

High-Performance Styrenic Thermoplastic Vulcanizates for Long-Term Application

Jushik Yun, Raman Patel, Darnell C. Worley II

Thermoplastic Elastomer Division, Teknor Apex Company, 505 Central Avenue, Pawtucket, Rhode Island 02861

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ABSTRACT: Styrenic thermoplastic vulcanizates (STPVs) were developed for long-term high-temperature applications. These STPVs consist of polypropylene as the continuous phase and a crosslinked modified hydrogenated styrenic block copolymer (mHSBC) as the dispersed phase. The present study compared STPVs with conventional TPVs (CTPVs) containing EPDM/PP. The STPVs showed a 20% improvement in solvent resistance after 500 h of immersion in IRM 903 oil at 125°C, and the swelling of oil did not increase with time. The elastic recovery was 50% better than with CTPVs. Tensile property retention was approximately 10% higher after aging for 1440 h at 125°C when compared to CTPVs.

These observed property improvements for STPVs relative to conventional TPVs can possibly be explained by the unique morphology of the resulting STPV compounds. These performance characteristics make STPVs more suitable for high-temperature air and chemical environmental applications. This new TPV technology is expected to bridge the gap between polypropylene/EPDM TPVs and more costly engineering TPVs. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2996–3005, 2007

Key words: morphology; elastomers; high temperature materials

INTRODUCTION

Thermoplastic vulcanizates (TPVs) are a subcategory of the broader thermoplastic elastomer (TPE) family. The introduction of dynamic vulcanization¹ significantly improved the properties of thermoplastic elastomers by crosslinking and dispersing the rubber phase as fine particles.^{2–4} The basic concept of a thermoplastic vulcanizate is to crosslink the rubber phase during melt mixing with appropriate thermoplastics. For example, melt-blending a thermoplastic like polypropylene (PP) and a crosslinkable rubber (EPDM) and then vulcanizing the rubber during processing. The resulting compound has a domain matrix morphology consisting of a continuous thermoplastic phase (PP) and a discrete thermoset rubber phase (crosslinked EPDM). The thermoplastic provides the processability, while the thermoset imparts elasticity characteristics.⁵

Thermoplastic vulcanizates have better tensile strength, a lower compression set, and high resistance to swell in oil compared with unvulcanized TPEs. Because of these characteristics, TPVs can compete with thermoset materials. TPVs can provide compositions that are very elastomeric in their performance (i.e., have reduced permanent set, increased oil resist-

ance, and low die swell for improved extrusion). Moreover, these TPVs can be rapidly fabricated into finished parts and also readily recycled.

Recently, TPVs based on the nonconventional polymer pairs EPDM and polypropylene have entered the marketplace. Zeon Chemicals developed a new type of TPV based on dynamic vulcanized polyacrylate rubber (ACM) and nylon.⁶ This TPV has good hot oil resistance and good high-temperature performance compared to the current generation of PP/EPDM TPVs and copolyester (COPE).

DuPont introduced its engineering TPV (ETPV), based on COPE.⁷ The ETPV has COPE as the thermoplastic phase, and a crosslinked ethylene acrylic elastomer is believed to be the dispersed rubber phase.⁸ It is claimed that ETPV has higher heat resistance and better oil and chemical resistance. For instance, 60 Shore A ETPV can withstand prolonged exposure to a 170°C environment while maintaining tensile strength at greater than 80% for up to 2000 h, and greater than 50% of elongation is retained with the use of an appropriate heat stabilizer.

Dow Corning has produced a silicone-based TPV called TPSiVTM,⁹ which is a polyamide and crosslinked silicone rubber alloy. It is said to retain a minimum of 50% of its mechanical properties after heat aging for 1008 hours at 150°C in air.

Tasaka et al.¹⁰ reported that TPVs of PP/polystyrene-*block*-poly(ethylene-*co*-propylene)-*block*-polystyrene (SEEPS or SEPS) had good oil resistance and a good compression set by generating intermolecular

Correspondence to: J. Yun (jyun@teknorapex.com).

TABLE I
TPV Types Used in This Experiment

Polymer	Type of TPV
STPV-65	Thermoplastic vulcanizate of HSBC, PP, and processing oil/peroxide cure; 65, 74, and 80 Shore A hardness.
STPV-74	
STPV-80	
CTPV1-64	
CTPV1-73	Thermoplastic vulcanizates of EPDM, PP, and processing oil/peroxide cure; 65, 73, and 80 Shore A hardness.
CTPV1-80	
CTPV2-64	Thermoplastic vulcanizates of EPDM, PP, and processing oil/phenolic resin cure; 64 Shore A hardness.
CTPV3-70	Thermoplastic vulcanizates of EPDM, PP and processing oil/hydrosilylation cure; 70 Shore A hardness.

crosslinking of poly(ethylene-*co*-propylene) (PEP) in the styrenic block copolymer.

Teknor Apex Company developed a new type of TPV based on a modified hydrogenated styrene block copolymer and polypropylene. This new TPV has excellent elastic recovery (lower compression set) and high solvent resistance at elevated temperatures. The elastic recovery properties show only small changes over 1400 h.

EXPERIMENTAL

Material

The styrenic TPV used in the present study is based on modified hydrogenated styrene block copolymer (HSBC) and polypropylene. Detailed structural information was not disclosed by the supplier. This HSBC is believed to have reactive groups in the main chain. Commercially available TPV (PP/EPDM) compounds

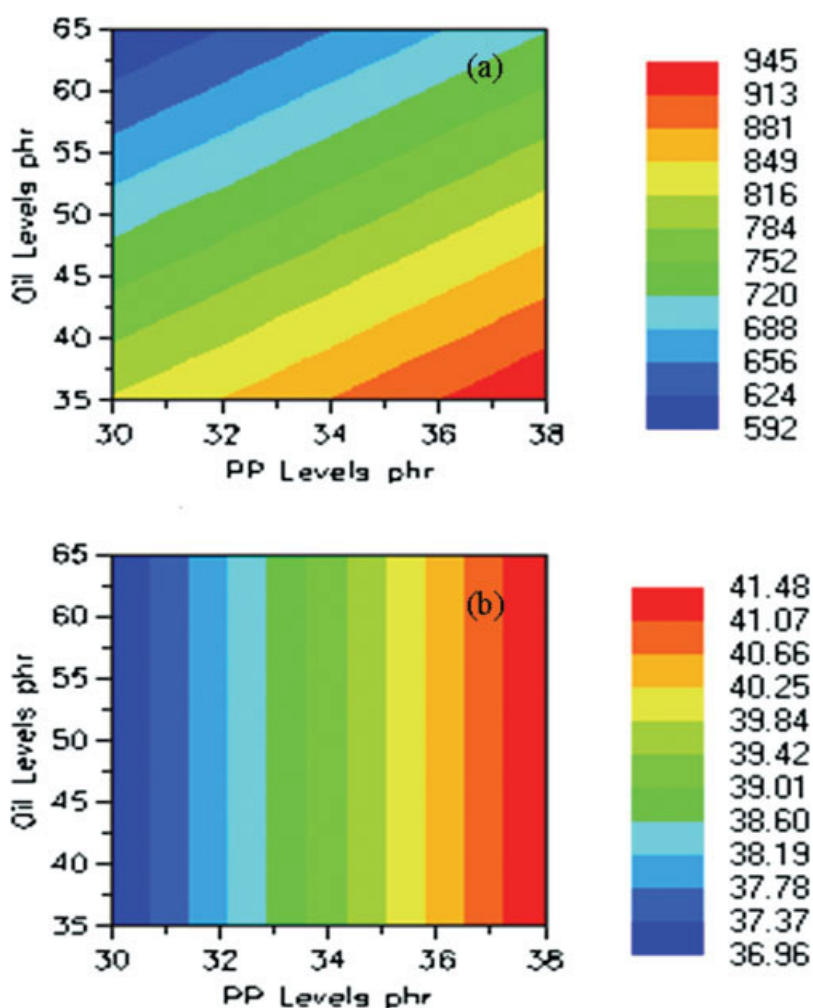


Figure 1 Contour graph showing the effects of oil and PP on TPV performance: (a) tensile strength at break (psi); (b) compression set %, 22 h, 125°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

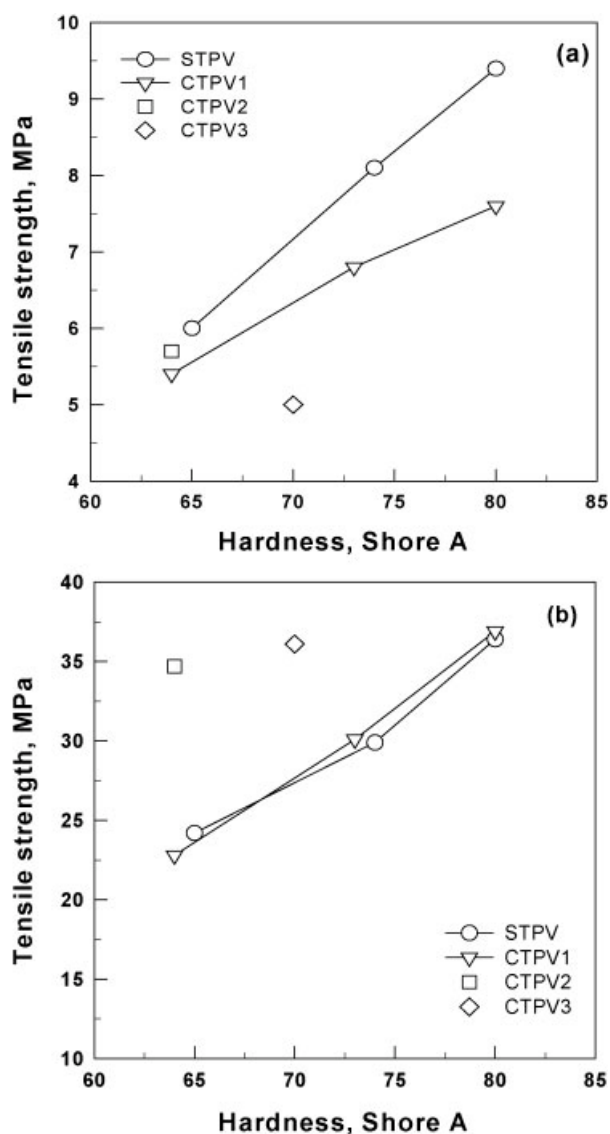


Figure 2 (a) Tensile strength and (b) tear strength as a function of hardness for various TPVs.

were acquired and used for the comparative study. The different TPV grades used in this work are shown in Table I, where STPV and CTPV are styrenic TPV and conventional EPDM/PP TPV, respectively. A proprietary curing process was used for this TPV system.

Standard factorial design

The design of experiments (DOE) for the compositional formulations was carried out using FastR&D[®] software from Quality Sciences Inc. The effect of each experimental formulation on STPV performance was investigated, and the resulting DOE made it possible to optimize this performance.

Sample preparation

The styrenic TPVs were prepared using a Berstorff twin-screw extruder (Berstorff L/D = 44, D = 40 mm).

The temperature profile went from 150°C to 200°C with a screw speed of 150–250 rpm. The styrenic TPV was produced by dynamically vulcanizing the rubber phase in rubber/plastic blends. The typical TPV formulations contained HSBC, polypropylene, processing oil, curatives, and additives.

Mechanical properties

After dynamic vulcanization, the test specimens were injection-molded. The injection-molding machine used was manufactured by Arburg Inc. (Lossburg, Germany) and had a clamping force of 250 tons. The temperature for injection molding was 200°C for all three zones.

Hardness was determined according to ASTM D 2240 and is expressed in Shore A units. Specific gravity of samples was measured according to ASTM D 792.

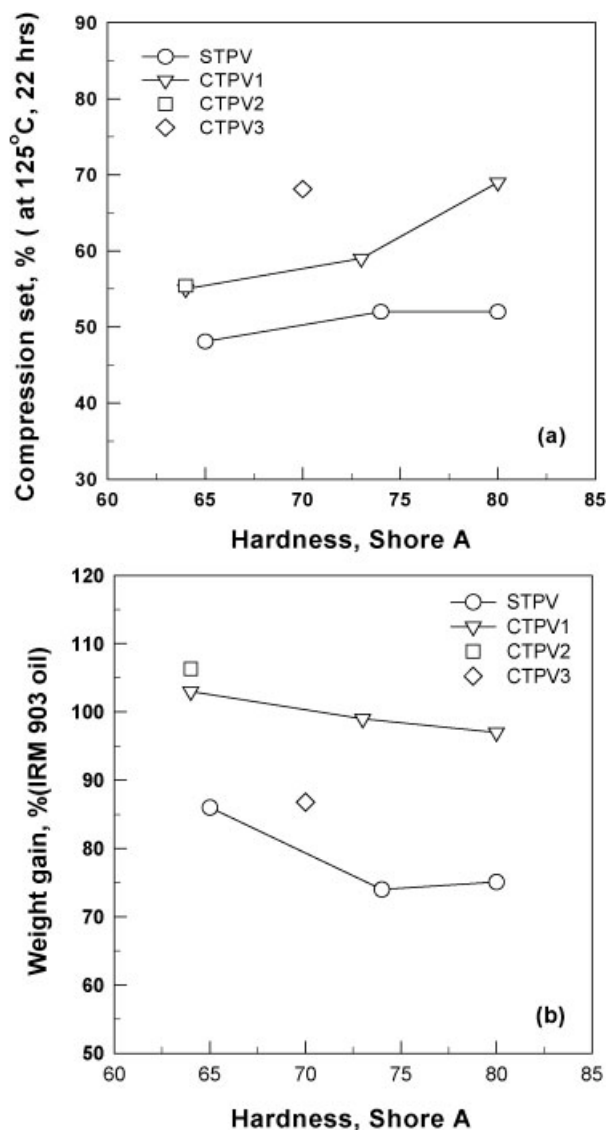


Figure 3 (a) Compression set and (b) weight gain in IRM #3 oil as a function of hardness for various TPVs.

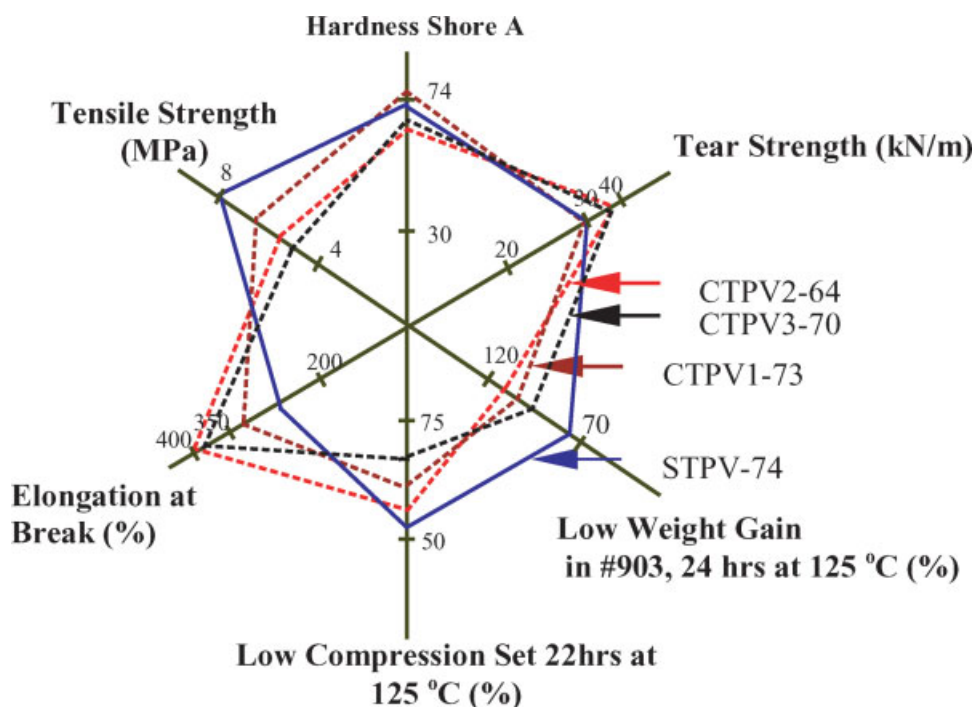


Figure 4 Comparison of performance of various TPVs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Tensile stress–strain properties were measured at 23°C according to ASTM D412 using injection molded dumbbell-shaped specimens. The testing was performed on an Instron Tensile Machine (Model 4077) (Norwood, MA) with a crosshead speed of 500 mm/min. Tear properties (die C) were also determined according to ASTM D624.

Rheology and dynamic mechanical properties

Dynamic mechanical properties were measured using an Advanced Rheometer AR 1000 (New Castle, DE). The tests were performed over temperature sweeps from -100°C to 200°C at 1 Hz with a ramp rate of $5^{\circ}\text{C}/\text{min}$ and a frequency sweep at 200°C under a constant strain of 0.25%. The dimensions of the sample, a torsion rectangle, were $63.5 \times 12.7 \times 3.18$ mm (L \times W \times T).

Long-term compression set and oil resistance

The compression set was determined at 25% deformation at 125°C according to ASTM D 395. Oil resistance measurements were made using IRM 903 oil at 125°C according to ASTM D 471, which was based on weight change.

Morphology

The samples were microtomed with an RMC Powerome XL with an RXL cryo attachment at a temperature

of -60°C . The resulting microtomed sections were approximately 1000 \AA thick. The sections were exposed to ruthenium tetroxide (RuO_4) for 15 min. Although osmium tetroxide (OsO_4) has traditionally been used to enhance the TEM contrast in diene copolymers,¹⁰

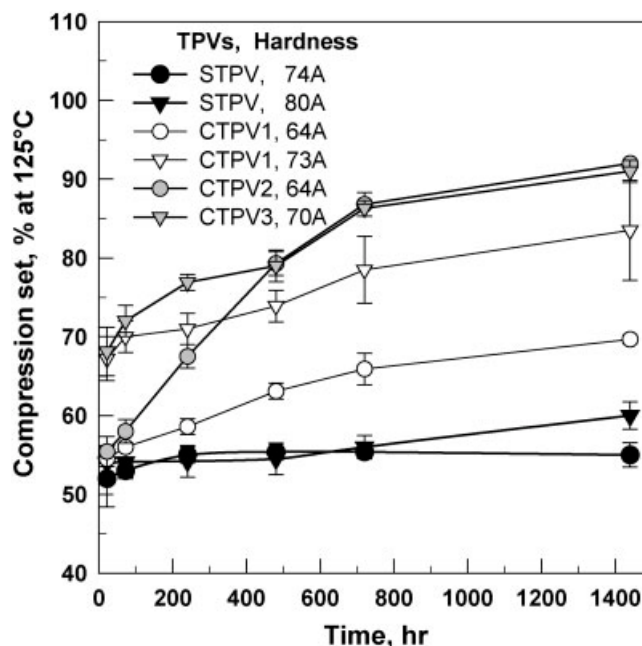


Figure 5 Long-term compression set at 125°C of various TPVs.

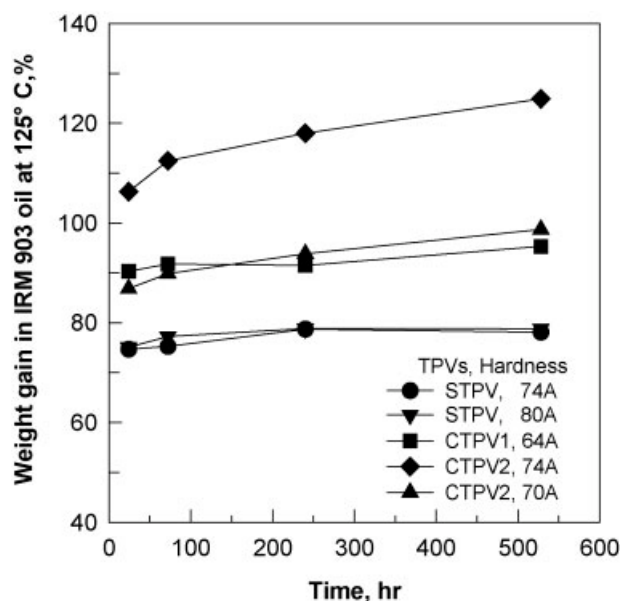


Figure 6 Long-term solvent resistance at 125°C of various TPVs.

RuO_4 was used because it has proven to be an effective staining agent for polymers without olefinic unsaturation.^{11,12} Otherwise, OsO_4 would be used because of its long history with diene copolymers. The samples were analyzed with a Philips EM 400 TEM interfaced with a Gatan Model 673 TV camera.

RESULTS AND DISCUSSION

Standard factorial design

Figure 1 shows the effect of polypropylene and oil on tensile strength [Fig. 1(a)] and the compression set [Fig. 1(b)]. As the level of polypropylene increased and the level of oil decreased, tensile strength increased.

Oil level had no effect on the compression set, but the compression set increased proportionally as polypropylene level increased. The contour graph shown in Figure 1 is an example of the kind of information a standard factorial design can generate. Based on this standard factorial design, it is possible to optimize the TPV formulation to obtain target properties as long as they can be generated in the compositional space evaluated. The styrenic TPVs (STPV-65, STPV-74, and STPV-80) were created from the results of this standard factorial design DOE.

Comparison with and conventional TPV

Changes in tensile strength and tear strength with hardness for several TPVs are shown in Figure 2(a,b), respectively. In general, as hardness increased, tensile strength [Fig. 2(a)] and tear strength [Fig. 2(b)] increased. Specifically, Figure 2(a) indicates that the STPV shows a tensile strength 10%–20% higher than that of conventional TPVs. The tear strength of the STPV shown in Figure 2(b) was similar to that of a per-

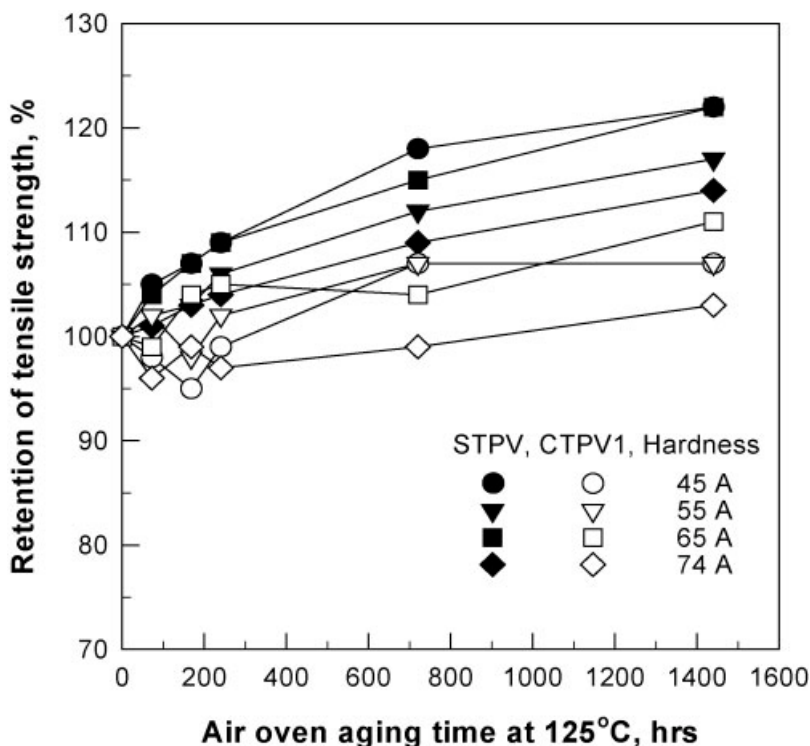


Figure 7 Retention of tensile properties as a function of time for various TPVs with differing hardnesses (solid symbol, STPV; open symbol, CTPV1).

oxide-cured conventional TPV (CTPV1). The tear strength of the phenolic-cured³ CTPV2 and the hydrosilylation-cured^{14,15} CTPV3 systems was higher than that of the STPV system. This suggests that the method of cure can affect tear strength. It should be noted that the one-to-one comparison of formulation components is not complete.

The compression set and weight gain versus hardness at 125°C are shown in Figure 3(a,b), respectively. The compression set of the STPV relative to various CTPVs was approximately 20% lower even at 125°C. Figure 3(b) shows that the STPV had a much smaller weight gain of approximately 20% in IRM 903 oil than did the conventional TPVs at 125°C.

A comparison of the performance of various TPVs in the same hardness range is shown in Figure 4. It can be observed that the properties of STPV-74 were well balanced compared to those of CTPV1-73, even though STPV had a slightly lower elongation at break. In particular, the tensile strength, the compression set, and the solvent resistance of STPV-74 were better than those of other CTPVs.

Long-term properties

The long-term compression set as defined above is represented graphically in Figure 5. The long-term compression set of the STPV at 125°C was almost un-

changed from the initial measurement of 52%. However, all the conventional TPVs showed an increase in the compression set as a function of time at elevated temperature. In particular, the compression set of CTPV2, a phenolic resin-cured system, showed an increase of 50% over 1440 h. The compression set of CTPV1, a peroxide-cured system, and CTPV3, a hydrosilylation-cured system, increased by approximately 20% after 1440 h of aging at 125°C. It can be concluded that crosslinks in STPV are thermally more stable than those in CTPVs.

Long-term solvent resistance is represented in Figure 6, which shows the effect of IRM #3 oil on various TPVs. STPVs had the lowest weight gain and rate of uptake over time. In contrast, conventional TPVs showed a higher weight gain and rate of uptake over the same 500-h period.

Furthermore, retention of tensile strength and elongation after heat aging for 1440 hours are shown in Figures 7 and 8 (solid and open symbols represent STPV and CTPV1, respectively). It was observed that retention of tensile strength of STPVs and CTPVs, shown in Figure 7, increased as aging time increased. More specifically, after 1440 h the retention of tensile strength of STPV was approximately 10% higher than that of CTPV1. Retention of elongation at break of the STPVs after 1440 h, shown in Figure 8, was about 10% higher than that of the CTPVs. Better

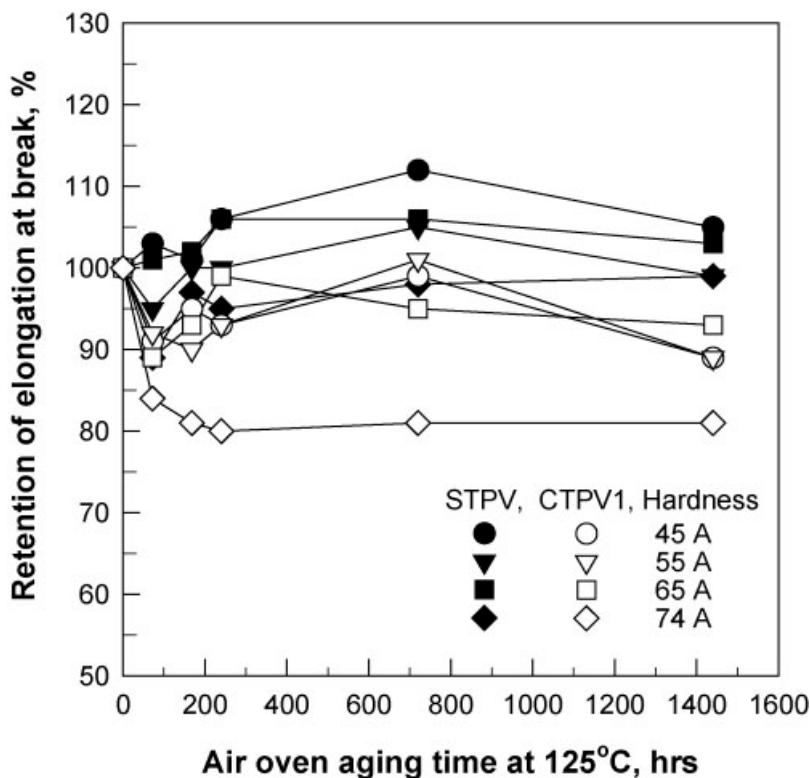


Figure 8 Retention of elongation properties as a function of time for various TPVs with differing hardnesses (solid symbol, STPV; open symbol, CTPV1).

retention performance is possibly related to the unique morphology of the STPVs, which is discussed later.

Heat stability

The heat stability of the injection-molded plaques is shown in Figure 9. An STPV before and after aging is shown in Figure 9(a,b), respectively, and CTPV1 before and after heat aging is shown in Figure 9(c,d), respectively. Visual observation after 30 min at 200°C showed the STPV had better shape retention [Fig. 9(b)] than did CTPV 1 [Fig. 9(d)].

The results show that this STPV has superior long-term elastic recovery and solvent resistance, better aging properties, and better heat stability relative to conventional TPVs. The improvement of the specified properties was driven by the difference between crosslinked EPDM and crosslinked mHSBC along with the resulting morphology. The mHSBC was designed to allow both the soft and hard segments to participate in crosslinking. This network resulted in less molecular

mobility between crosslink points. Therefore, improvement in the properties resulted from the tighter and more stable crosslink network of the mHSBC compared to that of the EPDM.

Rheology and dynamic mechanical properties of various TPVs

Storage modulus and loss tangent versus temperature are shown in Figure 10, which indicates the mHSBC had two glass-transition temperatures (T_g). The lower T_g was -44.6°C , corresponding to the soft block, and the higher T_g was 139°C , corresponding to the hard segment. Both peaks of the mHSBC were well defined. The resulting glass-transition temperatures for the new STPV were -52°C for the soft segment and 118°C for the hard segment. A shift in T_g was expected because of the mixing of formulation components.

In Figures 11 and 12 the complex viscosity, loss tangent, and storage modulus of the various TPVs are compared. STPV 74A and CTPV2 64A had similar complex viscosity values at high frequency (Fig. 11).

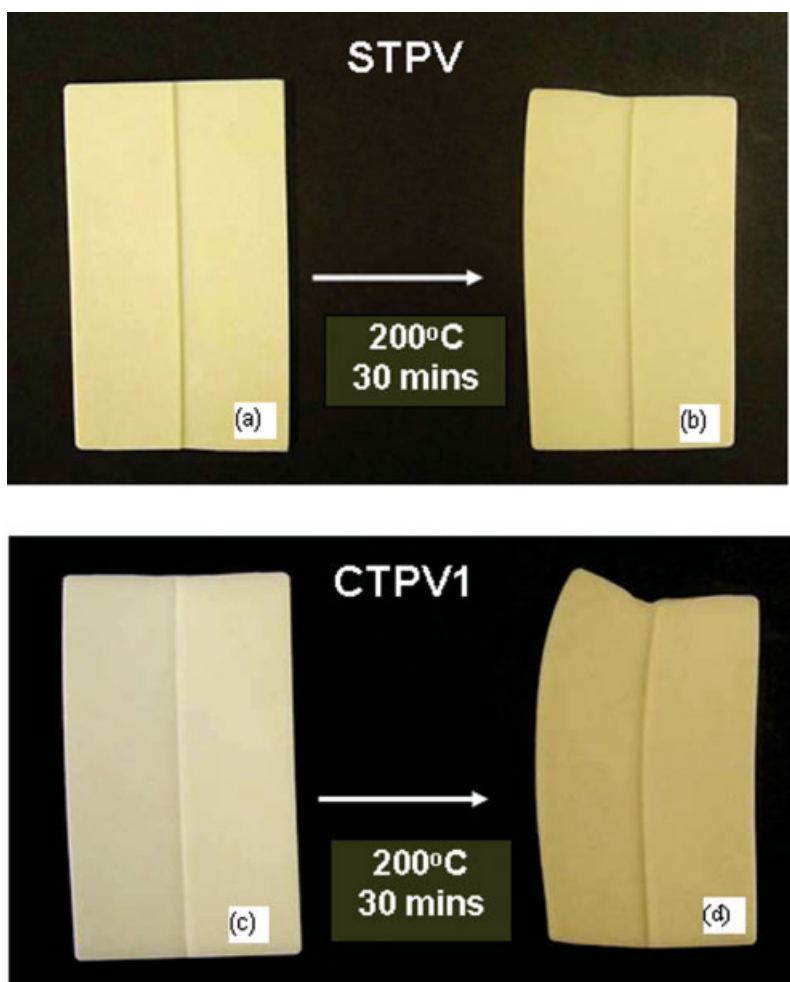


Figure 9 Heat stability of STPV and CTPV1 after oven aging at 200°C for 30 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

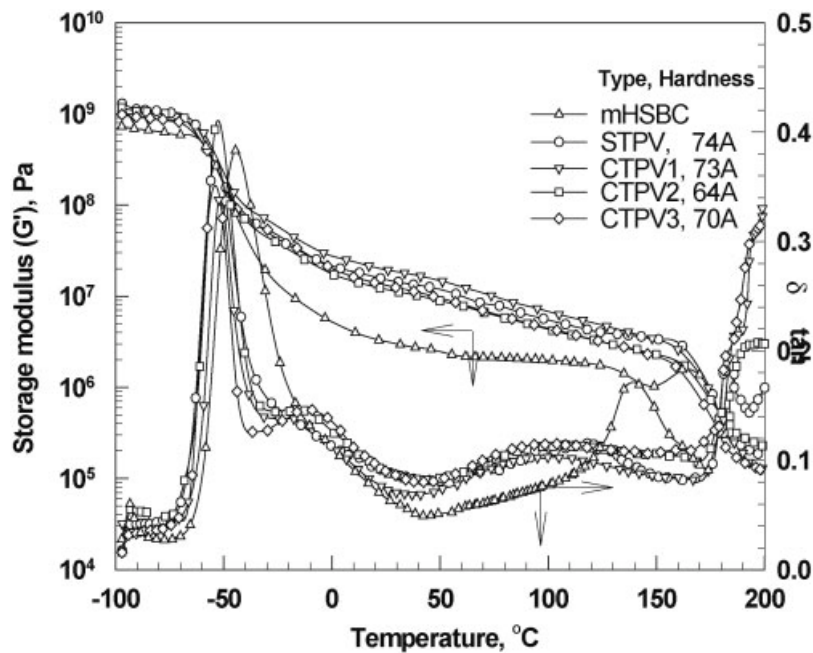


Figure 10 Dynamic properties as a function of temperature for various TPVs ($\omega = 6.28$ rad/s; strain = 0.25%).

STPV 74A showed the lowest loss tangent values compared with those of conventional TPVs. A comparison of storage modulus values is shown in Figure 12, indicating STPV 74A had the highest storage modulus over the frequency range of 10^{-1} to 10 rad/s. These results show that the STPV 74A has greater elasticity than conventional TPVs at 200°C. The observed differences are believed to be associated with the crosslink density generated by the hard and soft segments of the

mHSBC. This seems to also have affected the morphology of the resulting compound.

Morphology

The TEM micrographs of the various TPVs are shown in Figures 13 and 14. The morphology of the observed STPVs on a micron scale is shown in Figure 13(a). The STPV showed dark and irregularly shaped domains of

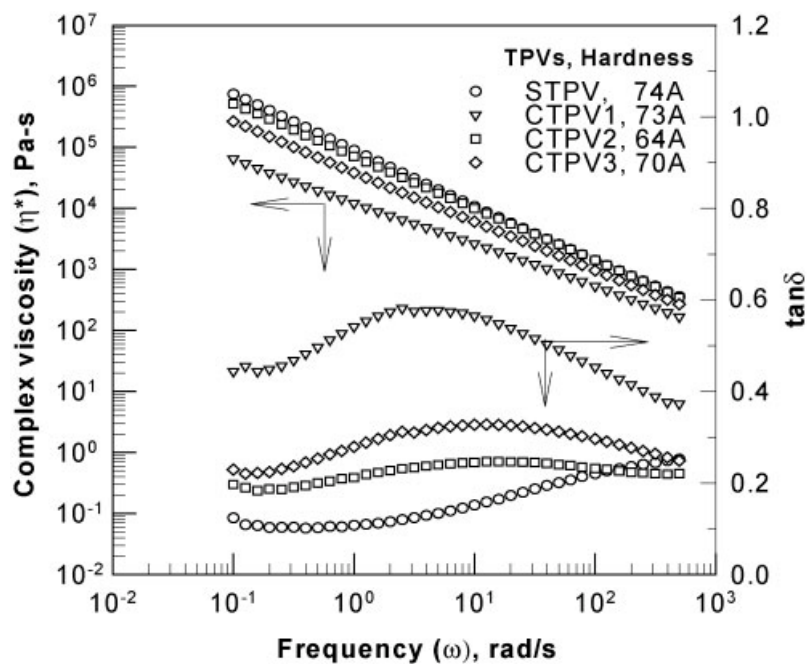


Figure 11 Complex viscosity and loss tangent versus frequency of various TPVs at 200°C and 0.25% strain.

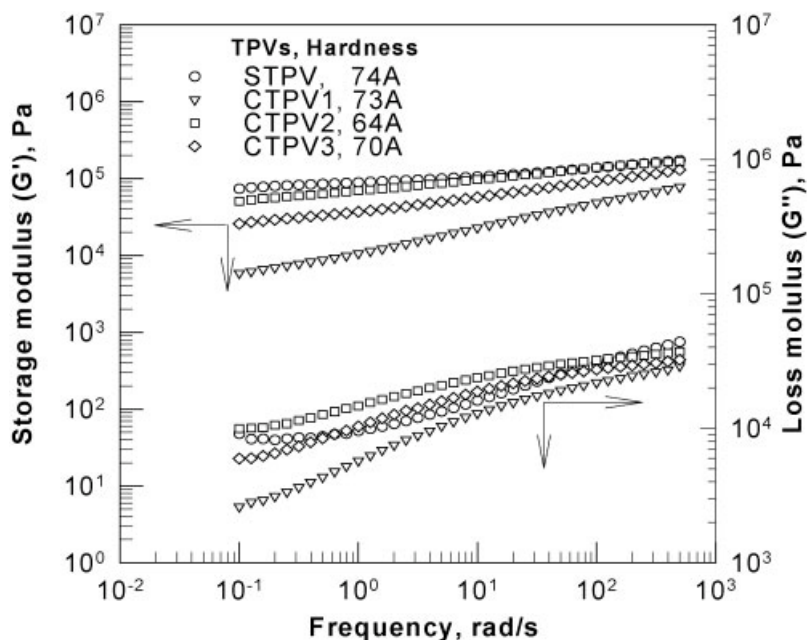


Figure 12 Storage modulus and loss modulus versus frequency of various TPVs at 200°C and 0.25% strain.

the dispersed crosslinked phase. These domains were approximately 0.5–2.0 μm in diameter. An analysis of these images indicated the STPV [Fig. 13(a)] had a denser and more interconnected domain morphology relative to the conventional TPVs.

The morphology of various TPVs on a nanometer scale is shown in Figure 14. At higher magnification a

substructure was observed within the rubber phase of the STPV [Fig. 12(a)]. There was no evidence of a substructure in the CTPVs [Fig. 12(b–d)]. The observed substructure was evenly distributed within domains approximately 30 nm in size. It is believed that these nanodomains are clusters of polystyrene hard segments, whereas the soft segments occupy the space

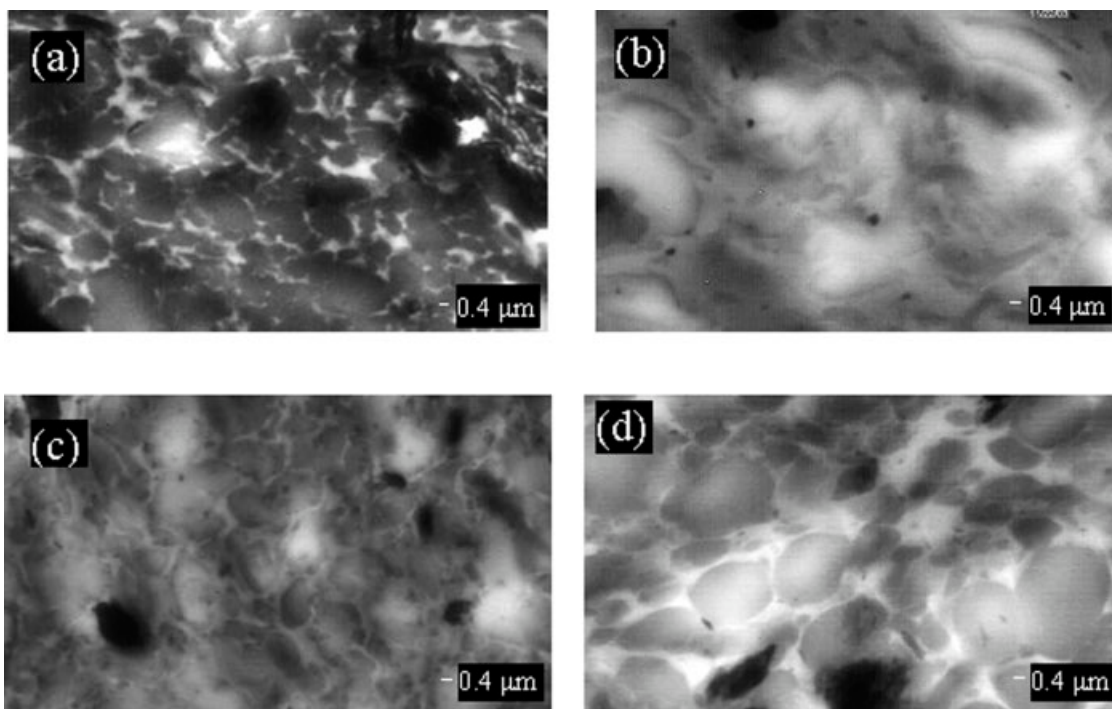


Figure 13 TEM morphology of various TPVs (shown on a micron scale): (a) STPV, (b) CTPV1, (c) CTPV2, and (d) CTPV3.

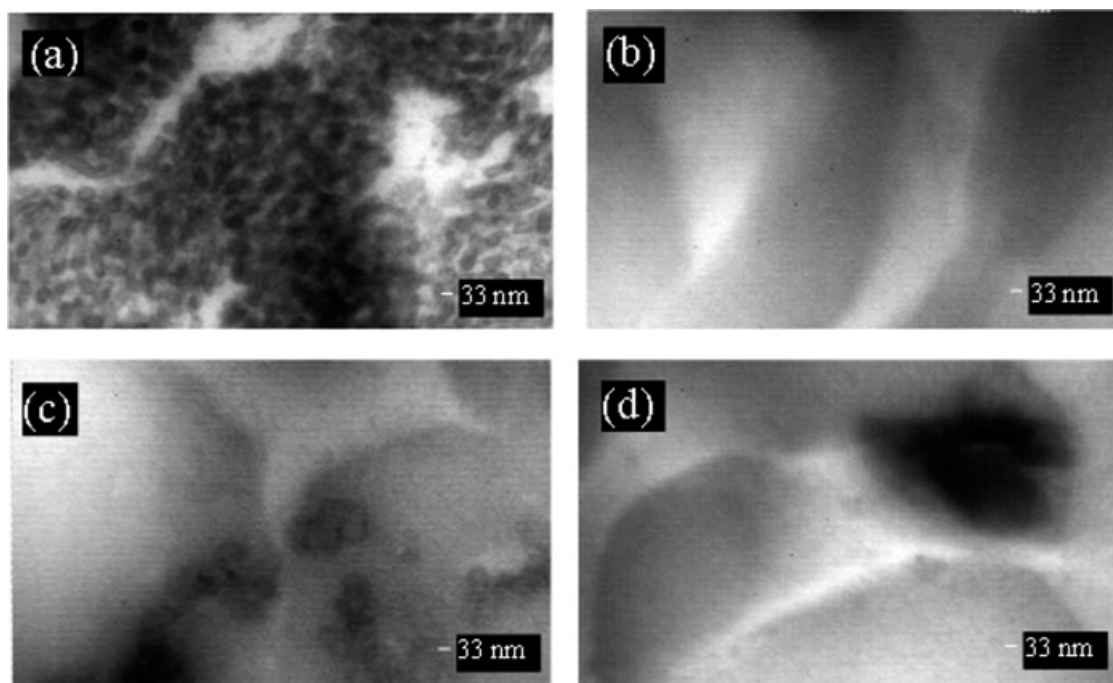


Figure 14 TEM morphology of various TPVs (shown on a nanoscale): (a) STPV, (b) CTPV1, (c) CTPV2, and (d) CTPV3.

between the dark clusters. Polystyrene block copolymers have hard block domains that are multifunction junction points that act as crosslinks.¹⁶

This dual-network morphology consisting of micron-sized rubber domains with a nanometer-sized substructure is the only difference in morphology between the STPVs and CTPVs. is part of the explanation for the excellent long-term elastic recovery, good solvent resistance, and better aging properties and heat stability of the STPVs. The nanodomain is the unique feature of STPV morphology; it is absent in a conventional TPV. The enhanced thermal and chemical properties of the STPVs makes them viable candidates use in many automotive and industrial applications.

CONCLUSIONS

As shown in the present study, development of an intermediate performance styrenic TPV (STPV) is possible. The STPV described here has an excellent, stable long-term compression set, improved hot oil resistance, and improved aging properties at 125°C compared to those of conventional PP/EPDM TPVs. The dual network generated by a modified HSBC (mHSBC) and thermally stable crosslinks explain these excellent long-term properties of STPV. This new technology is expected to bridge the gap between conventional TPVs and more costly engineering TPVs.

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