Mechanical and Thermal Properties of Silicone-Poly(tetrafluoroethylene) Blends

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Mixing and processing characteristics, mechanical properties and thermal characteristics of dimethyl vinyl silicone/poly(tetrafluoroethylene)(MVQ/PTFE) blends were investigated. With the rise Poly(tetrafluoroethylene) (PTFE) portion in blends, the values of both torque and total torque of blend materials decrease. In MVQ/PTFE blends, PTFE act as inactive filler and some mechanical properties decreases in blends compared to component polymers with the increases portion of plastic in blend compositions. The heterogenity of MVQ/PTFE blends was determined by thermomechanical analysis-dilatometry. Silicone (MVQ) and PTFE show separate T_{gs}*, which indicate that they are not compatible. Thermogravimetric analysis of these blends, show that with increased portion of PTFE in blends, the TGA characteristics* T_{beg} *and* $T_{5\%}$ *is moved at higher temperature, which mean increased of thermal blend stability.*

Keywords: blends, dilatometry, TGA,

Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science in the last few decades [1]. One of potential commercially important and immiscible polymer blends is that of dimethyl vinyl silicone (MVQ) and poly(tetrafluoroethylene) (PTFE). MVQ act as permanent plasticizer for PTFE in applications like wire and cable insulation, gaskets, and new applications in the medicine and automotive industry [2, 3]. PTFE offer some important properties such as good temperature resistance, chemical inertness, exceptional dielectric properties, toughness and flexibility, low coefficient of friction, non-stick behaviour, negligible moisture adsorption and good weather resistance. This plastic could improve these properties in blend with some elastomers such as silicone rubbers [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 resistances generally accepted as being better than that of any other elastomer [7]. The "useful life" for silicone at continuous elevated temperatures has been reported as 2 years at 150°C to 84 days at 260°C [8]. At low temperatures, general-purpose grades resist embitterment down to –75°C and retain flexibility at –50°C. Silicone elastomers retain good electrical properties at temperature extremes under moisture and ageing conditions. They have excellent resistance to water, steam, weather and oxidation. Abrasion resistance of standard types is poor. It is interesting to noticed that both, MVQ and PTFE are the best polymers when properties such as: low and elevated temperature resistance, good electrical properties, good weather resistance are needed to materials and products in applications in electrical and automative industry.

The object of this work is to investigate the mixing and processing characteristics, mechanical properties and thermal characteristics of MVQ/PTFE blends. A Haake Torque Rheometer has been used extensively for assessing the fusion characteristics and mechanical and thermal stability and processing characteristics of polymers and blends [9, 10, 11]. Such an investigation has been carried out on MVQ/PTFE blends using a Torque Rheometer, a Thermomechanic and a Thermogravimetric analyzer. The results of this evaluation are checked with mechanical and thermal properties of the blends. The compatibility for an immiscible system (MVQ/PTFE) was investigated using Thermomechanical analysis-dilatometry.

Experimental part

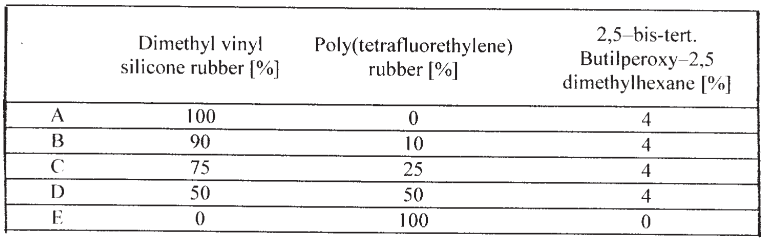
Materials

Polymers: Dimethyl vinyl silicone rubber (MVQ), Mooney viscosity ML 1+4 (100°C)= 15, density = 1,14 (SE 456 U General Electric) and polytetrafluorethylene (PTFE), density 2,175 (CFP 6000-Du Pont).

Curative: 2,5–bis-tert. Butilperoxy–2,5 dimethylhexane (Varox-Vanderbilt Co.).

The Compound formulations are shown in table 1.

Table 1
FORMULATIONS OF THE MIXES BASED ON MVQ RUBBER AND PTFE



	Dimethyl vinyl silicone rubber [%]	Poly(tetrafluorethylene) rubber [%]	2,5–bis-tert. Butilperoxy–2,5 dimethylhexane [%]
A	100	0	4
B	90	10	4
C	75	25	4
D	50	50	4
E	0	100	0

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The sample preparation of MVQ/PTFE polymer blends was carried out on a Torque Rheometer (HBI system 90, with mixing chamber–Rheomix 600), at rotor speeds: 25 rpm, 50 rpm, 75 rpm and 100 rpm. Mixing chamber is heated at 25 - 30°C and in the same time are added both MVQ and PTFE polymers. Mixing time for homogenized polymers was 15 min and then curative agent is added and compound was homogenized one minute in the mixer. In case of mixing blend MVQ/PTFE = 25/75 (with 75% PTFE) the quantity of MVQ rubber was not big enough to absorb a higher quantity of PTFE (filler) and compound was not homogenized (resulting compound looks like powder). From this reason, from further exploration are not used blend materials, which consist more than 50% of PTFE. After mixing, the blend compounds were moulded into 2 mm thick slabs for determining mechanical properties. The slabs were moulded 10 min in a hydraulic press at 175°C, and then cured 24 h at 200°C in oven.

Mechanical properties

The tensile properties of the vulcanizates were determined according to ASTM D 418, using dumbell specimens at 25 °C at a crosshead speed of 500 mm/min, with Monsanto Tensometer 10 [3]. Hardness was determined according to ASTM 2240.

Thermomechanical study

Thermal analysis of the blends was performed in the Thermomechanical analyser Perkin Elmer TMS–2 at a heating rate of 2.5 °C/min and temperature ranges from –170°C to 0°C and from 20°C to 150°C. From the diagram of temperature dependence of sample dilatation are determined: temperatures of phase transitions (crystallize temperature of silicone rubber and melting points of crystallization regions in silicone rubber) and glass transition temperatures (T_g) of silicone rubber and PTFE.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of different blends and pure components MVQ and PTFE were carried out using a Du Pont 951 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 25°C/min in temperature range from 50°C to 700°C. About 10 mg of the sample was used for each experiment.

Results and discussion

Processability

Studies on a Haake Torque Rheometer

The change in Haake viscosity (mixing torque) against time for component polymers and different blend compositions is presented in figures 1 and 2. Both initial and total torque of the blends is decreased with increase of PTFE portion in the blends. From the graphics (figs.1 and 2) it is evident that with the rise of PTFE portion in blends, at the equality rotor speed mixing, decrease of the values of initial and total torque were shown, which can be explained by the fact that PTFE is of lower viscosity and has good frictional properties.

The mixing of polymer blends MVQ/PTFE was carried out on a Haake Torque Rheometer at different rotor speed: 25 rpm, 50 rpm, 75 rpm and 100 rpm at temperature 25-30°C. On figure 3 is showed dependence of final (total) torque plotted against rotation speed (rpm) of mixing rotors for different blend compounds.

The initial torque as function of different blend compositions at different mixing times is shown in figure 4.

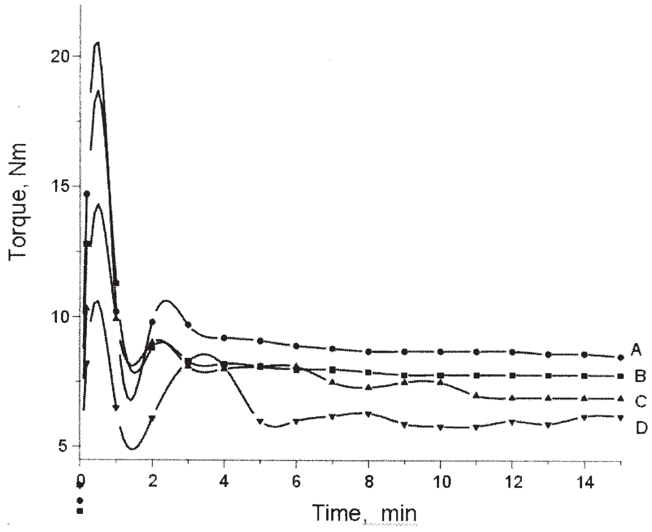

Fig. 1. Haake torque curves of MVQ and MVQ/PTFE blends as a function of mixing time

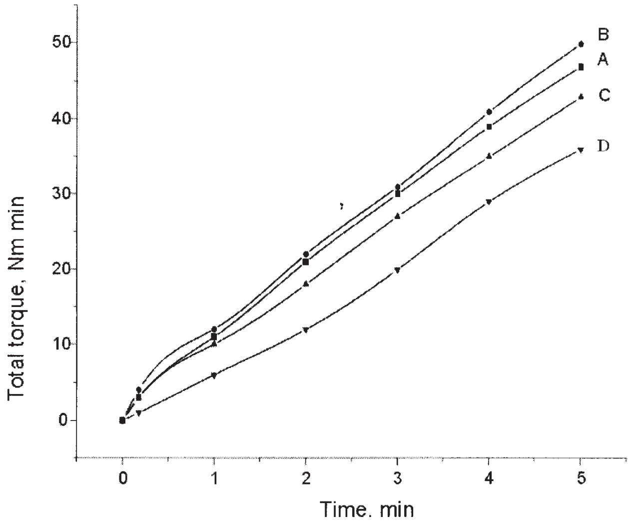

Fig. 2. Mixing total torque as a function of time mixing, for MVQ/PTFE blends

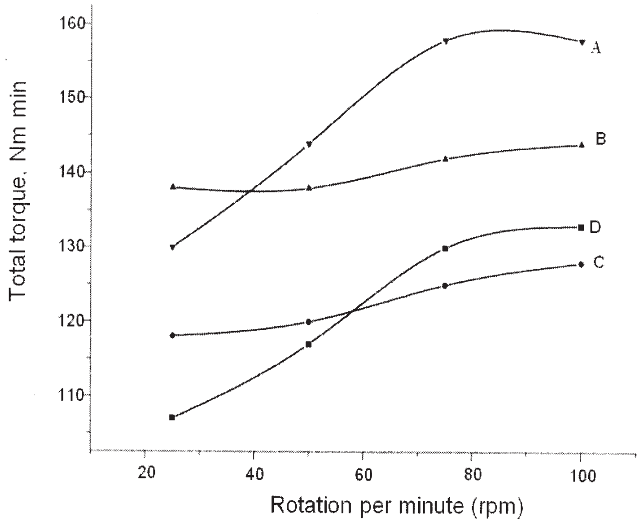

Fig. 3. Mixing total torque as function of speed mixing rotors (rpm), of MVQ/PTFE blends

With the increasing of rotor speed mixing, the resistance of blend material is increased too, and the total energy consumed for mixing is higher. Also, because of higher material friction, appearing during mixing process in case

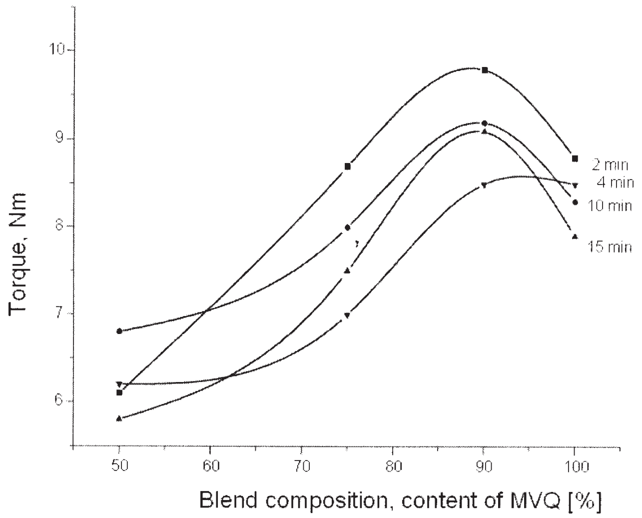

Fig. 4. Torque as function of MVQ/PTFE blend compositions, for different mixing time

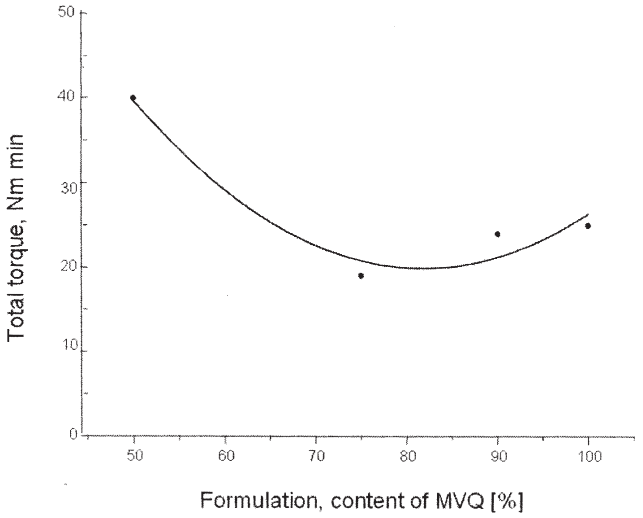

Fig. 5. Haake total torque of MVQ/PTFE blends as a function of content MVQ in blend formulations

of higher rotor speed, the rising in temperature of materials in mixing chamber has happened.

Viscosity of prepared MVQ/PTFE polymer blends, as parameter of rheology behaviour, was additionally determined, and the torque values during mixing in Haake Torque Rheometer for 5 min at temperature 125°C and speed of 25 rpm were measured. Figure 5 shows functional dependency of total torque of blend compositions. It is possible to noticed the rapid grow of viscosity in blend with 50% PTFE, compared to other compositions.

To compare different methods of determining viscosity of polymer blends of MVQ and PTFE, the torques on Monsanto Rheometer R-100, during 6 min at 125°C were measured. The lowest value of torque, determined at low shear rate is the measure of toughness and viscosity of uncured compound [12]. The viscosity of polymer blends determined as torque value and measured after 4 min from the beginning of testing, are showed in figure 6. It can be seen a good agreement curves of Monsanto torque values with torque values determined on Haake Torque Rheometer.

Mechanical properties

Mechanical characteristics are determined on cured polymer component MVQ and blends and the results are shown in table 2.

On the basis of values from table 2, it is shown that with the increased parts of plastic (PTFE) in blends, hardness is increased in blends compared to MVQ vulcanizate. Elongation at break decreases with increasing PTFE in blends (exception is blend B with 10% PTFE) and these means decreases of material ability for recovery deformations. In silicone rubber and PTFE polymer blends, PTFE has act as a inactive filler, because with the increasing portions of plastic in silicone matrix, hardness is increased, but tensile strength and elongation at break are decreasing at the same time. Disadvantages of these blends are poor (low) values of tensile strength.

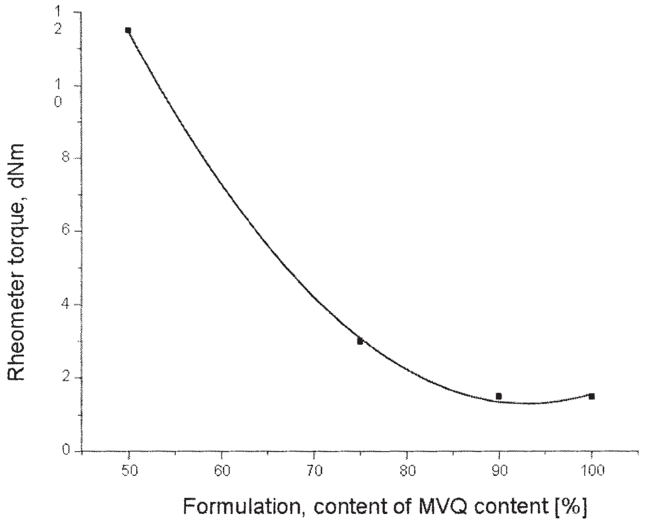

Fig. 6. Relationship rheometer torques of the composition MVQ/PTFE blends

Thermal characteristics

The results of testing polymer blends using thermomechanical analysis are given in figures 7 - 10.

Silicone rubber (MVQ) has very low value for T_g about –123°C and is one of most convenient elastomer for cryogenic application. Maximum speed of crystallization of silicone rubber happened in temperature interval –80 to –90°C and melting temperature of crystalline regions in rubber are in interval –70 to –85°C. Polytetrafluorethylene (PTFE) shown glass transition temperature T_g = 120°C and two secondary glass-glass transition temperatures; T_{gg1} on –93°C and T_{gg2} on –18°C. PTFE show two first order transitions (phase transformations): first on 22°C which is a consequence of changes in crystal structure (permeating); and second on 327°C when completely crystal melting is happened [12-15]. In figures 7 - 10

Table 2
MECHANICAL PROPERTIES OF MVQ/PTFE BLENDS

	A	B	C	D	E
Hardness, Shore A	56	56	60	80	90
Tensile strength, MPa	7.9	6.6	5.2	2.71	18.3
Elongation at break, [%]	533	590	393	183	120

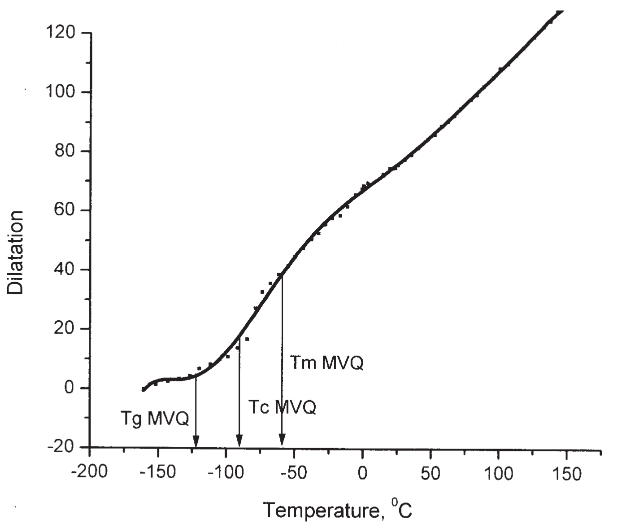

Fig. 7. TMA (dilatometry) plot of mix "A"

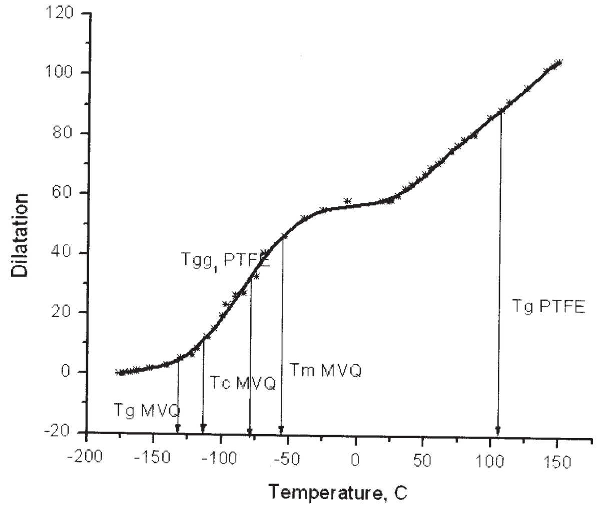

Fig. 9. TMA (dilatometry) plot of mix "C"

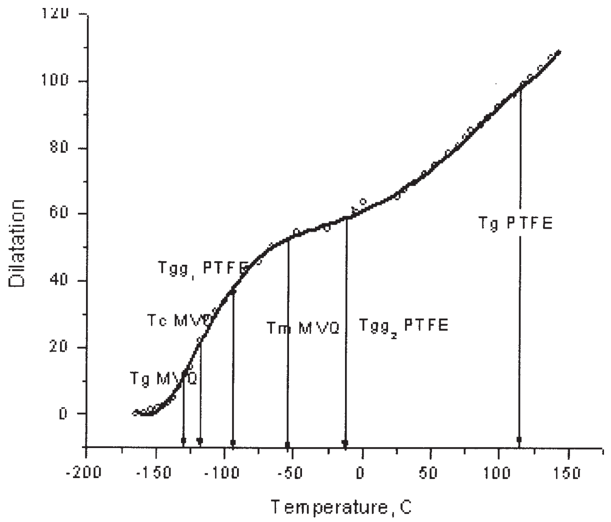

Fig. 8. TMA (dilatometry) plot of mix "B"

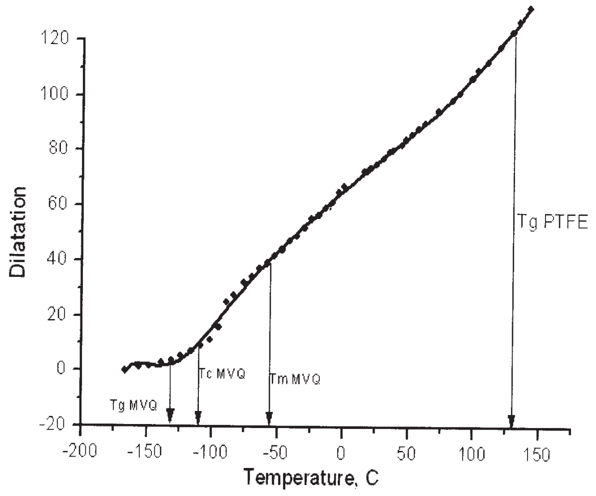

Fig. 10. TMA (dilatomtery) plot of mix "D"

Table 3
COEFFICIENT OF LINEAR THERMAL EXPANSION OF MVQ/PTFE BLEND

	-160 °C to T_{gMVQ}	T_{gMVQ} to T_{cMVQ}	T_{cMVQ} to $T_{gg1\,PTFE}$	$T_{gg1\,PTFE}$ to $T_{m\,MVQ}$	$T_{c\,MVQ}$ to $T_{m\,MVQ}$	$T_{m\,MVQ}$ To $T_{g\,PTFE}$	Above $T_{g\,PTFE}$
A	$1.07\ 10^{-4}$	$3.4\ 10^{-4}$	-	-	$3.34\ 10^{-4}$	-	$2.68\ 10^{-4}$
B	$1.67\ 10^{-4}$	$6.22\ 10^{-4}$	$4.2\ 10^{-4}$	$2.61\ 10^{-4}$	-	$2.47\ 10^{-4}$	-
C	$8.28\ 10^{-5}$	$3.1\ 10^{-4}$	$3.66\ 10^{-4}$	$2.16\ 10^{-4}$	-	-	$2.5\ 10^{-3}$
D	$9.97\ 10^{-5}$	$2.74\ 10^{-4}$	-	-	$1.06\ 10^{-3}$	$3.11\ 10^{-4}$	$4.75\ 10^{-4}$

temperature dependence curves of dimensione changes (dilatation) of tested samples are shown. In diagrams dependence dilatation from temperature could be seen.

Maximum on the curves which indicated glass transition temperature of silicone rubber are in the temperature interval from –118 to –134 °C (in literature, T_g is about –123°C) and T_g for PTFE are in temperature interval from 115 - 130°C (in literature, T_g is about 120 °C). Maximum on the curves (glass transitions) are not clearly visible, and a possible explanation can be that both polymers shown crystalline regions in their structure. MVQ/PTFE blends show separate T_{gs} which indicate that MVQ and PTFE are not compatible. Also, another transition on the curves corresponds well to temperatures from –80 to –100°C and that correspond to crystallization temperature T_c of silicone rubber (in lit. about –80°C).

In table 3 are given the blends values of coefficient of thermal expansion.

On the basis of these values it can be noticed that increasing the portion of PTFE in blends, the coefficient of linear thermal expansion has been increased, too. The most significant changes of these characteristics are in the region of glass transition temperatures of silicone rubber and PTFE, as other transitions in polymer blends during temperature changes are not significant for values changes of these coefficients.

Thermal stability (TGA analysis)

Being organic bodies, the polymers have limited thermal stability [16]. In the event of fire, due to a short circuit or other faults, the temperature of some potential products (cables, suits, gaskets) may go very high. So, the thermal stability of the polymer material is an important

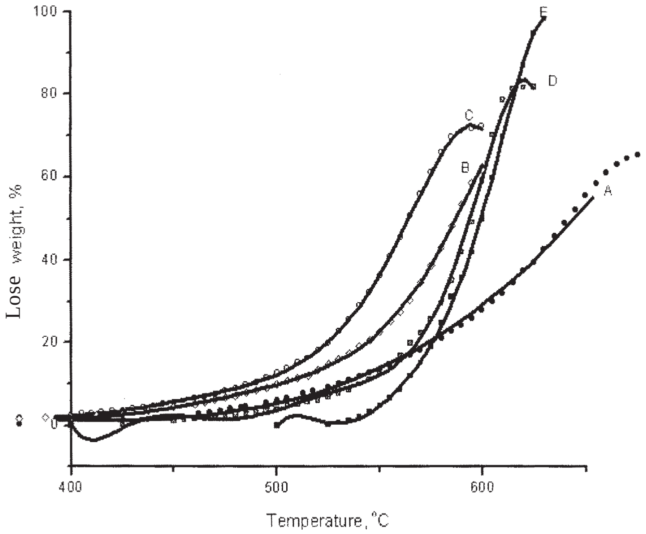

Fig. 11. Lose weight for MVQ/PTFE blends

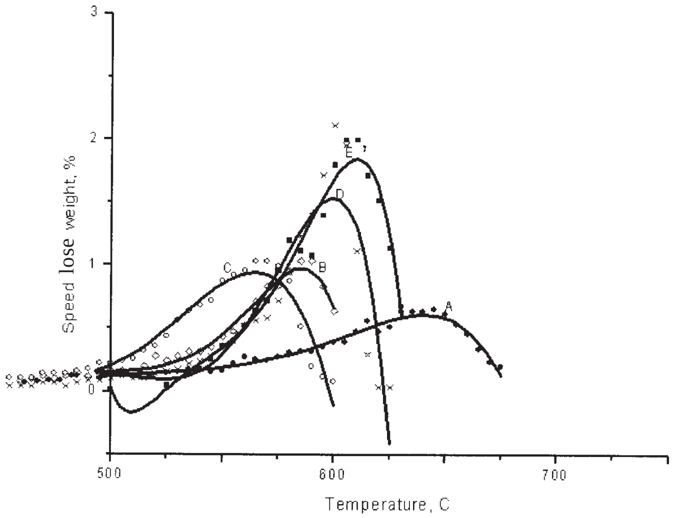

Fig. 12. Speed lose weight for MVQ/PTFE blends

Table 4
THERMOGRAVIMETRIC ANALYSIS OF CURED MVQ/PTFE BLENDS

Mix with content MVQ, [%]	Loose of weight mass on temperature 628°C (degradationof E) [%]	Loose of weight mass on temperature 595 °C (degradation of C) [%]	Height of DTG maximum (fig. 16)	Begining of degradation, °C	Temperature at which the speed of degradation is max., T_{max}	Temperature on which material loose 5 % of weight, $T_{5\%}$	End of degradation, °C
0 (E)	98.8	41.5	1.85	530	610	550	630
50 (D)	82.5	50.3	1.54	540	600	510	620
75 (C)	73.5	72.5	1.05	490	562	445	599
90 (B)	63.3	58.9	1.00	515	587	460	600
100 (A)	42.4	26.9	0.66	590	645	490	675

consideration for its selection for the products such as cable insulant. These two applicable polymers are different in structure, MVQ has inorganic bodies, while PTFE has fluor atoms in structure and both contribution to good thermal stability of these blends.

TGA analysis gives an idea of the thermal decomposition characteristics of different blends at elevated temperature. TGA plots for different blends are shown in figures 11 and 12 and gives the lose of weight and speed of material weight changes.

Thermal stability of binary polymer blends are determined based on TGA curves, by analyzing important parameters:

- temperature of the beginning of degradation;
- temperature on which material loses 5% of weight;
- temperature of maximum speed degradation.

The results of thermogravimetric analysis of MVQ/PTFE blends are shown in table 4.

On the base of TGA plots one can observe that pure PTFE had been unchanged for a long time, and then depreciated completely at increased speed, in relatively narrow temperature interval (530 to 630°C). This polymer is thermally stable up to temperature 530°C. Temperature (550°C) at which this material loses 5% of weight ($T_{5\%}$), is a very significant parameter from the aspect of application of polymer materials, and this is the highest temperature value compared to other testing temperature of blend materials. This means that PTFE is the most temperature stable material. Also, PTFE show the loose 98,8% of weight, which means completely degradation without residual up to the vaporized monomers on temperature 628°C. At the same time, silicone rubber at temperature 628°C, has shown only 42.4% lose of weight, which can be explained with its structure (high contain of inorganic silicon).

The blends C and B with content 75% and 90% MVQ has shown the lowest values of $T_{5\%}$, and T_{max}, which means that these materials are not thermally stable compared to component polymers and this indicated to incompatibility of these blends, too. The blend materials shown maximum degradation speed (T_{max}) at lower temperatures, compared to component MVQ and PTFE polymers.

With the increased portion of PTFE in blends, the temperature of the beginning of the degradation ($T_{beg.}$) and temperature on which material loses 5% of weight ($T_{5\%}$), are moved (shift) to higher temperature, which means the increasing of thermal material blends stability.

Conclusions

PTFE and MVQ formed incompatible blends. The higher the PTFE portion, the larger is the heterogenity of the system.

PTFE/MVQ blends behaviour as heterogenity system in which PTFE acts as an inactive filler. This is noticeable in deteriorating mechanical properties of vulcanizates of blends compared to component polymers, MVQ and PTFE.

The results of polymer blends viscosity showed a good agreement of Monsanto torque values with torque values determined on Haake Torque Rheometer.

Thermomechanical analysis (TMA) of polymer blends shows separate T_{gs} which indicates that PTFE and MVQ are not compatible.

The results of thermogravimetric analysis of this blends, show that with increased PTFE in blends, the values of $T_{beg.}$ and $T_{5\%}$ are moved at higher temperature increasing the thermal blend stability.

The properties of MVQ/PTFE blends indicate that possible use for this blend materials might be classified as follows:

Replacement of some rigid plastics such as: PVC, PP, etc. in applications with extreme temperatures,

- replacement of cured rubbers in products where high temperature resistance are essential (hoses, wire and cable insulations, gaskets, etc.);
- new applications, especially in the medicine and automative industry.

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Manuscript received: 3.02.2009