

Influence of Engage[®] copolymer type on the properties of Engage[®]/silicone rubber-based thermoplastic dynamic vulcanizates

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Received 22 August 2008; accepted in revised form 30 October 2008

Abstract. Thermoplastic vulcanizates (TPVs) are a special class of thermoplastic elastomers, which are produced by simultaneously mixing and crosslinking a rubber with a thermoplastic polymer at an elevated temperature. Peroxide-cured TPVs based on blends of silicone rubber and thermoplastic Engage of two different types, mainly ethylene-octene and ethylene-butene copolymers at different blend ratios have been developed. A detailed comparative study of ethylene-octene vs. ethylene-butene based TPVs are mainly focused in this paper. These TPVs exhibit very good overall mechanical and electrical properties. With increasing amount of Engage in the blends at a fixed concentration of peroxide and coagent, tensile strength, modulus and hardness of the TPVs were found to increase considerably. Ageing characteristics and recyclability of silicone rubber based TPVs are also found excellent. Rheological studies confirm the pseudoplastic nature of these TPVs.

Keywords: polymer blends and alloys, silicone rubber, ethylene-octene, ethylene-butene and peroxide

1. Introduction

Thermoplastic elastomers (TPEs) based on rubber-plastic blends are relatively new class of polymeric materials, where properties can be more easily tailored by simply changing the ratio of the rubber to plastic in the blends. These TPEs are normally phase separated systems, in which one phase is soft and rubbery at room temperature while the other is hard and solid. They possess the elasticity of a rubber and the thermoplasticity of a plastic; yet retain unique features of its components such as good ultraviolet and ozone resistance, solvent resistance and high deformation temperature. Furthermore, they can be processed very easily by extrusion, injection moulding, and blow moulding etc. to provide commercially attractive products that show the softness, extensibility and resilience of conven-

tional thermoset rubbers. The most important feature of this class of materials is that the scrap can be recycled several times without significant deterioration of properties [1–3]. As a result, many commercial TPEs have been developed for various applications particularly in the automotive, electrical, medical and construction industries etc.

The first TPE was introduced to the market in 1972 by Fisher [4]. Significant improvements in the properties of these blends were achieved in 1978 by Coran, Das and Patel by fully vulcanizing the rubber phase under dynamic shear, while maintaining the thermoplasticity of the blends [5, 6]. These blends were further improved by Sabet Abdou-Sabet and Fath [7] in 1982 by the use of phenolic resins as curatives. A series of extensive studies on dynamically vulcanized TPEs or TPVs were car-

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ried out by Coran and Patel in 1980s [8–15]. Generally, it is easy to combine a rubber and plastic of similar polarities and solubility parameters to produce a useful thermoplastic elastomer, such as polypropylene (PP)/ethylene-propylene-diene copolymer (EPDM), epoxidized natural rubber (ENR) and poly (vinyl chloride) (PVC), acrylonitrile-butadiene rubber (NBR) and nylon etc. However, it is difficult to produce a TPE using a plastic and an elastomer having different polarities and solubility parameters. This is due to the existence of a high interfacial tension between the two polymers. Bhowmick *et al.* [16–24] also reported various TPEs and TPVs. Recently Naskar *et al.* [25–30] extensively studied the effect of various peroxides including multifunctional peroxides as crosslinking agents in PP/EPDM TPVs. They are typically characterized by finely dispersed (micron-sized) crosslinked rubber particles distributed in a continuous thermoplastic matrix. Generally the rubber particle size varies in the range of 0.5–2 μm . A literature survey indicates that there is enough opportunity to generate new materials by blending the existing polymers, especially to improve properties, to cover up the deficiency of one polymer by another and also to reduce cost. This survey also reveals that there is a growing interest of the use of thermoplastic vulcanizates (TPVs) in the last couple of decades. Currently TPVs comprise of the fastest growing elastomer market with an annual growth rate of about 15%.

Only limited researches have been pursued so far in the field of silicone rubber. A few research works in related field have been patented by Dow Corning Corporation [31–33]. Very recently Basuli *et al.* [34, 35] studied the properties of TPVs based on

silicone rubber at a fixed blend ratio of the blend constituents. Potential areas of application of silicone based TPVs could be in wire and cable industries and soft-touch appliances.

The main objective of the present work is basically to study the influence of the type of Engage on the properties of silicone rubber and Engage-based TPVs at varied blend ratios. Two different types of Engage, namely, ethylene-octene and ethylene-butene were taken for this study.

2. Experimental

2.1. Materials

Silicone rubber (polydimethyl siloxane, PDMS) was supplied by GE Silicones, India having a specific gravity of 0.9 g/cm^3 and a Mooney viscosity ML_{1+4} at 100°C of 45. Engage-8440 (Ethylene-octene grade) and Engage-7256 (Ethylene-butene grade) were supplied by DuPont Dow elastomers, USA. Table 1 [36] shows various properties of Engage-8440 and Engage-7256, which have crystallinity of 27 and 23% respectively. Dicumyl peroxide (DCP) (98%) and triallyl cyanurate (TAC) (50%) were obtained from Akzo Nobel Polymer Chemicals, The Netherlands. DCP was used as the crosslinking agent and TAC was used as the co-agent (booster for peroxide).

2.2. Preparation of TPVs

The TPV compositions employed for the present work is shown in Table 2. The experimental variable is the ratio of blend constituents. All TPVs were prepared by a batch process in a Brabender Plasti-Corder PLE 330, Germany having a mixing

Table 1. Various properties of Engage-8440 (ethylene-octene grade) and Engage-7256 (ethylene-butene grade)

Type of Engage	Density [g/cm^3]	Melt index [dg/min] (190°C, 2.16 kg)	Mooney viscosity ML_{1+4} at 121°C	Total crystallinity [%]	Hardness [Shore A]	DSC melting peak [°C] (rate 10°C/min)
Engage-8440	0.897	1.6	16	27	92	94
Engage-7256	0.885	2.0	16	23	79	73

Table 2. TPV compositions in phr (parts per hundred rubber) at varied PDMS/Engage blend ratios at a fixed DCP/TAC concentration

Components	E ₁	E ₂	E ₃	E ₄	E ₅	E ₆	E ₇	E ₈	E ₉	E ₁₀
PDMS	100	100	100	100	100	100	100	100	100	100
Engage-8440	25	50	75	100	125	–	–	–	–	–
Engage-7256	–	–	–	–	–	25	50	75	100	125
DCP (98%)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
TAC (50%)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

chamber volume of 70 cm³. The mixer temperature was kept at 120–130°C with a constant rotor (cam type) speed of 80 rpm. Engage and silicone rubber (PDMS) were first mechanically melt-mixed. After 6 min of mixing, the co-agent (TAC) was added, followed by the addition of DCP. The mixing was continued for another 4 min to complete the dynamic vulcanization process in the Brabender. Immediately after mixing, the molten mass was passed through a cold two-roll mill to achieve a sheet of about 2 mm thickness. The sheet was cut and pressed (2 mm thick) for 4 min in a compression molding machine (Moore Press) at 130°C. Teflon sheets were placed between the molded sheet and the press plates. The sheet was then cooled down at room temperature under pressure. Test specimens were then die-cut from the compression molded sheet and used for testing after 24 hrs of maturation at room temperature.

2.3. Testing procedures

2.3.1. Curing characteristics

Curing characteristics of only silicone rubber (without any Engage) containing cross-linking agents, DCP/TAC were carried out by using Monsanto Rheometer R100S (an oscillating disc rheometer, ODR) at 130°C for 30 minutes.

2.3.2. Mechanical properties

Tensile tests were carried out according to ASTM D 412-98 on dumb-bell shaped specimens using a Zwick tensile testing machine, Zwick 1445, Germany at a constant cross-head speed of 500 mm/min. Three specimens were tried for each condition and average value (having a very little standard deviation in all samples) was reported. Hardness of the samples was measured with a Durometer (Shore A and Shore D, as per ASTM D2240). Tension set test was carried out at room temperature after stretching the samples for 10 min at 100% elongation according to ASTM D 412-98.

2.3.3. Rheological characteristics

Processing and rheological characteristics of the samples were carried out using a Monsanto Processability Tester (MPT), USA at 120°C at varied shear rates (0.05, 0.10, 0.25 and 0.40 in/min).

2.3.4. Ageing test

Ageing test was carried out keeping the samples in the ageing oven at 70°C for 72 hrs to get a preliminary idea about the ageing characteristics of the samples.

2.3.5. Recyclability study

Recyclability tests were carried out by putting the residual molded TPV samples again in the Brabender Plasticorder at 110–120°C, followed by molding the samples at 130°C and subsequently testing them.

3. Results and discussion

Peroxide crosslinking chemistry has been known for many years. The mechanism of peroxide crosslinking of rubber is less complicated as compared to sulfur vulcanization. The crosslinking process of high polymers like silicone rubber by organic peroxides (DCP) can be divided into three successive steps [35]. The first step is the homolytic decomposition of DCP and generation of cumyloxy free radicals. This step is the rate-determining step of the overall reactions. These cumyloxy radicals can further undergo β chain scission to produce highly reactive methyl radicals and acetophenone. The second step is the abstraction of hydrogen atoms from the silicone polymer, resulting in stable peroxide silicone polymeric radicals. The final step consists of the combination of two such decomposition products such as methane, acetophenone, and 2-phenyl propanol-2 and silicone polymeric radicals to produce a stable C–C crosslink, which has very high bond strength. Increases in the tensile strength, modulus, and hardness of TPVs can be explained by the higher extent of crosslinking in the PDMS phase. It should be noted, however, that there is a possibility that DCP could also take part in crosslinking the Engage phase to some extent because of its chemical structure. However, crosslinking in the PDMS phase is predominating here and is mainly controlling the final phase morphology and consequently the properties of the blends. In addition, during the process of dynamic vulcanization of silicone rubber and ethylene-octene or ethylene-butene copolymer in the presence of DCP/TAC, there is a possibility of generation of in situ graft links of silicone rubber

Table 3. Formulations of the samples used for the ODR experiments (phr) at 130°C and corresponding data

Sample	PDMS	DCP (98%)	TAC (50%)	Minimum ML [dN m]	Maximum MH [dN m]	Max – Min torque [dN m]	T ₉₀ [min]
R-1	100	1.0	2.0	4.50	73.00	68.50	17
R-2	100	2.0	2.0	5.00	77.00	72.00	21
R-3	100	2.5	2.0	7.50	83.00	75.50	20
R-4	100	3.0	2.0	7.50	88.00	80.50	13

and ethylene-octene or ethylene-butene copolymer at the interface (which is very difficult to prove by any analytical technique because of the extremely small amount of grafts being generated), which can in turn enhance the compatibility between the two phases and also can improve the final mechanical properties of the TPVs.

Table 3 shows formulations of the samples for rheograms containing only PDMS, DCP, and TAC and corresponding results. In order to achieve a better in-sight into chemistry involved with dynamic vulcanization in PDMS/Engage blends in presence of DCP, vulcanization characteristics of PDMS gum compounds at different DCP concentrations for ODR study. The delta torque (maximum torque–minimum torques) values, as obtained from the ODR generally correlate with the crosslinking efficiency of the peroxide, which is defined as the number of moles of chemical crosslinks formed per mole of peroxide. It should be noted, however, that the latter could be measured by static vulcanization only in the absence of Engage; which is not exactly a one-to-one comparison to dynamic vulcanization, because of the lack of a high shear rate and the longer timescales.

3.1. Physical and mechanical properties

Table 4 illustrates various physical properties of the TPVs at varied PDMS/Engage blend ratios at a

fixed peroxide concentration of 2.5 phr. Table 4 shows that the tensile strength, modulus at 100% (M100), at 200% (M200) and at 300% (M300) of PDMS/Engage-8440 and PDMS/Engage-7256 based TPVs as a function of the amount of Engage. With increasing amount of Engage-8440 from 25 to 125 phr, the tensile strength increases from 3.3 to 11.0 MPa, M100 from 1.1 to 3.2 MPa and M300 from 2.0 to 4.2 MPa respectively. Table 3 also shows the Shore A hardness values of the TPVs as a function of the concentration of Engage-8440. An increase in hardness (40–68 Shore A) is seen with increasing amount of Engage.

In case of Engage-7256, tensile strength increases from 3.3 to 6.4 MPa, M100 from 1.0 to 2.0 MPa and M300 from 1.6 to 2.8 MPa respectively. Table 4 also shows the Shore A hardness values of the TPVs as a function of the concentration of Engage. An increase in hardness (40–58 Shore A) takes place with increasing amount of Engage. The general reason for the increased tensile strength, modulus, hardness, and tension set of TPVs with increasing amount of Engage in PDMS/Engage blend, as seen in Table 4, can be explained by the incorporation of higher amount of thermoplastic hard component in the blends. At low concentration of thermoplastic Engage, both types of TPVs shows more or less similar physico-mechanical properties up to 50 phr of Engage; however beyond 50 phr ethylene-octene grade shows better improvement in

Table 4. Physical properties of PDMS-Engage TPVs at varied blend ratios

Sample No.	Tensile strength [MPa]	Elongation at break [%]	Modulus [MPa]			Hardness [Shore A]	Hardness [Shore D]	Tension set [%]
			M100	M200	M300			
E ₁	3.3	350	1.1	1.5	2.0	40	8	4
E ₂	4.5	570	1.9	2.2	2.7	52	11	7
E ₃	6.4	641	2.4	2.8	3.4	56	13	11
E ₄	8.8	755	2.8	3.2	3.8	61	16	15
E ₅	11.0	854	3.2	3.6	4.2	68	19	19
E ₆	3.3	900	1.0	1.3	1.6	40	8	4
E ₇	3.6	950	1.3	1.7	1.9	50	11	8
E ₈	4.9	1025	1.6	1.9	2.2	53	13	12
E ₉	5.8	1100	1.9	2.2	2.5	56	14	16
E ₁₀	6.4	1200	2.0	2.5	2.8	58	15	20

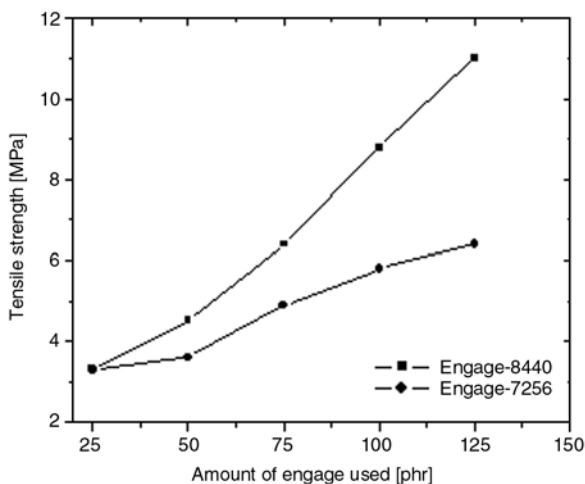


Figure 1. Tensile strength of TPVs as a function of amount of Engage

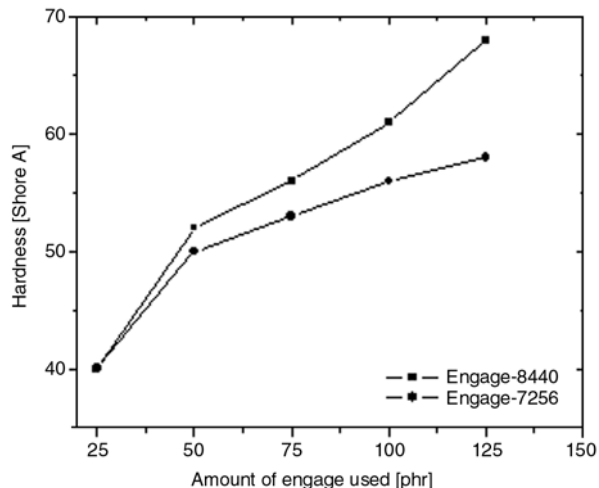


Figure 4. Hardness of TPVs as a function of amount of Engage

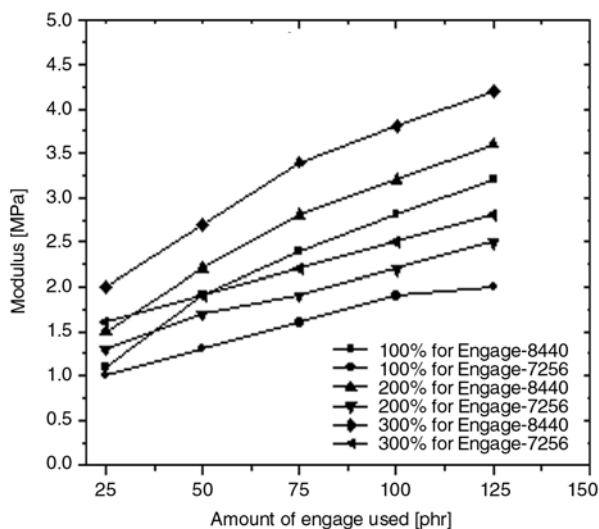


Figure 2. Modulus at different elongation of TPVs as a function of amount of Engage

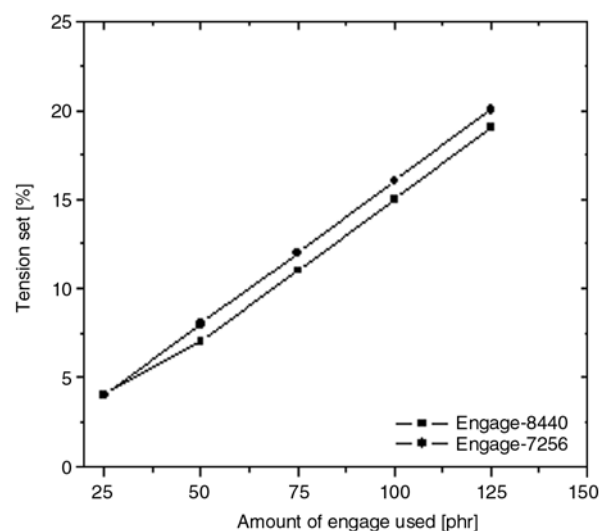


Figure 5. Tension set of TPVs as a function of amount of Engage

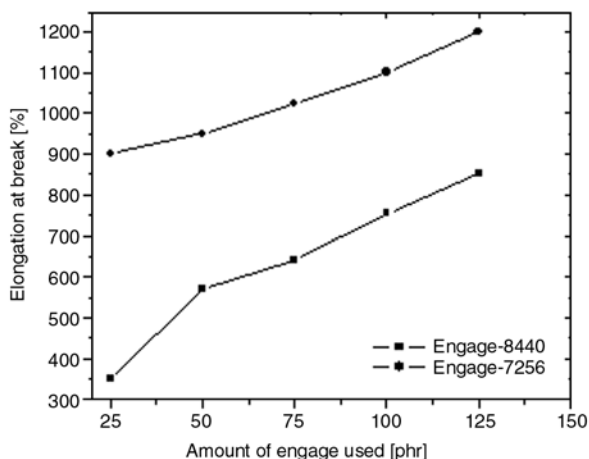


Figure 3. Elongation at break of TPVs as a function of amount of Engage

properties than ethylene-butene grade. Hardness of these TPVs are found to be almost same, only little

difference is observed of two different TPVs of same amount of two different Engage grades. This is due to the slight difference in their crystallinity values. Engage-8440 with PDMS always shows better properties; however, Engage-8440 i.e. ethylene-octene co-polymer is more expensive material because of the presence of octene monomer as compared to ethylene butene.

Figures 1–5 show various mechanical properties of Engage-8440 and Engage-7256 based TPVs at varied amounts of Engage.

3.2. Rheological study

Figures 6 and 7 show the plot of apparent shear stress vs. apparent shear rate and apparent viscosity vs. apparent shear rate respectively for Engage-

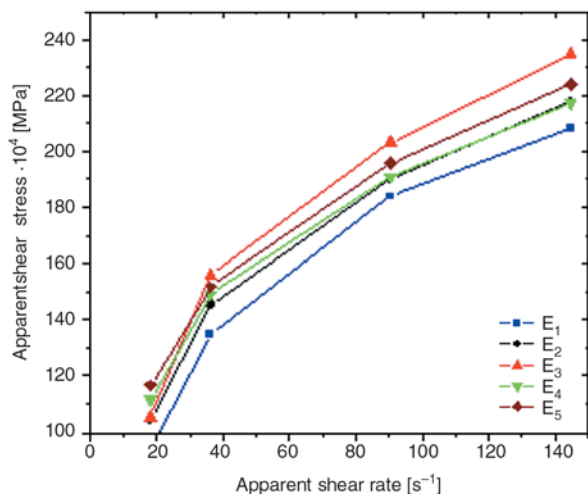


Figure 6. Relation between apparent shear stress and apparent shear rate for PDMS/Engage-8440 TPVs

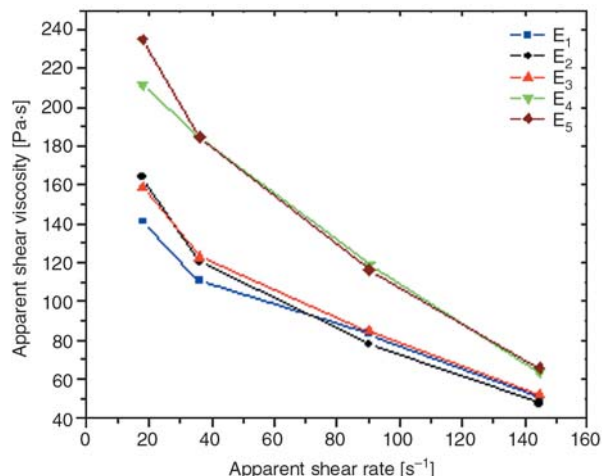


Figure 9. Relation between apparent viscosity and apparent shear rate for PDMS/Engage-7256 TPVs

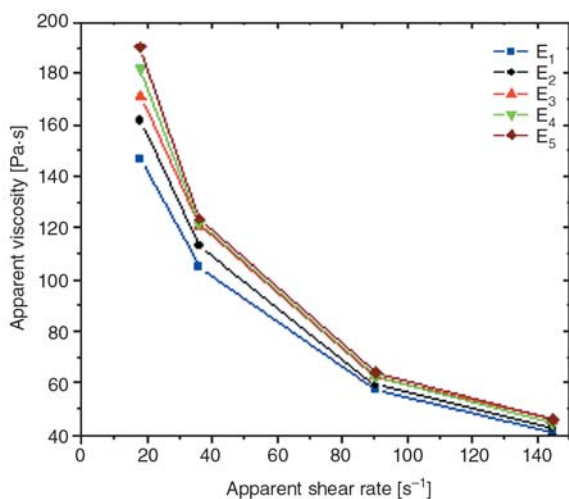


Figure 7. Relation between apparent viscosity and apparent shear rate for PDMS/Engage-8440 TPVs

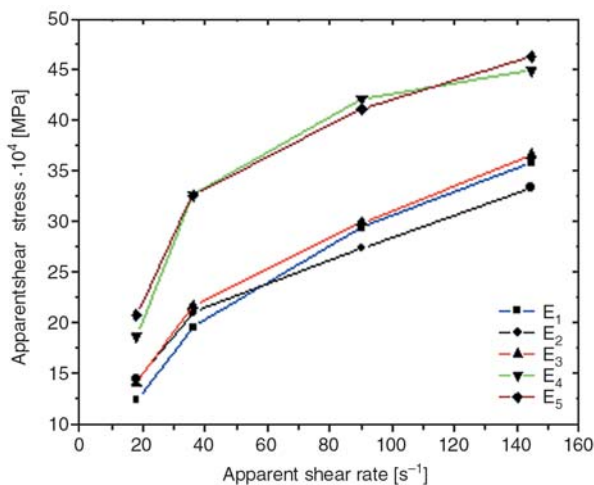


Figure 8. Relation between apparent shear stress and apparent shear rate for PDMS/Engage-7256 TPVs

8440. Apparent shear stress of the TPVs increases with increasing apparent shear rate and apparent viscosity decreases with increasing shear rate. However, at a particular shear rate, TPV containing higher level of Engage-8440 exhibits higher shear stress as compared to a TPV containing lower amount of Engage-8440. On the other hand, Figures 8 and 9 show the plot of apparent shear stress vs. apparent shear rate and apparent viscosity vs. apparent shear rate respectively for Engage-7256. Apparent viscosity of the TPVs decreases with increasing shear rate indicating pseudoplastic behaviour. From the MPT experiment, it is also observed that viscosity increases with increasing amount of Engage.

3.3. Ageing study

Table 5 shows the ageing result of PDMS/Engage TPVs. It can be seen that even after ageing at 70°C for 72 hrs., the PDMS/Engage TPV still keeps a relatively high tensile strength and elongation at break. Only the M100 of the PDMS/Engage-7256 TPVs slightly changes with ageing. However, no linear behavior for the parameters has been observed in a comparison of the influence of Engage before and after aging. Most of the TPVs show very good retention of properties even after aging, and this indicates good resistance to heat. Peroxide curing provides strong C–C linkages as crosslinks, and this is reflected in the better aging behavior. More or less similar results were observed for PDMS/Engage-8440 and PDMS/Engage-7256 TPVs.

Table 5. Change of tensile strength, elongation at break, modulus of the TPVs due to ageing (72 hrs at 70°C)

Sample No.	Tensile strength [MPa]			Elongation at break [%]			M100 [MPa]			M300 [MPa]		
	Before ageing	After ageing	Change [%]	Before ageing	After ageing	Change [%]	Before ageing	After ageing	Change [%]	Before ageing	After ageing	Change [%]
E ₁	3.3	2.9	-8.3	350	325	-3.9	1.1	0.8	-27.3	2.0	2.0	0
E ₂	4.5	3.0	-33.3	570	360	-36.8	1.9	2.2	+15.8	2.7	2.7	0
E ₃	6.4	5.3	-21.8	641	605	-5.6	2.4	2.7	+12.5	3.4	3.7	+8.8
E ₄	8.8	7.3	-17.0	755	630	-16.6	2.8	3.1	+10.7	3.8	3.9	+2.6
E ₅	11.0	9.0	-18.2	854	708	-17.1	3.2	3.3	+3.1	4.2	4.3	+2.4
E ₆	3.3	1.3	-60.0	900	550	-39.0	1.0	1.3	+30.0	1.6	2.0	+25.0
E ₇	3.6	2.5	-31.0	950	700	-26.0	1.3	1.6	+30.0	1.9	2.8	+47.0
E ₈	4.9	2.8	-43.0	1025	950	-7.0	1.6	2.0	+25.0	2.2	2.5	+14.0
E ₉	5.8	3.5	-40.0	1100	1025	-7.0	1.9	2.0	+5.0	2.5	2.5	0
E ₁₀	6.4	3.8	-41.0	1200	1060	-12.0	2.0	2.1	+5.0	2.8	2.6	-7.1

Table 6. Change of tensile strength, elongation at break, modulus of the TPVs after recycling

Sample No.	Tensile strength [MPa]			Elongation at break [%]			M100 [MPa]			M300 [MPa]		
	Before	After	Change [%]	Before	After	Change [%]	Before	After	Change [%]	Before	After	Change [%]
E ₁	3.3	2.9	-12.1	350	400	+14.3	1.1	1.8	+64	2.0	3.0	+50
E ₂	4.5	4.5	0.0	570	450	-21.0	1.9	2.8	+58	2.7	4.4	+63
E ₃	6.4	8.0	+25.0	641	640	0.0	2.4	3.0	+25	3.4	4.4	+29
E ₄	8.8	8.8	0.0	755	700	-7.3	2.8	3.0	+7	3.8	4.1	+8
E ₅	11.0	13.0	+18.2	854	785	-8.2	3.2	3.8	+19	4.2	5.2	+24
E ₆	3.3	2.0	-39.0	900	310	-65.0	1.0	1.3	+30	1.6	2.0	+25
E ₇	3.6	4.2	+17.0	950	670	-29.0	1.3	1.6	+23	1.9	2.8	+47
E ₈	4.9	3.5	-26.0	1025	650	-37.0	1.6	1.7	+6	2.2	2.5	+14
E ₉	5.8	5.0	-14.0	1100	1100	0.0	1.9	1.8	-5	2.5	2.5	0
E ₁₀	6.4	5.1	-20.0	1200	1130	-6.0	2.0	2.0	0	2.8	2.9	+4

3.4. Recyclability study

One of the most important criteria of TPEs is its recyclability. Table 6 shows the data of recycling test, which shows very good recyclability of both types of TPV samples. Table 6 also illustrates tensile strength, M100 and M300 and elongation at break values for various systems before and after recycling. All the systems show a slight decrease in tensile strength and modulus after recycling. More or less similar results were observed for PDMS/Engage-8440 and PDMS/Engage-7256 TPVs.

4. Conclusions

Thermoplastic vulcanizates based on blends of silicone rubber and thermoplastic Engage have been developed. These TPVs exhibit very good overall mechanical properties with respect to two different types of Engage (Engage-8440 and Engage-7256). With increasing amount of Engage in the blends at a fixed DCP concentration of 2.5 phr, tensile

strength, elongation at break, modulus and hardness of the TPVs were found to increase considerably. This can be explained by the incorporation of more thermoplastic hard component in TPVs. Ageing characteristics and recyclability of these TPVs are also found very good. Peroxide cured Silicone rubber/Engage TPVs exhibit very good overall performance towards heat ageing resistance, processability and recyclability. PDMS/Engage-8440 system was compared with PDMS/Engage-7256 system for physical properties, heat aging, processability, and morphology studies. PDMS/Engage-8440 system was found to exhibit better behavior in all respect. However, Engage-8440 i.e. ethylene-octene co-polymer is more expensive because of the presence of octene monomer, as compared to ethylene-butene grade. MPT shows good correlation with shear stress vs. shear rate and shear viscosity vs. shear rate. Rheological studies also confirm the pseudoplastic nature of these TPVs.

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