



## Comparison of co-agents in peroxide-cured of thermoplastic vulcanized (TPV)

F. Nokandi<sup>1</sup>, M. Dana<sup>1,2</sup>, S. Asadi Shahidi<sup>1</sup>, S. Yazdanbakhsh<sup>1</sup>, G. H. Zohuri<sup>3\*</sup>

<sup>1</sup> Department of Materials Engineering, Pouya Gostar Khorasan Co. of Part Lastic Group, Mashhad, Iran.

<sup>2</sup> Department of Polymer & Materials Chemistry, Faculty of Chemistry and Petroleum Science, Shahid Beheshti University, GC, 1983969411 Tehran, Iran.

<sup>3</sup> Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran.

\* Correspondence to: Gholamhossein Zohuri ([zohuri@um.ac.ir](mailto:zohuri@um.ac.ir))

### Abstract

Styrenic thermoplastic vulcanizates (STPV) were developed for long-term high-temperature applications. These STPVs consist of polypropylene as the continuous phase and a crosslinked hydrogenated styrene block copolymer (SEBS) as the dispersed phase. Effects of two co-curing agents, triallyl cyanurate (TAC) and bismaleimide (BMI) in a peroxide curing system for the preparation of STPV are studied. The compound is prepared in an industrial-scale twin-screw extruder. Mechanical study reveals an increase in tensile strength, hardness (15s) and elongation at break (from 5.92 to 6.89, from 45 to 56 and 897% to 1082% respectively) of the STPV when using BMI as a co-curing agent. Heat ageing study (85 °C for 168 h) and compression set (70 °C and 22 h, rest at 70 °C) on the STPV, however, slightly was raised with using TAC co-curing agent compared to BMI. The melt flow index (190 °C, 5 kg) is not changed with BMI co-agent.

**Keywords:** styrenic thermoplastic vulcanizates, co-agent, polypropylene, twin extruder, triallyl cyanurate, bismaleimide.

### Introduction

Thermoplastic vulcanizates (TPVs) are a subcategory of the broader thermoplastic elastomer (TPE) family. The introduction of dynamic vulcanization [1] significantly improved the properties of thermoplastic elastomers by crosslinking and dispersing the rubber phase as fine particles [2–5]. The basic concept of a thermoplastic vulcanizate is to crosslink the rubber phase during melt mixing with appropriate thermoplastics.

Tasaka et al.[6] reported that TPVs of PP/polystyrene-block-poly(ethylene-co-propylene)-block-polystyrene (SEEPS or SEPS) had good oil resistance and good compression set by generating intermolecular crosslinking of poly(ethylene-co-propylene) (PEP) in the styrenic block copolymer.

The present study compared TAC and BMI as co-curing agents in the STPV compound containing SEBS/PP.

### Experimental

Dynamic cross-linking process based on SEBS/PP was carried out in a co-rotating twin-screw extruder (Model CTE 65, COPERION Co. Germany) in one step.

The composition was moulded at 210 °C into sheets. The TPVs have the same proportion of SEBS/PP in two curing systems by mass, as shown in Table 1. The number indicates the amount in php (weight parts per 100

parts of polymer) added. The amount of each component is listed in Table 1.

### Results and discussion

The ultimate tensile strength, the stress at 100 and 200% of elongation and the elongation-at-break were determined, and the values are listed in Table 2. It can be observed that the blend STPV1 has poor mechanical properties compared to the BMI cross-linked compositions (STPV2).

**Table 1** designation of STPV1 and STPV2.

material	STPV1	STPV2
SEBS	35	35
PP	10	10
PE	1-10	1-10
peroxide	0.1-2	0.1-2
TAC	0.1-1	-
BMI	-	0.1-1
Irganox 1010	0.1-1	0.1-1
Irgafos 168	0.1-1	0.1-1
tackifier	1-15	1-15
oil	5-30	5-30
filler	1-20	1.20

Compositions STPV1 and STPV2 exhibited different performances, with a value of ultimate tensile strength close to 5.92 and 6.89 MPa and an elongation-at-break near 897 and 1082%, respectively. The STPV1 system



exhibited a low value for the ultimate tensile strength and elongation, which increased as the co-curing agent changed (STPV2). We can see that the ultimate tensile strength and the elongation-at-break depend on the curing system that is applied. As reported in the literature [7], the stress-strain properties of the TPVs are strongly dependent on morphology.

Given the advantages of processing and recycling, TPVs can replace thermoset rubber in many applications. However, they have limitations in regards to hardness and compression set. The hardness of a thermoplastic is higher than a thermoset rubber. Thus, the hardness of TPVs is determined mainly by the thermoplastic phase; only a small contribution is provided by the rubber domains and the crosslink density of the rubber phase [7,8]. The hardness values of the STPV1 and STPV2 were reached to 50 Shore A and 57 Shore A, respectively. The compression set, i.e., the amount of deformation (expressed as a percentage of the original dimensions) retained by a material at a given temperature after compressive stress is released, is a very important property for many applications. However, the fact that the plastic phase begins to suffer irreversible deformation at a specific temperature limits the application of TPV even at relatively low temperatures compared with the applicable temperatures of thermoset rubbers; so the dynamic vulcanization of the rubber phase is essential for the ultimate properties of the TPV. [9]. Given this limitation, knowing the compression set values of TPV is very important for defining the range of temperature for its application. The compression set values of the STPVs under investigation are shown in Table 2 and were almost 38%. So both of the curing systems have the same performance.

**Table 2** Properties of the prepared STPV1 and STPV2

test	STPV1	STPV2
Tensile strength (MPa)	5.92	6.89
Elongation at break %	897	1082
Tensile, 20% Elongation	2.7	3.16
Tensile strength with aging (% , 85 °C, 7day)	19.93	8.6
Elongation with aging (% , 85 °C, 7 days)	42.12	11.3
Hardness change (Shore A, 85 °C, 7 days)	45	56
MFI (190 °C/ 5 kg, g/10 min)	6.7	6.7
Hardness, shore A	50	57
Compression set (25%, 22 h, 70 °C, rest 70 °C)	37.8	38

### Conclusion

The two crosslink systems were applied to obtain STPVs based on SEBS/PP in a composition of 35/10 by mass, by dynamic vulcanization in the extruder. The mechanical performance of the TPVs depends on their morphologies, which, in turn, depend on the curing system used for the dynamic vulcanization. The mechanical performance of the STPV2 was better compared to STPV1, due to decreased degradation of the plastic phase. MFI and

compression set measurements indicated that the crystallization of the plastic phase is not significantly affected by dynamic vulcanization. These results show that the system developed here has great potential for a technological application given the fact that both polymers and curing systems are well known in the technology of thermoplastic elastomers as well as easily available. It is believed that the processability of this material in a twin screw extruder could improve its properties.

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### References

- [1] Gessler, A. M. and Haslett, W. H., U.S. Pat. 3,037,954 (1962).
- [2] Coran, A. Y., Das, B. and Patel, R., U.S. Pat. 4,104,210 (1978).
- [3] Coran, A. Y. and Patel, R., U.S. Pat. 4,271,049 (1981).
- [4] Coran, A. Y. and Patel, R., "Rubber-Thermoplastic Compositions. Part I. EPDM-Polypropylene Thermoplastic Vulcanizates", Rubber Chem. Technol., 53, 141–150 (1980).
- [5] Yun, J., Patel, R. and Worley II, D. C., "High-Performance Styrenic Thermoplastic Vulcanizates For Long-Term Application", J. Appl. Pol. Sci., 105, 2996-3005 (2007).
- [6] Tasaka, M.; Tamura, A.; Mori, R., "The Effect of Several Kinds of Oils on the Oil Resistance Behavior of Polystyrenic Thermoplastic Vulcanizate", SPE ANTEC papers (1998).
- [7] de Risi, F. R. and Noordermeer, J. W. M., "Effect of Methacrylate Co-Agents on Peroxide Cured PP/EPDM Thermoplastic Vulcanizates", Rubber Chem. Technol., 80, 83–99 (2007).
- [8] Cheremisin-off, N. P., In *Elastomer Technology Handbook*, Morganville, New Jersey, (1993).
- [9] Fagundes E. C. M. and Jacobi M. A. M., "Influence of a crosslinked system on the morphology and properties of TPVs based on PA/NBR", J. Appl. Pol. Sci, 23, 3072–3080 (2012).