

**Application of Diene-Based  
Thermoplastic Polyurethanes  
in Rubber Compounding**

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## ABSTRACT

Thermoplastic polymeric materials (TPEs) are widely used in applications where the ability to transition between effectively thermoset and plastic states provides a benefit in the manufacturing process. Global expansion of TPEs is predicted, led by increased use of styrenic-based products. However, polyolefin and polyurethane TPEs enjoy wide application and offer competition to styrenics for market share replacing natural and synthetic rubbers.

Thermoplastic polyurethanes (TPUs) are typically based on polyether or polyester soft segments. However, a TPU based on polybutadiene can increase the compatibility with rubber compounds by presenting a new form with both rubber-like soft segments and urethane linkages. Polybutadiene-based TPUs are desired for their hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature elasticity.

The present study introduces the technology associated with 7840 TPU resin, and the application of this new polybutadiene-based TPU material in traditional rubber compounding is explored. The use of diene-based TPU as a co-curable adhesive tie layer between rubber compounds and a polyurethane component will be demonstrated. Additionally, the results from a study mixing diene-based TPU as an additive into traditional rubber formulations are provided. Comparative data

using other commercially available TPUs and TPEs is included in order to assess the performance of the new polybutadiene TPU.

## INTRODUCTION

Thermoplastic polyurethanes (TPUs) are typically based on polyether or polyester soft segments. Unlike styrenic triblock thermoplastic elastomers (TPE) products, these TPUs are not widely utilized in traditional rubber compounding. The polar forms are not very soluble in diene rubbers, or effectively vulcanized with sulfur curatives. However, a TPU based on diene prepolymers can increase the compatibility with rubber compounds by presenting a new form with both rubber-like soft segments and urethane linkages. Polybutadiene-based TPUs are desired for their hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature elasticity.<sup>1,2,3</sup> Previously available diene-based urethane materials were produced from radical polymerized polybutadiene polyols, and were not thermoplastic.<sup>4,5</sup> New thermoplastic products are made from anionically-prepared telechelic polybutadiene diols which are linear and uniform in chain length. Reaction with diisocyanate and a chain-extending diol results in a thermoplastic material which can be characterized by chemical and physical properties intermediate to that of currently available TPU and TPE grades. Figure 1 provides a schematic comparing urethane and styrenic thermoplastic materials.

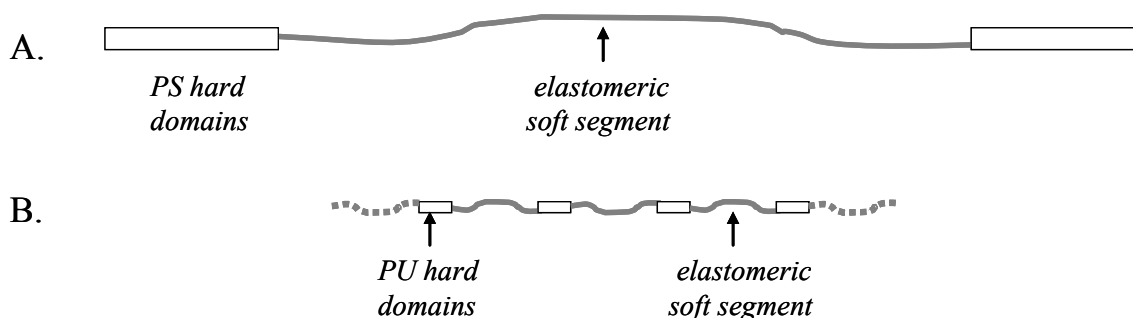


Figure 1. Typical styrenic triblock TPE (A) and multiblock TPU (B) macrostructure.

7840 TPU resin (Cray Valley Company) is produced from Krasol<sup>®</sup> polybutadiene prepolymer by a reactive extrusion process. 7840 TPU has been designed to be compatible with rubber systems. The present study introduces the technology associated with polybutadiene-based TPU materials. Physical characteristics of the 7840 TPU product are presented. Possible applications of TPUs in traditional rubber compounds are explored. The use of 7840 TPU as a co-curable adhesive tie layer between rubber compounds and a polyurethane component will be demonstrated. Additionally, the results from a study mixing 7840 TPU as an additive into traditional rubber formulations are provided. Comparative data using other commercially available TPUs and TPEs is included in order to assess the performance of the new polybutadiene TPU.

## EXPERIMENTAL

In addition to 7840 TPU, several other commercially available thermoplastic materials were included and used as received. Table I provides characterization data of 7840 TPU resin compared to other TPU and TPE products.

Table II details the formulation used as substrates with virgin thermoplastic materials in adhesion studies. The formulation in Table III was used to prepare compounds in which the thermoplastic materials are used as a direct additive. A Banbury-style internal mixer was used to prepare the rubber compounds. Mixing was accomplished in two stages with the non-productive compound milled between stages and prior to curing. A thermoset polyurethane was used also as a substrate. Adiprene<sup>®</sup> L 100 (Uniroyal) is a TDI- terminated polyether based prepolymer that produces a vulcanizate with approximately 90 Shore A hardness when cured with 4,4' - methylene-bis(2-chloroaniline).

Table I. Structural and physical properties of thermoplastic materials.

Typical Property	7840 TPU	polyether TPU	polyester TPU	SBS	SEBS
Type	TPU	TPU	TPU	TPE	TPE
Soft Segment	polybutadiene	polyether	polyester	polybutadiene	ethylene/butylene
Hard Segment	polyurethane	polyurethane	polyurethane	polystyrene	polystyrene
Shore A Hardness	80	82	85	74	72
Tensile Strength (MPa)	14.0	36.6	44.8	9.3	26.8
Elongation (%)	550	670	550	785	630
100% Modulus (MPa)	5.6	5.2	5.5	3.2	2.9
Glass Transition Temp (C)	-35	-49	-32	-61	-55
Vicat Softening Point (C)	52	70	85	~100	~100

Table II. Rubber substrate formulations.

	Ingredient	phr
<b>Non-Productive</b>	BR or IR <sup>a</sup>	100.0
	Carbon Black (N330)	50.0
	Process Oil (paraffinic)	10.0
	Antioxidant (TMQ) <sup>b</sup>	1.0
	Zinc Oxide	5.0
	Stearic Acid	2.0
<b>Productive</b>	Sulfur	2.5
	Accelerator (TBBS) <sup>c</sup>	0.7

<sup>a</sup>solution *cis*-polybutadiene; solution *cis*-polyisoprene

<sup>b</sup>2,2,4-trimethyl-1,2-hydroquinoline

<sup>c</sup>N-*t*-butylbenzothiazole-2-sulfenamide

Table III. Model compound formulation.

	Ingredient	phr
<b>Non-Productive</b>	ESBR (1502) <sup>a</sup>	100.0
	Carbon Black (N330)	60.0
	Process Oil (aromatic)	20.0
	Antioxidant (IPP) <sup>b</sup>	2.0
	Antioxidant (TMQ) <sup>c</sup>	1.0
	Zinc Oxide	3.0
	Stearic Acid	2.0
	Thermoplastic Elastomer	0, 5.0, 10.0, 25.0
<b>Productive</b>	Sulfur	2.0
	Accelerator (CBS) <sup>d</sup>	1.4

<sup>a</sup>emulsion styrene-butadiene rubber, 23.5% styrene

<sup>b</sup>N-isopropyl-N'-phenyl-p-phenylenediamine

<sup>c</sup>2,2,4-trimethyl-1,2-hydroquinoline

<sup>d</sup>N-cyclohexylbenzothiazole-2-sulfenamide

## RESULTS AND DISCUSSION

### Adhesion Study

The application of urethane materials in traditional rubber compounding has been limited, primarily due to poor compatibility between the systems. Urethane polymers have very little solubility in diene-based elastomers and are not readily cured by sulfur-based vulcanization systems. As elastomeric components, urethane materials possess many desirable properties such as excellent abrasion resistance, good flexural properties, low hysteresis, and good solvent resistance.<sup>6</sup> Benefits could be realized in many engineered rubber product applications if a simple means of incorporating urethanes could be established. Today, adhesives and other applied methods are required to generate adhesion between urethane and rubber components in a laminate. The concept of using diene-based TPUs as a tie layer between unsaturated rubber compounds and urethane materials has been promoted.<sup>7</sup> However, previous work resulted in a thermoset polyurethane *in-situ* using branched polybutadiene prepolymers with higher functionality ( $f > 2.0$ ). Commercial development of 7840 TPU resin allows for improvement in such applications. By creating a material that possesses both unsaturated soft segments and hard segments of urethane linkages, diene-based TPUs can promote adhesion between the dissimilar components. In addition, the thermoplastic form allows for easy processing from the melt.

Adhesion properties of 7840 TPU were compared to other thermoplastic materials. Adhesion to an uncured polybutadiene compound (Table II) was first evaluated. Thin sheets of thermoplastic material (<2 mm thickness) were placed against the uncured rubber compound. The laminate was then compression molded in a press at 160°C to the  $t_{90}$  cure time of the rubber layer. Upon cooling, adhesion between the layers was assessed qualitatively. In some cases, delamination between the layers was easily achieved (adhesive failure). Good adhesion resulted in cohesive failure of the rubber or thermoplastic layer. Results are provided in Table IV. As expected, those materials capable of co-curing with the rubber compound displayed cohesive failure, while the saturated products gave adhesive failure.

Adhesion between the different thermoplastic materials was also studied. Using an identical procedure, thermoplastic laminates were prepared. The results are given in Table V. 7840 TPU produced good adhesion and cohesive failure against polyether or polyester urethane substrates. Laminates of the TPUs and SBS TPE produced adhesive failure only.

Subsequently, the adhesion between the thermoplastic products and various substrates was assessed quantitatively. Peel adhesion testing, based on ASTM D1876-01, was performed at Akron Rubber Development Laboratory, Inc. The test was modified by restricting adhesion area to a 3" by 0.25" window by masking with a nylon insert between the substrates. Figure 2 summarizes the peel adhesion results only for the cured laminates which displayed cohesive failure (other laminates failed adhesively at the interface). Both the cis-polybutadiene (BR) and cis-polyisoprene (IR) based rubber compounds were used as substrates.

Table IV. Adhesion testing (rubber).

Component A	Component B	Failure
rubber compound	7840 TPU	<i>cohesive</i>
rubber compound	polyether TPU	<i>adhesive</i>
rubber compound	polyester TPU	<i>adhesive</i>
rubber compound	SBS	<i>cohesive</i>

Table V. Adhesion testing (thermoplastics).

Component A	Component B	Failure
7840 TPU	polyether TPU	<i>cohesive</i>
7840 TPU	polyester TPU	<i>cohesive</i>
7840 TPU	SBS	<i>adhesive</i>
SBS TPE	polyether TPU	<i>adhesive</i>
SBS TPE	polyester TPU	<i>adhesive</i>

Auto-adhesion (self) of the cured rubber compounds is shown. In comparison, the adhesive force between the in-situ cured rubber compounds and the SBS thermoplastic and 7840 TPU is provided. Since the failure mode was cohesive for all samples, actual adhesive force is also dependent upon the modulus of the failed component. 7840 TPU was the only TPU to produce an adhesive bond to the cured rubber substrates. By incorporating curatives into the TPU prior to laminate curing, the cohesive strength and, ultimately, the adhesive force may be increased.

Figure 3 outlines the data from peel adhesion testing between 7840 TPU and other polyurethanes. Both thermoplastic and thermoset polyether-based polyurethanes were used as substrates. With 7840 TPU, cohesive failure was seen in all cases (the SBS product produced only adhesive failures). The highest adhesive force is achieved when the thermoset polyurethane was cast in-place against the diene-based TPU prior to testing.

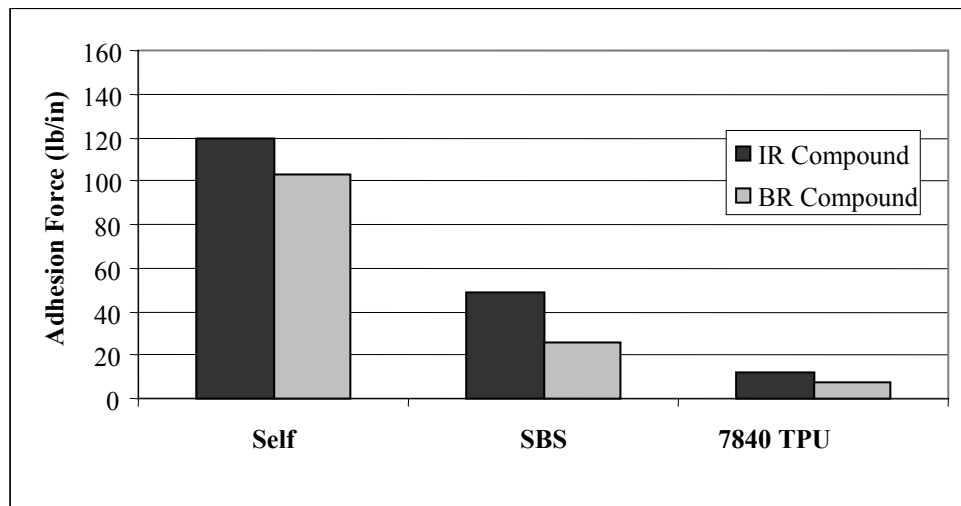


Figure 2. Peel adhesion results for cured laminates resulting in cohesive failure.

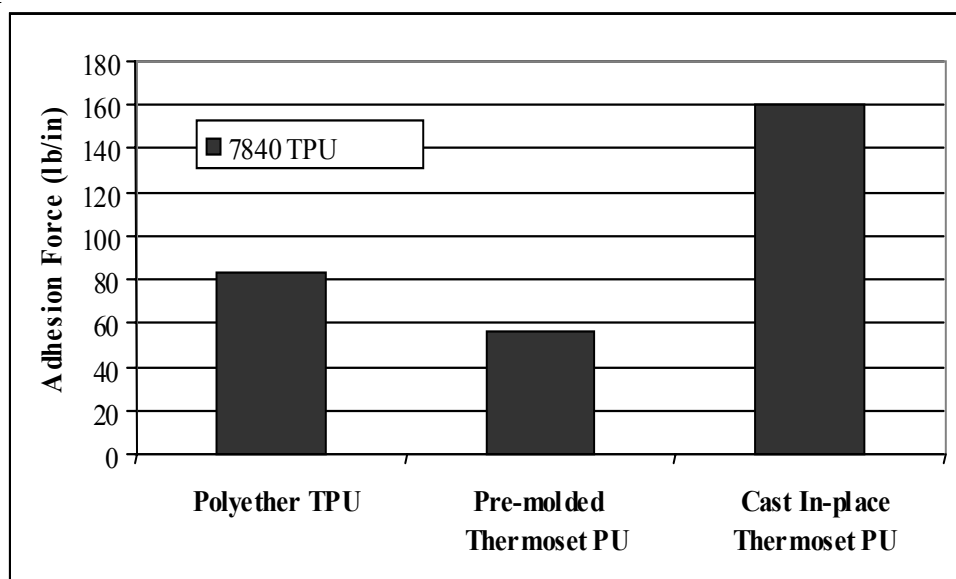


Figure 3. Peel adhesion results for 7840 TPU and polyurethane substrates.

Only the diene-based TPU effectively adhered the two dissimilar layers, producing cohesive failure at each interface. The structure of 7840 TPU includes both regions of unsaturated hydrocarbon capable of co-curing to rubber compounds and hard segments that promote interaction with similar structures in the urethane layer. Additionally, the diene-based TPU may improve adhesion between compounds based on elastomers with very different polarity, or as an adhesion aid to polar fabrics. The diene-based TPU may provide utility as an intermediate tie-layer in multi-component articles including hose, belt, and tires.

### Rubber Compounding

The various thermoplastic materials were directly compounded as additives in a rubber formulation in order to determine how and to what extent the physical properties are affected. 7840 TPU, polyether TPU, SBS, and SEBS were mixed in the rubber formulation given (Table III). The polyester TPU did not readily mix into the formulation and resulted in a compound with visible inhomogeneity which was not tested.

Results presented are normalized to the control. The normalized values coincide with the directionality of

the actual results. The effect of thermoplastic additives on cure kinetics and state of cure were evaluated (Tech Pro MDpt, ASTM D 5289, 160°C). Delta torque decreases with loading of the additives, regardless of type (Figure 4). It is important to realize that the torque value associated with the cure state may be attributable to reasons other than crosslink density derived through the generation of sulfur linkages. At higher loadings a larger percentage of the apparent crosslinks are of the reversible type inherent to the thermoplastic additive. Cure was measured above the softening point of the TPU materials, and close to that of the triblock TPES. In addition, 7840 TPU has a lower molecular weight (~ 30,000 g/mol, relative to polystyrene standard). It is common to lose some cure density as a result of incorporating low molecular weight polydienes. An increase in the cure package loading is typically recommended.

Trends in tensile properties of compounds containing increasing loadings of 7840 TPU are summarized in Figure 7 (Thwing-Albert Materials Tester, ASTM D 412 and D 624-C). Testing was conducted under ambient conditions. Tensile strength, 300% modulus and tear strength increased, elongation decreased, and 100% modulus remained constant with TPU loading.

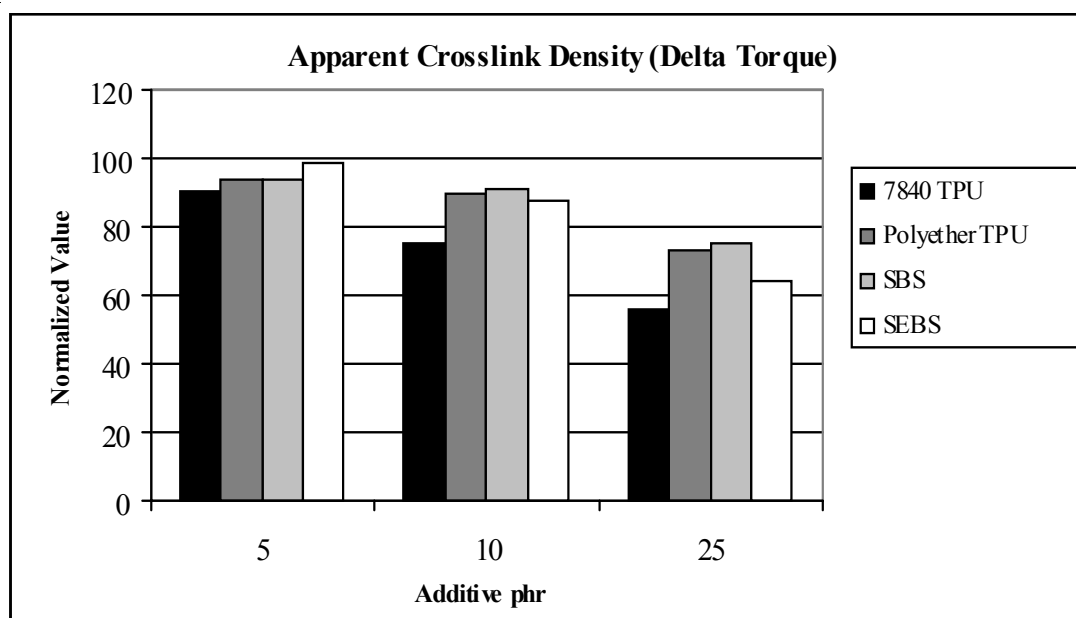


Figure 4. Delta torque as a function of additive loading (control = 100).

The cured compounds containing the thermoplastic additives were submitted to a dynamic (tension) temperature sweep (TA Instruments DMA 2980, -100°C to 100°C at 11 Hz and 0.1% strain amplitude). Tangent delta was plotted as a function of temperature to determine how the response of the base compound (control) is affected with additive loading (5, 10, and 25 phr). Such a method is useful in ascertaining if gross phase morphology exists in these composites. The results for 7840 TPU and SBS are provided in Figures 6 and 7.

According to the results in Figure 6, it appears that at 5 and 10 phr of 7840 TPU, the TPU is soluble in the compound but forms a discrete phase at 25 phr loading. A single peak (-30°C) was seen at 5 and 10 phr, decreasing slightly in height with increased loading. However, at 25 phr an additional peak appeared at approximately -10°C. The difference in peak temperatures (D 20°C) correlates with that for the Tgs of the individual polymers (-55°C for 1502 ESBR and -35°C for 7840 TPU). Only a single peak was

seen for the SBS material up to 25 phr loading (Figure 6). The SBS appeared to be largely soluble in the system, however the Tg of the polystyrene blocks register at > 100°C.

The utility of phase separated morphology with a polyurethane-containing discrete phase was explored. DeMattia flex fatigue testing (ASTM D 813) was performed on the above compounds both below (10 phr thermoplastic additive) and above (25 phr thermoplastic additive) the apparent compatibility limit of 7840 TPU in ESBR. Figures 8 and 9 provide the data, respectively. The compounds were cured to the same 100% strain modulus values (2.0 MPa at 10 phr additive, 2.4 MPa at 25 phr additive). At 10 phr loadings, each thermoplastic additive provided a slight improvement in crack growth resistance. However, at 25 phr loading, only the TPU additives provided the larger reduction in fatigue resistance. It is evident that the flexural fatigue performance is enhanced by the addition of a phase separated thermoplastic component.

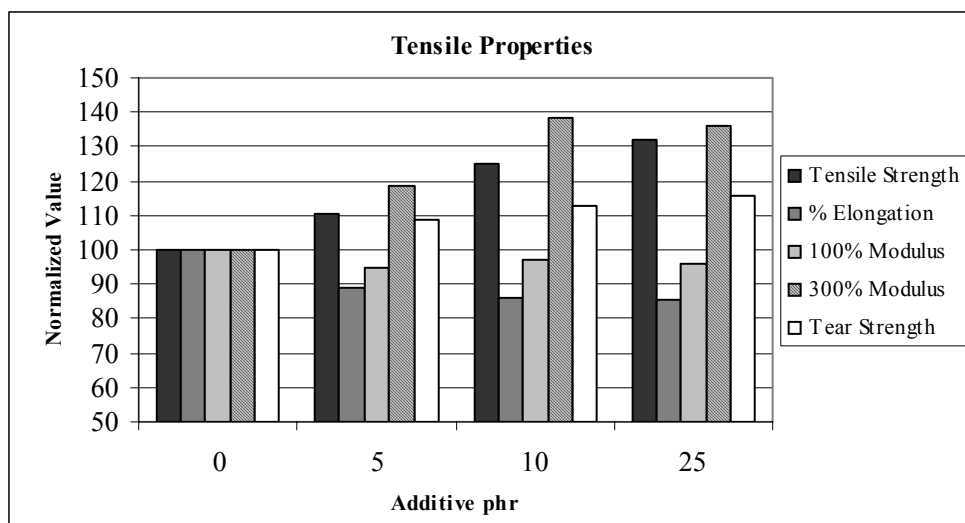


Figure 5. Tensile properties as a function of 7840 TPU loading.



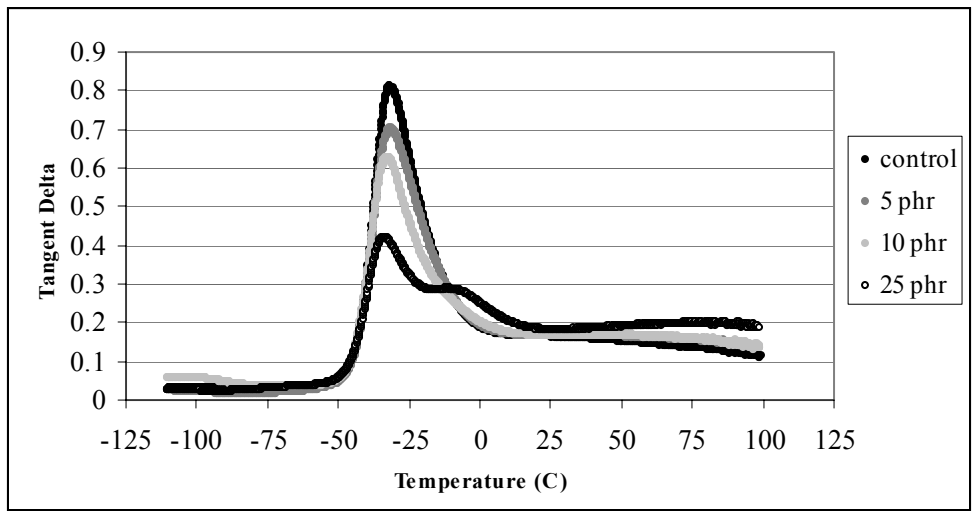


Figure 6. Temperature sweep for vulcanizates containing 0, 5, 10, and 25 phr 7840 TPU.

Figure 7. Temperature sweep for vulcanizates containing

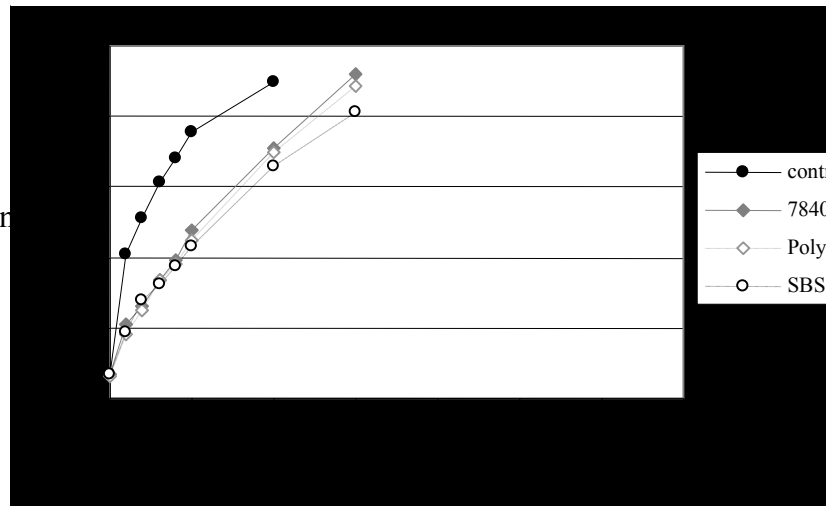


Figure 8. DeMattia flex fatigue results as a function of thermoplastic additive (10 phr).

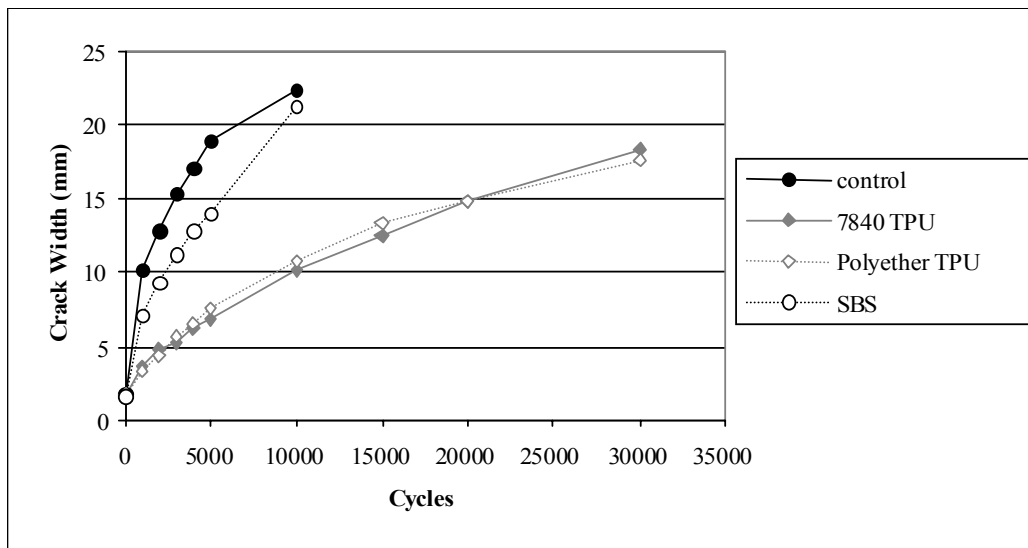


Figure 9. DeMattia flex fatigue results as a function of thermoplastic additive (25 phr).

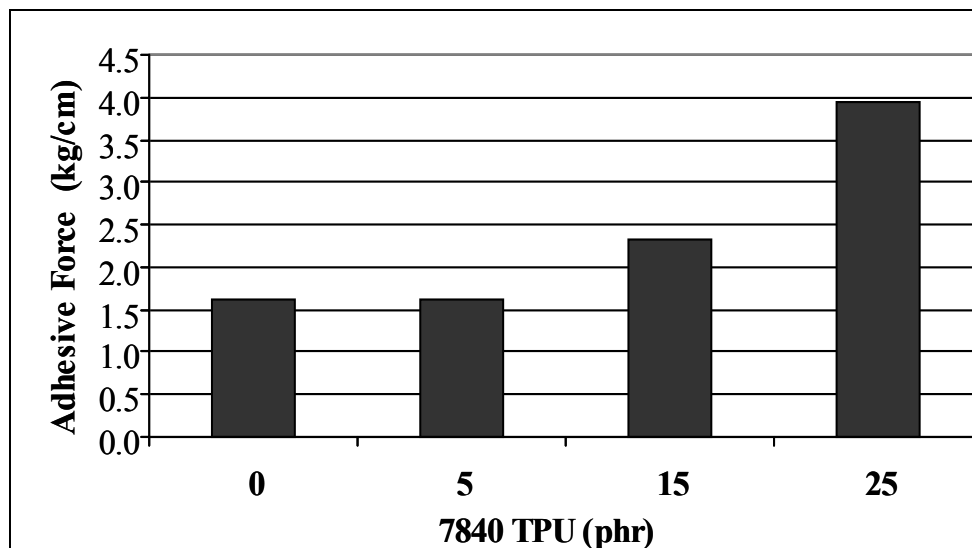


Figure 10. Peel adhesion force as a function of 7840 TPU loading in cis-IR compound.

The phase-separated TPU can also enhance adhesion to other polyurethanes. Using the same model formulation in Table II (*cis*-IR), 7840 TPU was added at 5, 15, and 25 phr. DMA analysis showed a second peak corresponding to the TPU evolves between 5 and 15 phr. Peel adhesion laminates were constructed again, but no thermoplastic layer was used. Laminated samples were cured in-situ. A polyether TPU substrate was used for adhesion testing purposes. The results are provided in Figure 10. The adhesive force is constant at loadings below phase separation, but increases as a function of loading when a discrete TPU phase is formed.

Considering the structure-property relationships of the thermoplastic additives, the diene-based TPU provides not only the ability to co-cure into the formulation (reducing hysteresis), but also has smaller hard segments unlike the very hysteretic styrene blocks associated with the triblock TPEs. Such a combination of structural properties is unique to 7840 TPU, and may provide new opportunities in formulating for molded tire applications.

## SUMMARY AND CONCLUSIONS

7840 TPU resin is compatible with rubber compounding, as the diene segments are capable of co-curing with compounds employing sulfur or peroxide vulcanization. Linear urethane linkages allow for not only thermoplastic quality but also the ability to bond with other urethane materials. The novel diene-TPU structure facilitates its use as an adhesive layer between rubber (uncured) and urethane compounds.

When used as an additive in rubber compounds, the performance of 7840 TPU can be differentiated from polyether TPUs or SBS TPEs. Unique processing and green strength properties as well as improved hysteresis may be explained in part by the evolution of phase morphology with increased TPU loading. Results are preliminary but suggest an interesting opportunity to add urethane characteristics to traditional rubber compounds, improving performance in a wide variety of applications from molded and extruded articles such as gaskets, shoe soles, cable sheathing and hose to multi-component products such as tires, belts, and other automotive parts.

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