Dynamically Vulcanized PP/EPDM Blends:Effects of Different Types of Peroxides on the Properties

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ABSTRACT : Thermoplastic vulcanizates (TPV) or dynamic vulcanizates are thermoplastic elastomers produced by simultaneous mixing and crosslinking of a rubber and a thermoplastic. The objective of the present work is to investigate the effects of different types of peroxides as curing agents on the properties of PP/EPDM TPVs. The mechanical properties change significantly with the chemical nature of the peroxides and the extent of crosslinking at a fixed PP/EPDM blend ratio. The tensile strength of the TPVs obtained with the various peroxides can be related to the solubility parameters of the polymers and of the peroxides. The Young's modulus of the peroxide-cured TPVs can be correlated with the delta torque values of equivalent thermoset EPDM vulcanizates, corresponding to the crosslinking efficiencies of the peroxides.

I. Introduction

A thermoplastic elastomer (TPE) is a rubbery material with properties and functional performance similar to those of conventional vulcanized rubber, yet it can be processed in a molten state as a thermoplastic polymer.[1] The field of TPEs based on polyolefin rubber/ thermoplastic compositions has grown along two distinctly different product-lines or classes: one class consists of a simple blend and classically meets the definition of a thermoplastic elastomeric olefin (TPO); in the other class, the rubber phase is dynamically vulcanized, giving rise to a thermoplastic vulcanizate (TPV) or dynamic vulcanizate. TPVs are characterized by finely dispersed micron-size crosslinked rubber particles distributed in a thermoplastic matrix. If the elastomer particles of such a blend are small enough and if they are fully vulcanized, then the properties of

the blend are generally improved.[2] Examples of such improvements are:
- Reduced permanent set and better elastic recovery;
- Higher ultimate mechanical properties;
- Improved fatigue resistance;
- Greater resistance to attack by fluids e.g. hot oils;
- Improved high temperature utility;
- stability of phase morphology in the melt;
- Higher melt strength.

TPVs are generally prepared by melt-mixing techniques either by batch processes (typically in an internal batch mixer) or by a continuous process (typically co-rotating twin-screw extruder).

The dynamic vulcanization process was first claimed by Gessler[3] in 1962 and then further developed by Fisher,[4] Coran et al.[5,6] and Sabet Abdou-Sabet and Fath.[7] TPVs based on EPDM/PP blends are the most important from a commercial point of view, although TPVs based on IIR/PP,[8] NR/PP[9] and NBR/PP[2] blends are also commercially available.
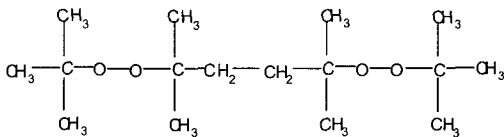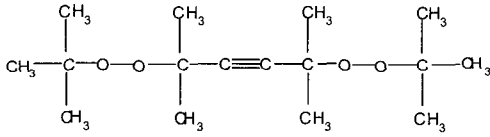
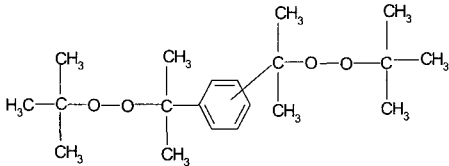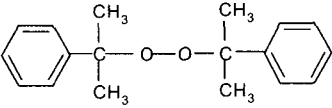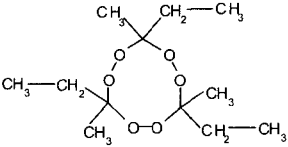† 대표저자(*e-mail : j.w.m.noordermeer@ct.utwente.nl*)

These systems show a close match in overall pro-
perties with regularly cured rubbers within a hard-
ness range of Shore A 40-90.

Several crosslinking agents have been employed
to crosslink the EPDM phase in PP/EPDM blends,
e.g., activated sulfur, co-agent assisted peroxides,
activated phenol-formaldehyde resins (resol), plati-
num catalyzed hydrosiloxane, vinyltrialkoxysilane/
moisture, bisazide and catalyzed quinonedioxime

etc. The objective of the present work is to widen
the possible use of peroxides in the production of
TPVs. The main advantages of peroxide crosslinking
in comparison with e.g., sulfur cure are:
- Ability to crosslink unsaturated as well as satu-
  rated rubbers
- High temperature resistance; and
- Good compression set properties, particularly at
  elevated temperatures.[10]

Table 1. Commercial names and chemical names / structures of peroxides employed

Commercial name	Chemical name / structure
Trigonox 101-40D (40%) (di-alkyl type)	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane
Trigonox 145-45B (45%) (di-alkyl type)	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3
Perkadox 14-40B (40%) (alkyl-aralkyl type)	Di(tert-butylperoxyisopropyl)benzene
Perkadox BC-40B (40%) (di-aralkyl type)	Dicumyl peroxide
Trigonox 301 (40%) (cyclic type)	3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxane

When peroxide is added to a PP/EPDM blend, two competing processes take place simultaneously: EPDM crosslinking and polypropylene degradation by β-scission.[11,12] There is a need for a proper peroxide in combination with a suitable co-agent for PP/EPDM TPVs to diminish the extent of PP degradation and improve the degree of EPDM cross-linking. The objective of this work is to investigate the effect of different types of peroxides on the properties of PP/EPDM TPVs.

II. Experimental

1. Materials

Ethylidene norbornene (ENB)-containing EPDM rubber, which includes 50 wt % of paraffinic oil, was obtained from DSM Elastomers, the Netherlands. The EPDM contains 63 wt % of ethylene and 4.5 wt % of ENB; it has a Mooney viscosity, ML 1+4 @ 125℃ of 52. Polypropylene was obtained from DSM Polypropylenes, the Netherlands. The melt flow index of the PP, measured at 230℃ and 2.16 kg is 0.3 g /10 min. Several types of peroxides, obtained from Akzo Nobel, the Netherlands, were employed for this study. The commercial names and chemical names / structures of the five peroxides under investigation are given in Table 1.

The typical crosslink temperature of all these peroxides[10] is in between 170-185℃. Triallyl cyanurate, TAC (50%) (Perkalink® 300) was also obtained from Akzo Nobel. Two stabilizers, Irganox® 1076 and Irgafos® 168 were obtained from Ciba Geigy.

2. Preparation of pp/epdm tpvs

The TPV composition employed is shown in Table 2. The experimental variable is the level of peroxide curing agent. All TPVs were mixed by a batch process in a Brabender Plasti-Corder PL-2000, having a mixing chamber volume of 50 cc. The mixer temperature was kept at 180-190℃ with a constant rotor (cam type) speed of 80 RPM. Poly

Table 2. TPV Composition

Component	Phr
EPDM	200.0
PP	50.0
Irganox 1076	0.4
Irgafos 168	0.4
Peroxide (40% or 45%)	Varying doses (0.0 - 7.0)
Perkalink 300 (TAC) (50%)	0.4

propylene, stabilizers (Irganox 1076 and Irgafos 168) and EPDM Rubber were first mechanically melt-mixed. After 4 minutes of mixing, the co-agent (TAC) was added, followed by the peroxide. The mixing was continued for another 5 minutes to complete the vulcanization process. Vulcanization was monitored by the mixing torque or by the mixing energy consumption during the mixing process. Immediately after mixing, the composition was removed from the mixer and while still molten, passed once through a cold two-roll mill to achieve a sheet of about 2 mm thick. The sheet was cut and pressed (2 mm thick) in a compression molding machine (WLP 1600/5*4/3 Wickert laboratory Press at 210℃, 4 minutes and 125 bar pressure). Aluminum foil was placed between the molded sheet and the press plates. The sheet was then cooled down to room temperature under pressure. Test specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

3. Testing procedures

Tensile tests were carried out on dumb-bell shaped specimens (Type 2) using a Zwick Tensile Testing machine Z020 at a constant cross-head speed of 500 mm / min (ISO 37). The Young's modulus was determined from the initial slope of the stress-strain curve (0.1 to 0.25 % of strain) at a cross-head speed of 50 mm / min.

Compression set tests were performed at 70℃ for 22 hours (ISO 815).

Hardness of the samples were measured by a

Zwick Hardness-meter (Shore A Type, ISO R868).

A Rubber Process Analyzer RPA-2000 (Alpha Technologies), which is a type of moving die rheometer, was used to measure the cure-characteristics of the different types of peroxides (at a fixed concentration of 9 milli-equivalents relative to the EPDM) in pure EPDM-compounds (no PP added) at 180℃.

Ⅲ. Results

The effects of the different types of peroxides were investigated using a fixed amount of 4 phr co-agent TAC.

Figure 1 shows the tensile strength as a function of concentration of the peroxides (milli-equivalents per 100 grams of pure EPDM rubber) for the different types of peroxide-cured PP/EPDM TPVs. In most cases it is seen that with increasing concentration of the peroxide the tensile strength first increases, then reaches a plateau at a concentration of 9 milli-equivalents of peroxide. Perkadox BC-40B reaches the highest plateau whereas Trigonox 145-45B stops at the lowest level. Trigonox 301 is the overall lowest, but does not reach a plateau and keeps on increasing.

Figure 2 shows the elongation at break as a function of concentration of the peroxides. It is seen that with increasing concentration of the peroxide the elongation at break decreases. With respect to the elongation at break, overall little difference between the various peroxides is noticed; Perkadox BC-40B shows the highest value whereas Trigonox 145-45B shows the lowest levels, except for Trigonox 301, which shows very high elongation at break relative to the others.

In Figure 3 the Young's modulus as a function of concentration of the peroxides is given. In most cases, the Young's modulus increases with increasing concentration of the peroxide, then reaches a plateau at a concentration of 9 milli-equivalents of peroxide. Overall little difference between the various peroxides is observed; Trigonox 301 is the
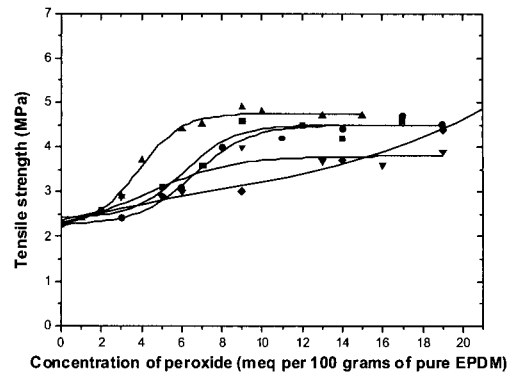

Figure 1. Tensile strength as a function of concentration of peroxides: ▲, Perkadox BC-40B; ■, Perkadox 14-40B; ●, Trigonox 101-40D; ▼, Trigonox 145-45B; and ◆, Trigonox 301.
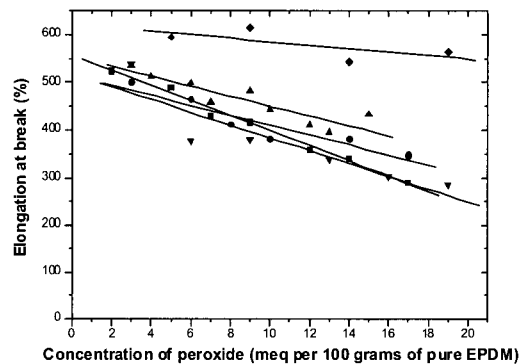

Figure 2. Elongation at break as a function of concentration of peroxides. Symbols as in figure 1.
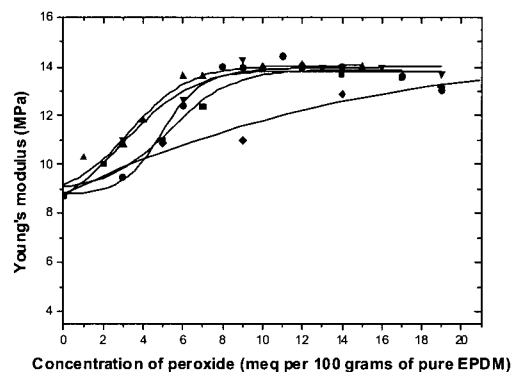

Figure 3. Young's modulus as a function of concentration of peroxides. Symbols as in figure 1.
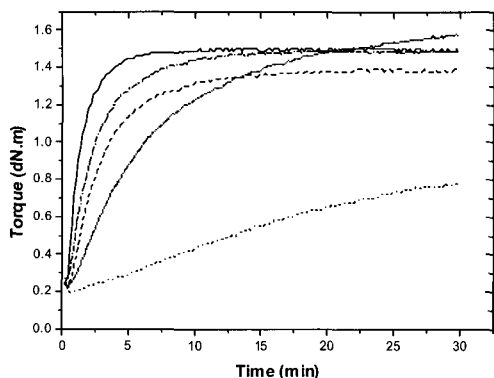
Figure 4. Rheograms for different types of peroxide-cured EPDM vulcanizate at 180℃ : —, Perkadox BC-40B; —.—., Perkadox 14-40B ; ----, Trigonox 101-40D; ......, Trigonox 145-45B; and . . . ., Trigonox 301.
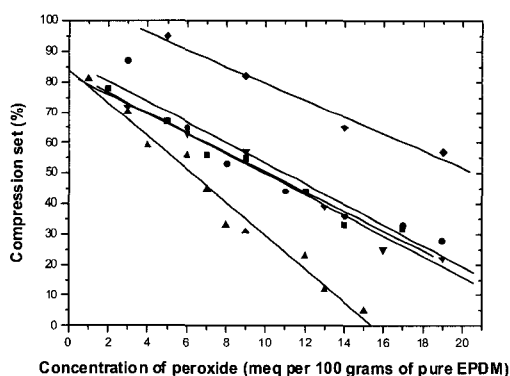

Figure 5. Compression set as a function of concentration of peroxides. Symbols as in figure 1.

overall lowest, but does not reach a plateau and keeps on increasing.

An attempt can be made to interpret the results of the Young's modulus in peroxide-cured TPVs in terms of the delta torque values (maximum torque - minimum torque), obtained from RPA rheograms on equivalent EPDM-compounds with 9 milliequivalents of peroxide added. This correlates with the cross-linking efficiency of the peroxides, which is defined as the number of chemical crosslinks formed per mole-equivalent of peroxide decomposed. The maximum theoretical number is fixed to 100 %, assuming that one mole-equivalent of
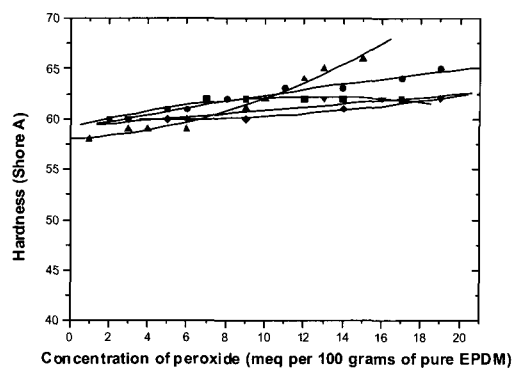

Figure 6. Hardness as a function of concentration of peroxides. Symbols as in figure 1.

peroxide results in one crosslink. Figure 4 shows the performance of the peroxides obtained from the rheograms of the 'equivalent' thermoset EPDM vulcanizates using the RPA at 180(C.

Compression set as a function of concentration of peroxides is shown in Figure 5. With increasing concentration of peroxide the value of the compression set decreases. Perkadox BC-40B is the best, whereas Trigonox 301 is the worst. No significant difference is seen for the other three.

Figure 6. shows the hardness versus the concentration of peroxides. Only a small increase in the hardness values is noticed. The average values of the hardness vary in between 60-65 Shore A. Perkadox BC-40B tends to increase at higher peroxide concentrations, whereas Trigonox 301 is more or less in the same line with the others.

Ⅳ. Discussion

EPDM/PP blends essentially are a two-phase system, where the EPDM-phase has a slightly different solubility parameter than PP. At the temperature where the addition of the peroxide is made, the solubility parameter of the latter will be of great importance for which of the two phases it is most preferred: the EPDM-phase to perform crosslinking or the PP-phase, where degradation of the PP will mainly occur. Therefore, it is an important question

with the series of peroxides investigated in this paper to obtain an impression about the distribution of all peroxides over the two phases.

Solubility parameters (δ) of non-electrolytes can be determined from their cohesive energy density (CED) and consequently their heat of vaporization:

$$\delta = (CED)^{1/2} = \left\{ \frac{H_v - RT}{V_m} \right\}^{1/2} \tag{1}$$

where H_v = heat of vaporization, R = gas constant, T = absolute temperature and V_m = molar volume.

However, as it is very difficult to measure the solubility parameters of the different components at the mixing temperature, an attempt was made to calculate those. Solubility parameter can be calculated using group contribution methods, which are based on additive contributions of different functional groups. Using the values of molar attraction constants (based on heat of vaporization values) given by Small, the solubility parameters of different peroxides were calculated by Hogt.[13] The solubility parameters were also experimentally determined by Hogt from the molar heats of vaporization of various peroxides using a differential scanning calorimeter operating at a reduced pressure of 2 mbar and at a heating rate of 5K min.[-1] For

most peroxides, an excellent correlation was found between the solubility parameters determined experimentally and those calculated according to Small's group contribution method for a temperature of 25℃: Table 3. The calculation of the solubility parameters by the method of Small gave values of 16.6 $(J/cm^3)^{1/2}$ for PP and 17.2 $(J/cm^3)^{1/2}$ for the EPM copolymer (70-80 wt % ethylene),[14] also at 25℃. In order to correlate these values at 25℃ now with the mixing temperature, the solubility parameter values of the peroxides at a mixing temperature of 180℃ were calculated using the following equation[15]:

$$\ln \delta_T = \ln \delta_{298} - 1.25\alpha \, (T\text{-}298) \tag{2}$$

where α = the co-efficient of linear thermal expansion of the peroxides. These were estimated from density measurements[13] up to 80℃ and were about $10^{-3} \, K^{-1}$. The solubility parameter values of PP and EPDM at the higher temperature of 180℃ were calculated using the following equation[16]:

$$\ln \delta_T = \ln \delta_{298} - \alpha \, (T\text{-}298) \tag{3}$$

As the co-efficient of linear thermal expansion for PP a value of 6.3 $\times$ $10^{-4} \, K^{-1}$ was taken[17] and 2.3

Table 3. Solubility parameters of polymers and peroxides at 25℃ and 180℃

Type of Polymer/ peroxide	Molar volume, (cm^3/mole)	Heat of vaporization, (kj/mole)	Solubility parameter at 25℃ (Exp.) $(J/cm^3)^{1/2}$	Solubility parameter at 25℃ (Calc.) $(J/cm^3)^{1/2}$	Solubility parameter at 180℃ (Calc.) $(J/cm^3)^{1/2}$
EPDM				17.2	16.6
PP				16.6	15.1
Perkadox BC-40B	260	84.1	17.7	17.7	14.6
Perkadox 14-40B	358	79.3	14.6	15.5	12.8
Trigonox 101-40D	335	66.5	13.8	14.1	11.6
Trigonox 145-45B	324	76.8	15.1	13.9	11.5

$\times$ 10^{-4} K^{-1} for EPDM.[18] Table 3 gives the values of the experimental as well as calculated solubility parameters of the polymers and peroxides at 25 and 180℃.

For all peroxides, their solubility parameters are lower than for PP and even more so for EPDM. Consequently, there is the tendency for the peroxide to preferably partition towards the PP phase. Higher solubility parameters of the peroxides correlate with a decreased difference with the solubility parameters of EPDM and correspondingly a higher tendency to partition towards EPDM.

The decreasing order of the solubility parameters of the peroxides parallels the same order in the tensile strength of PP/EPDM TPVs, as shown in figure 7: it shows the correlation between the tensile strengths of the PP/EPDM TPVs and the solubility parameters of the corresponding peroxides.

The effect of different types of peroxides at a fixed concentration of peroxide on the Young's modulus of PP/EPDM TPVs can be partially correlated with the delta torque values, as shown in the figure 8. It should be noted however that the latter was measured by a static vulcanization in absence of PP and high shear. This is not exactly a one-to-one equivalence to dynamic vulcanization due to the lack of high shear and longer time scales which translate to a different crosslinking efficiency.

Similarly, the higher extent of crosslinking in the EPDM phase results in a better elastic recovery and therefore lowers the compression set.

V. Conclusions

The physical properties (tensile strength, elongation at break, Young's modulus compression set and hardness) change significantly with the chemical nature of peroxides and the extent of crosslinking at a fixed PP/EPDM blend ratio. Solubility parameters of the polymers and of the peroxides turn out to play an important role in determining the physical properties. The tensile strength of the TPVs with the various peroxides can be related to the
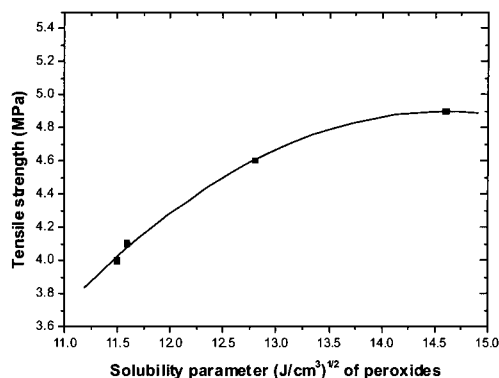

Figure 7. Tensile strength of PP/EPDM TPVs as a function of solubility parameter of the peroxides.
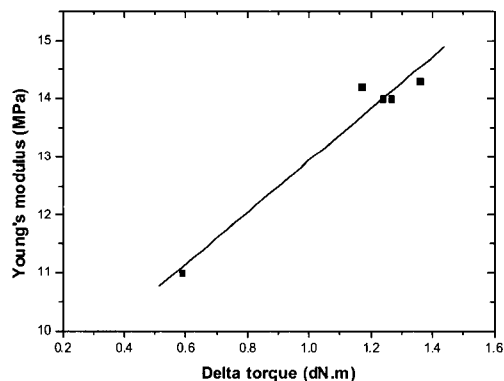

Figure 8. Young's modulus of PP/EPDM TPVs as a function of delta torque.

solubility parameters of the various components: the closer the solubility parameter of the peroxide to that of the EPDM, the higher the tensile strength. On the other hand, the Young's modulus of peroxide-cured TPVs can be correlated with the delta torque values of RPA measurements on equivalent thermoset EPDM vulcanizates. This corresponds to the crosslinking efficiencies of the peroxides. Dicumyl peroxide (Perkadox BC-40B), out of five different types of peroxides for PP/EPDM TPVs, gives the best balance of all properties. 3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxane (Trigonox 301) is the worst.

Acknowledgement

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