# Processibility, Mechanical and Thermal Characteristics of MVQ / PP Elastomer / Plastic Composites

#### RADIVOJ POPOVIC1, RUZICA POPOVIC2, DRAGAN MILENKOVIC3\*

- <sup>1</sup> Faculty for Design, Belgrade
- <sup>2</sup> Technical Testing Center, Belgrade
- <sup>3</sup> High scool for technology Krušvac, Kosanciceva 36, 37000 Kruševac, SRBIJA.

Mixing and processing characteristics, mechanical and thermal characteristics of MVQ/PP composites were investigated. Both initial and total torque of these materials are increased with increase in the PP concentration of the blend composite. The area under the torque-time curve represents the mechanical energy cosumed during blending. The energy required for blending decreases with increase in MVQ concentration. A lower value for final torque (viscosity) implies better processibility with lower energy consumption during mixing and further processing such as extrusion, calandering and moulding. Also, with the increased PP in blends, some properties such as, hardness, tensile strength and impact strength are increased in blend materials compared to silicone rubber vulcanizate. The heterogenity of MVQ/PP composites was determined by thermomechanical analysis. MVQ and PP show separate T, which indicates that they are not compatible. These characteristic properties (high softening point, high impact strength, easy and low cost processability) indicate that these composites might replace some vulcanized rubbers and some rigid plastics in applications, especially in the automative industry.

Keywords: processing, mechanical properties, blend, composites

Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science [1]. About 75% of all elastomers are used as blends rather than alone [2]. The ultimate goal of blending two or more polymers is usually a practical one of achieving materials that are commercially viable by virtue of having certain properties which cannot be obtained by other means or show lower cost [3]. In this blends MVQ acts as a permanent plasticizer for PP. On the other hand, PP improves ozone ageing, chemical resistance of elastomers such as silicone rubber. In applications like wire and cable insulation, tubes, gaskets, etc., PP also vastly improves abrasion resistance, tear resistance and tensile properties in blend with some elastomers (NR, EPDM) [4,5].

A key attribute of silicone rubber is its ability to retain a large proportion of its initial properties after long periods of time over a wide range of temperature [6]. Tensile strength is generally lower than for organic elastomers. Compression set resistance is generally accepted as being better than that of any other elastomer [7]. The "useful life" for silicone at continous elevated temperatures [8] has been reported as 2 years at 150°C to 84 days at 260°C [9]. At low temperatures, general-purpose grades resist embrittlement down to -75 °C and retain flexibility at -50 °C. Silicone elastomers retain good electrical properties at temperature extrems under moisture and ageing conditions. They have excellent resistance to water, steam, weather and oxidation. Abrasion resistance of standard types is poor.

In principle MVQ/PP blends can be made from any of the PP homopolymer marketed under different brand names. For most purposes polymers with a MFI of about 4(ASTM D 1238) will give blends having good properties and processibility. MVQ/PP blends retain their shape up to about 100°C. A wide service temperature range is important in vehicle components such as car bumpers and semi rigid panels [3].

It is well known that organic peroxides cause oxidative degradation of polypropylene at elevated temperatures and for fully cross-linked materials alternative cross-linking systems such as bismaleimide or an accelerated sulpfur system have been used [3,10. It has been confirmed that in MVQ/PP a peroxide initiates degradation of the polypropylene.

In literature and industrial practice are well known blend materials based on PP such as: EP(D)M/PP blends, PP/EPDM/Ionomer ternary blends, NR/PP blends etc., [3,11-13].

When MVQ/PP blends are prepared by intensive mixing, the mixing temperature must be higher than the melting point of PP (165°C). These two polymers form incompatible blends, typical heterogeneus systems of two mutually incompatible components. Higher viscosity (medium-low MFR) polypropylene grades are preferred when plastic like blends are required which display excellent cold-impact properties, together with still acceptable stiffnes and creep resistance at elevated temperatures.

The object of this work is to investigate the mixing and processing characteristics, mechanical properties and thermal characteristics of MVQ/PP blends. A Haake Torque Rheometer has been used extensively for assesing the fusion characteristics and mechanical and thermal stability and processing characteristics of polymers and blends [14-16]. Such an investigation has been carried out on MVQ/PP blends using a Torque Rheometer. The results of this evaluation are checked with mechanical and thermal properties of the blends.

### **Experimental part**

Materials

Polymers. Dimethyl vinyl silicone rubber (MVQ), Mooney viscosity ML  $1+4(100\ C)=15$ , density  $=1.14\ (SE\ 456\ U$ -General Electric) and polypropylene (PP), MFI =5.6; density  $=0.9\ (Moplen\ C\ 30G$ - Montecatini Edison).

<sup>\*</sup> email: divm@ptt.yu or milenkovic\_dragan@yahoo.com

Curative. 2.5-bis-tert. butilperoxy-2,5 dimethylhexane (Varox- Vanderbilt Co.)

The compound formulations are shown in table 1.

**Table 1** FORMULATION OF THE MIXES

Mix	Silicone rubber	Polypropylene	Varox (peroxide)
A	100	0	4
В	70	30	-
С	50	50	-
D	30	70	-
Е	0	100	-

Studies on a Haake Torque Rheometer

The sample preparation of MVQ/PP polymer blends was caried out on a Torque Rheometer (HBI system 90, with mixing chamber-Rheomix 600), rotor speed 50 min<sup>-1</sup>. Mixing chamber is heated to temperature 170 °C and then are added MVQ and PP respectively; mixing needs 15 min. After MVQ are cooled to the room temperature, the curative agent is added to the silicone rubber and the compound was homogenised 1 min in the mixer. During the time when peroxide was added in MVQ/PP blend, the material crumbles becomes difficult to handle and loosed viscosity consistence. This can be explained by the fact that peroxides are causing polypropylene degradation at high temperature [3]. From this reason, in sample preparation, the adding curative in blend compound was only in case of preparing pure silicone compound, signed as A.

Evaluation of Mechanical and Thermal properties

For meassuring the mechanical properties, the blend containing 30, 50, 70 % PP, and pure materials MVQ and PP speciments were prepeared by compression moulding at 180 °C (table 1). Thensile properties were then determined using Zwick Universal Testing Machine according to ASTM D 412 [12]. The dumbbell-shaped specimens were obtained from vulcanized sheet. A Shore –A type durometer was used for determining the hardness of the blends as per ASTM 224D. A Charpy Impact strength was determined on Zwick aparatus according to JUS G.S2.616 at a pendelum speed of 650 mm/min. Vicat melting point was determined on KPM/V Heraeus aparatus, temperature ranges up to 350°C. Thermal analysis of the blends was performed in the Thermomechanical analysator Perkin-Elmer TMS-2 at a heating rate of 2,5°C/min and temperature ranges from –70°C to 0°C and from 24°C to 215°C.

#### **Results and discussion**

Studies on a Haake Torque Rheometer

For all the tests run on the Torque Rheometer, MVQ was added initialy attaineding the required temperature. After giving 15 seconds time for the rubber to heat up and homogenised in the mixer, PP was added. The polymers were blended for 15 min. The study was repeated for the other combinations of blends and pure MVQ and PP [1]. The change in Haake viscosity (mixing torque) against time for pure components and different blend compositions are presented in figures 1 and 2. Both initial and final (totalized) torque of the blends increase with increase in the PP concentration of the blend. The area under the torque-time curve represents the mechanical energy consumed during blending [17]. The energy required for blending decreases with increase in MVQ concentration. The final (totalized) torque is plotted against time in figure 2. A lower value for final torque (viscosity) implies better processibility with lower energy consumption during

mixing and further processing such as extrusion, calandering and moulding.

The mixing studies in the Torque Rheometer showed that the blends of polymers generated much higher torques than MVQ polymer and less than PP polymer. The Torque Rheometer curves for the blends of MVQ and PP indicate that the systems go through an initiation-compaction-fusion sequence and the torques observed at the fusion peaks are higher than that observed for MVQ polymer.

Figure 1 shows the Haake torque curves at 170 °C drops down rapidly after peaks (0,5 min to 2 min), than drops down slightly in range (2 min to 4 min), and then stabilizes to torque value at the end of mixing (15 min). This behaviour in PP and blends when the torque goes down in range (0,5 min to 4 min) is the consequence that the PP be not fully melted at this temperature, and this differences in torque might have occured predominantly due to two factors: an overall tendency for the viscosity to come down due to the rise in the temperature and the tendency of the PP phase to enhance the viscosity by melting more of that phase [1]. From (4 min to 15 min.) the difference in torque remains the same, indicating that these two factors continue to exert almost the same influence.

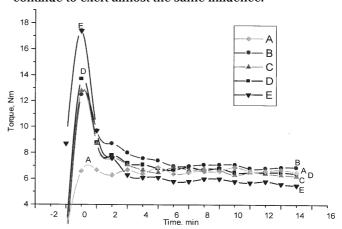


Fig. 1 Haake torque curves of MVQ, PP and MVQ/PP blends as a function of mixing time

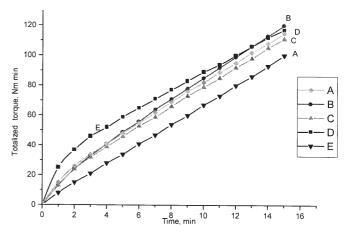


Fig. 2 Haake totalized torque curves of MVQ, PP and MVQ/PP blends as a function of mixing time

Mechanical properties

Mechanical characteristics are determined on pure polymer components and blends and the results are shown in table 2. The slabs were moulded in a hydraulic press using moulding condition at 180°C for 10 min. After moulding the slabs were cooled slowly in a cold mould settled in a press. This way it was it prevented the leakages

 Table 2

 MECHANICAL PROPERTIES OF POLYMER BLENDS

Mix	A	В	С	D	Е
Hardness, Shore A Hardness, Shore D	50 -	83 25	85 36	90 50	95 60
Tensile strength, MPa	5.9	1.3	5.6	12.6	28.8
Elongation at break, %	410	40	30	26	20
Charpy impact strength, kJ/m <sup>2</sup>	3.4	6.2	8.0	10.1	15.6
Vicat softening temperature, °C	*	84	121	154	171

<sup>\*</sup>Measured value can not be determined because on room temperature momentaly break up of material was happened

 Table 3

 COEFFICIENT OF LINEAR THERMAL EXPANSION OF MVQ/PP BLENDS

Mix	Coefficient of linear thermal expansion α, °C <sup>-1</sup> , for temperature intervals						
	$-70$ °C to $T_{\rm mMVQ}(-60$ °C)	$T_{\rm mMVQ}$ to $T_{\rm gPP}(-5^{\rm o}{\rm C})$	24 °C to T <sub>m PP</sub>	T <sub>m PP</sub> to 215 °C			
Α	2.867 10 <sup>-3</sup>	$3.33 \cdot 10^{-4}$	2.815 10 <sup>-4</sup> *	-			
В	$2.79 \cdot 10^{-3}$	2.33 10 <sup>-4</sup>	2.98 10 <sup>-4</sup>	1.60 10-3			
С	1.99 10 <sup>-3</sup>	1.97 10-4	1.68 10 <sup>-4</sup>	5.48 10 <sup>-4</sup>			
D	8.695 10 <sup>-4</sup>	9.56 10 <sup>-5</sup>	8.18 10 <sup>-5</sup>	4.4 10 <sup>-4</sup>			
E	1.16 10 <sup>-4</sup> **	-	0.239 10-4	9.76 10 <sup>-6</sup>			

<sup>\*</sup>For the temperature ranges 24 °C to 215 °C, there is no PP in compound

of melting mass, which is thermoplastic in high level, because of the influences of polypropylene presence.

On the basis of values from table 2, it is shown that with the increased thermoplastic polymer PP in blends, some properties such as hardness, tensile strength and impact strength are increased in blends compared to MVQ vulcanizate. Elongation at breaks decreases with increasing of PP in blends, this leading to the decreasing of the material ability for recovery deformations..

It can be concluded that resulting blending materials represented the combination of component polymer properties, and on that manner it can be possible to modificate thermoplastic (PP) with the rubber (MVQ) or oposite to modificate elastomer with the thermoplastic polymer. In these MVQ/PP blends the increased tensile properties with the addition of PP is significant, and the resulting material had similar properties as thermoplastic polymer. Disadvantages of these blends are the low values of elongation at break (26% to 40%).

# Thermal characteristics

The thermomechanical analysis data of samples of PP, MVQ, and their blends are shown in figures 3 to figure 7. From the plots of temperature dependency of sample strain are determined phase temperature transition (polypropylene melting point ( $T_{\rm m}$ ) and melting of crystaline regions in silicone rubber) and PP glass temperature ( $T_{\rm m}$ ). Silicone rubber glass temperature could, not be determined because the testings were done on temperature above –70°C, while  $T_{\rm g}$  of silicone rubber is about –125°C.

From literature [18] is known that PP has T at about  $-5^{\circ}$ C and melting temperature ( $T_{\rm m}$ ) at about  $150^{\circ}$ C, while silicone rubber has T at about  $-125^{\circ}$ C, and crystaline  $T_{\rm m}$  in range from  $-60^{\circ}$ C<sup>g</sup> to  $-85^{\circ}$ C. From the plots can be determined:

- Pure silicone rubber exibits a distinct melting point at about -60 °C;
- at the temperature at about 170°C phase transition which corresponded to polypropylene melting point;
- at the temperature at about -5°C, second order transition corresponded to glass temperature of PP;

- at the temperature at about 133°C, transitation is occured, which probably significate some polymer interactions in the blend.

On the basis of TMA plots it can be concluded that changes in polymer compositions are not affected on materials phase temperature transitions during the examinations. The corresponding blends spanning the comlete composition range also show that the T<sub>g</sub> of PP remains essentially invariant with changes in the MVQ concentration. In addition, the melting temperature of the MVQ component is invariant with PP concentration. These results confirm that this blend series is immiscible over the entire composition range. In table 3 are given the blends values of coefficient of thermal expansion.

Silicone rubber show greater values of coefficient of thermal expansion compared to PP in all testing temperature ranges (table 3). Also, values of thermal expansions of blends are changes in all temperature ranges. That fact is in agreement to theoretical background that this thermal characteristic is changed during the phases and other transitions in polymers. Vicat softening point is showing that heat performance limits values for blend B are lower than 100°C.

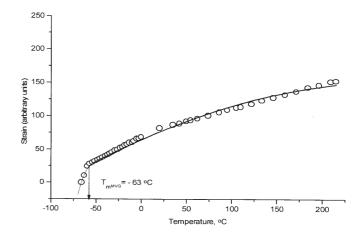


Fig. 3 TMA plot of MVQ

<sup>\*\*</sup> For the temperature range -70 °C to 0 °C, there is no MVQ in compound

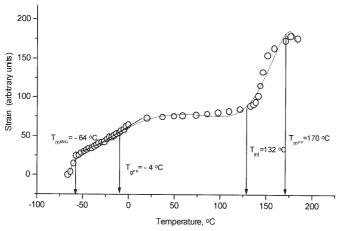


Fig. 4 TMA plot of MVQ/PP " blend B

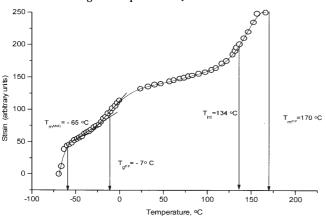


Fig. 5 TMA plot of MVQ/PP " blend C

#### **Conclusions**

When MVQ are blended with homopolymer PP to an extent of 10% to 50% by weight, a family of thermoplastic material is produced. They are relatively low priced and show high levels of tensile strength and impact strength.

Thermoplastic rubbers (TRs) have some notable properties with MVQ/PP blends:

-high softening point;

-high impact strength properties;

-lower production costs than vulcanised rubbers;

-easy and low cost processability;

-easy available raw materials.

These properties indicate that the markets for which MVQ/PP blends could be assessed and may be classified as follows:

-replacement of high modulus vulcanised rubbers in products where high reselience and elongation at break are not essential,

-replacement of rigid plastics such as: PVC, PP, etc.;

-new applications, esspecially in the automative industry.

Having described the preparation and properties of MVQ/PP blends it remains the question of their potential to become a commercial reality. As for any new material this will depend on both technical and economic factors. Mechanical properties of such blends are similar to those of RMPP (EPDM rubber modified PP), the only exception is elongation at break, with which it might be expected to compete in the same markets. Higher prices of these MVQ/PP blend materials compared to EPDM/PP blends could be limitation to the broadening automative technical uses.

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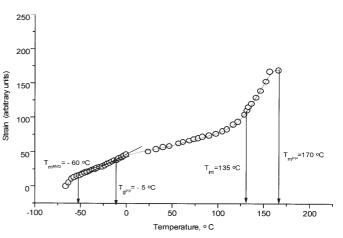


Fig. 6 TMA plot of MVQ/PP " blend

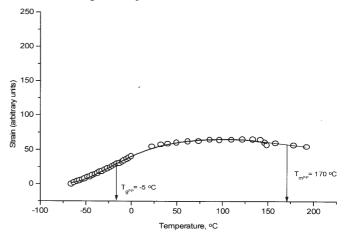


Fig. 7 TMA plot of PP

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