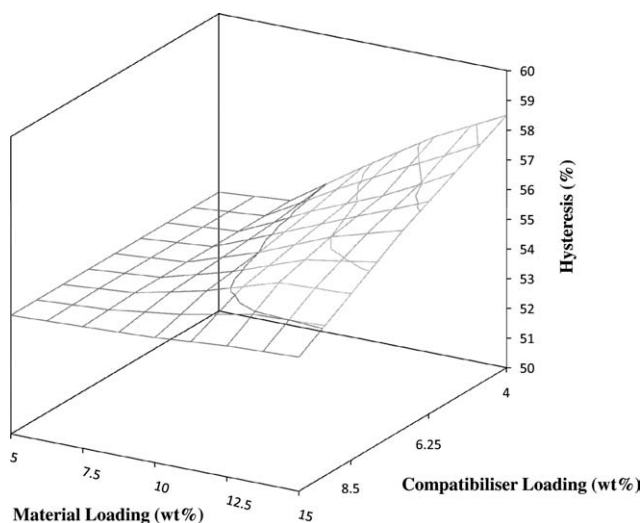
**Figure 4** Hysteresis response surface plot from Design Expert® for blends prepared using Kraton compatibilizer.
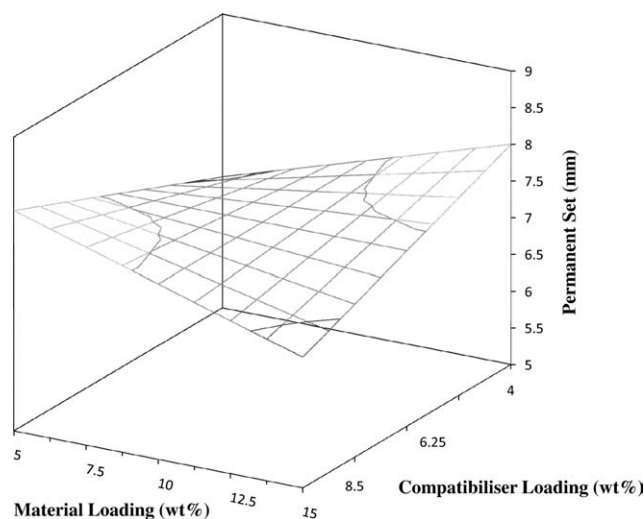


**Figure 5** Permanent Set response surface plot from Design Expert® for blends prepared using Kraton compatibilizer.

Analysis of variance (ANOVA), which was carried out on each response using the Design Expert® software, is an analysis method which determines the significance of a set of data by studying the amount of variance of the data around the model mean.

In general, it was observed that blends with 5 wt % PA6 had better properties compared to blends with higher levels of PA6. 88/5/7K from the second-order DOE, had one of the lowest recorded hysteresis levels at 53.1 ± 0.5% and a permanent set of 7.1 ± 0.2 mm. One of the highest recorded hysteresis levels in this study was for a blend containing 30 wt % PA6 (68/30/2K from the first-order DOE had a hysteresis of 78.8 ± 0.7%).

From this it appeared that increasing the loading level of PA6 in SEPS did not lead to improvements in retraction properties. However, analysis of factor interactions using DOE showed that particular compositions containing higher levels of PA6 actually had exceptionally good retraction properties. The response surface plot in Figure 4 clearly illustrates that the hysteresis increased significantly with increasing PA6 content only when lower loading levels of compatibilizer were used. At the upper loading levels of compatibilizer, the hysteresis remained at the lower levels irrespective of the PA6 content.

The response surface plot for permanent set presented in Figure 5 also illustrates interaction between compatibilizer loading and PA6 loading for blends containing Kraton compatibilizer. It can be seen that the permanent set increased with increasing PA6 loading at low loading levels of compatibilizer but reduced with increasing PA6 loading at high loading levels of compatibilizer. In addition the permanent set increased with increas-

ing Kraton loading at low PA6 loading but reduced with increasing Kraton loading at high PA6 loading.

This is evident when comparing 81/15/4E to 75/15/10E, both from the second-order DOE. Tensile retraction curves for these two blends are presented in Figure 6 (a tensile retraction curve for virgin SEPS is also presented here for reference). The former blend had a hysteresis of 70.9 ± 2.8% and a permanent set of 11.3 ± 1.2 mm. The latter, which was a blend with the same PA6 content but with a higher Exxelor content of 10 wt %, had a significantly reduced hysteresis of 58.4 ± 0.7% and permanent set of 8.4 ± 0.2 mm. When the compatibilizer content was increased in blends with lower levels of PA6, a reduction of this magnitude was not evident. This strongly suggests that an increase in compatibilizer
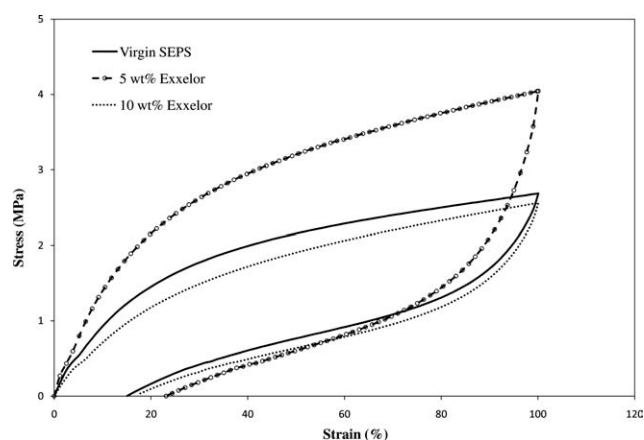


**Figure 6** Tensile retraction curves for virgin SEPS and for blends containing 15 wt % PA6 with two different levels of Exxelor compatibilizer.
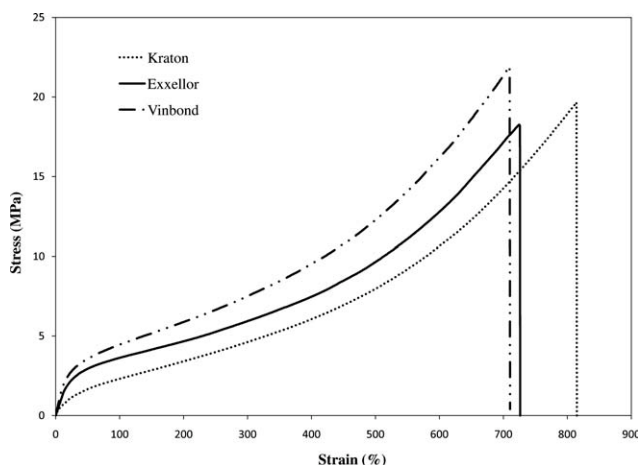
**Figure 7** Tensile stress–strain curves for blends containing 10 wt % PA6 and 4 wt % compatibilizer.

content was essential when higher levels of PA6 were present to increase compatibility and improve the retraction properties.

It is therefore clear that good retraction properties were attainable with high loading levels of PA6 provided that a higher level of compatibilizer was also added to achieve a critical PA6 to compatibilizer threshold ratio. For example, 75/15/10K from the second-order DOE, contained 15 wt % PA6 and had a hysteresis value of 55.7 ± 0.6% and a permanent set of 7.2 ± 0.2 mm, which are exceptionally good retraction properties.

With regard to the twin-screw compounding parameters, the tensile properties of the blends improved when higher barrel temperatures were used. It was found that there was a 95.19% probability that increasing the barrel temperature would give rise to a reduction in hysteresis of the blends. It is probable, therefore, that the higher compounding temperature led to an improvement in the compatibilizing mechanism in the blends. This may have been due to a higher degree of reaction between the maleic anhydride and the PA6 or due to a reduced melt viscosity of the polymeric blend components at the higher temperature promoting improved dispersion.

DOE studies showed that the compatibilizer type also had a significant effect on the tensile properties of the blends. It was found in the first-order DOE that there was a 99.47% chance that changing compatibilizer type during the experiment affected the hysteresis level. The first-order DOE showed that Kraton was the most successful compatibilizer in terms of improving tensile retraction properties. In terms of ultimate tensile properties it was also found that blends containing Kraton generally had the highest tensile strength and strain at break.

It is evident from the stress–strain plots in Figure 7 that, not only did the blend prepared using Kraton

compatibilizer have the highest strain at break, but that it also had a significantly lower secant modulus than the other blends at all strains. The blend prepared using Kraton was therefore softer and more flexible than the other three blends. This probably reflects increased compatibility, and thus increased PA6 phase dispersion, in this blend; the PA6 would therefore have been less likely to have a stress concentrating effect in the blend prepared using Kraton.

Further investigation using torque rheometry was carried out to assess the effect of the different compatibilizers on the melt viscosity during mixing. The purpose of this technique was to compare the interactions that occurred when different compatibilizers were melt-blended with the SEPS/PA6 mix. An increase in torque observed during blending may be attributed to the interfacial reaction occurring between the polymers at that time. Torque rheometry has been widely used for this purpose in the past.[16,17,20,25–28] The conventional test method for torque rheometry involves adding the all of the blend components together into the mixing chamber. However, it was found that this method did not allow a valid comparison of the different compatibilizers due to the effect of the different compatibilizer pellet size on the mixing torque. A modified test method was devised for this work whereby the SEPS and compatibilizer components were added to the mixing chamber at the start of the test and allowed to mix for a 4-min period (by which time it had been established that these components were fully melted). After this time period had elapsed the PA6 was added to the mixing chamber. Figure 8 shows the percent increase in torque 40 s after addition of the PA6 component into the mixing chamber for each compatibilizer. Measurements showed that the increase in viscosity was highest for the blend containing Kraton, suggesting that the level of grafting
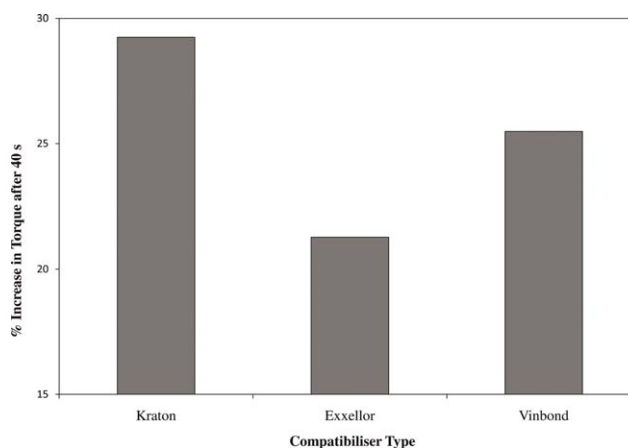


**Figure 8** Percentage increase in torque after addition of 10 wt % PA6 into a blend of 86 wt % SEPS/4 wt % compatibilizer.

between the maleic anhydride and the PA6 was greatest in this blend; this further supports the earlier observations that blends containing Kraton generally had superior tensile properties.

The reason for Kraton's superior performance as a compatibilizer in this blend system is, almost certainly, attributed in some way to its chemical composition. As outlined previously in Table I, Kraton FG-1901X is a maleic anhydride functionalized SEBS copolymer containing 2.0 wt % maleic anhydride. Exxelor VA 1803 is a maleic anhydride functionalized EP copolymer and has a nominal maleic anhydride content of 0.8 wt %. The base polymer in Vinbond P100 is a polypropylene homopolymer, which is chemically modified with grafted maleic anhydride at a content of 1.0 wt %. Therefore, of these compatibilizers, Kraton had the highest content of maleic anhydride. It is possible that this promoted an increased degree of interaction between the compatibilizer and the PA6 and thus increased compatibility in the blends. However, it is also likely that the nature of the polymeric component of the compatibilizers played an important role; the polymeric component of Kraton, SEBS, may have been more compatible with the SEPS component of the blend than the polymeric component of Vinbond or Exxelor.

While the first-order DOE suggested that Kraton was unequivocally the best of the three compatibilizers, on closer examination in the second-order DOE it was actually found that blends containing Exxelor could perform equally as well as Kraton but only at low loading levels of PA6.

## CONCLUSION

DOE was successfully applied to the blend development process in that factors and factor interactions that were critical in determining the mechanical properties of the blend system were identified. Furthermore, response measurements were accurate and sensitive to the changes made to each of the blends. As certain blends had better retraction properties than the virgin SEPS material it is probable that it was the presence of PA6 in the SEPS matrix, in conjunction with a compatibilizer, which led to the lower levels of hysteresis and permanent set. Thus, it is reasonable to conclude that the thermoplastic PA6 phase improved the resistance to irreversible deformation in the SEPS material during extension. This is consistent with observations by Okada et al.[16,17] in their study of ethylene–propylene/PA6 blends.

A possible mechanism, which supports these findings is that the rigid PA6 phase formed additional hard segment domains in the SEPS matrix and, through the formation of covalent bonds via the reactive compatibilizers, provided resistance to the flow of the elastomeric chain segments of the SEPS.

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