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Thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends: Selection of optimal peroxide type and concentration in relation to mixing conditions

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Abstract

A proper balance between degree crosslinking of ENR and degradation of PP-phase, and the tendency of peroxide to form smelly by-products, in particular acetophenone are investigated on a 60/40 ENR/PP TPV. Four types of peroxides were used at two mixing temperatures: 160 and 180 °C. The maximum and final mixing torques are clearly related to the intrinsic decomposition temperature of the particular peroxide used, where DCP and DTBPIB turn out to be effective at 160 °C, whereas the other two type of peroxides require a higher temperature of 180 °C. The best mechanical properties are obtained at lower mixing temperature with DCP and DTBPIB, presumably due to less degradation of the PP and ENR. Unfortunately, these two types of peroxides form more smelly by-products and blooming than those of the DTBPHY and DTBPH. Dependent on the requirements of the pertinent application, a balanced selection needs to be made between the various factors involved to obtain an optimal product performance of these ENR/PP TPVs.
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1. Introduction

Thermoplastic vulcanizates (TPVs) have become very well accepted as thermoplastic elastomers since their introduction in 1981. These materials have the processing characteristics of a thermoplastic and the functional performance of a conventional vulcanized rubber. The best way to prepare TPVs is through dynamic vulcanization, wherein the elastomer is preferentially vulcanized under dynamic shear to generate finely dispersed micron-sized elastomer particles of a high crosslink density embedded in a thermoplastic matrix [1–3]. The dynamic vulcanization process was first described by Gessler and Haslett [4] in 1962 and later developed by Fisher [5] and Coran and Patel [6,7]. This discovery

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was further advanced by Abdou-Sabet and Fath through the use of preferred curing agents to achieve improvement in elastomeric properties and flow characteristics, which led to a successful commercialization of dynamic vulcanization technology [8,9].

There is a wide variety of commercially available rubbers and plastics that can be considered for blending and preparation of TPVs. In a previous article in this series we have reported on the effects of peroxide types and mixing conditions on Natural Rubber (NR)/PP TPVs [10]. Epoxidized natural rubber (ENR) is a chemically modified natural rubber. The presence of the epoxide groups in the rubber chain provides it excellent properties such as oil resistance, low gas permeability, good wet grip, and high damping characteristics [11]. The oil resistance of ENR is due to the polarity of the epoxide group. The resistance of ENR to hydrocarbons improves with increasing epoxide level [12,13]. TPVs based on ENR have been investigated trough blending with polar thermoplastics such as poly(vinyl chloride) [14–17], poly(ethylene-co-acrylic acid) [18] and poly(methyl methacrylate) [13]. Furthermore, semi-crystalline thermoplastic polyolefins, especially polypopylene were also studied. Dynamic vulcanization of ENR/PP TPVs was done by using either a sulfur-based system or peroxides [19–22].

The technique of crosslinking rubbers with peroxides has been known for many years. The general advantages of peroxide-based crosslinks are good high temperature resistance, good elastic behavior in particular compression set, and no discoloration of the finished products [23,24]. The rate at which peroxide crosslinking takes place is dependent on the decomposition temperature of the selected peroxide, because the initial and rate determining step in the crosslinking process is the first-order formation of free alkoxy radicals. A proper peroxide should therefore be selected on the basis of its decomposition rate at the approximate processing temperature [25,26].

Another selection criterion for the peroxide type is its tendency to show a blooming effect and decompose into smelly by-products. In particular the formation of acetophenone as by-product of aromatic moieties contained in the peroxide structure is a well-known cause of notorious smell [27,28]. The aromatic nature of peroxides is related to the decomposition temperature of the peroxides, being lower with the higher the aromatic content.

The purpose of the present work is to investigate the effect of different types and concentrations of peroxides in combination with mixing temperatures on the mechanical properties of 60/40 ENR/PP TPV. This is to select the optimal peroxide for these products with respect to mechanical properties and oil resistance. Also the tendency of the peroxides to form smelly by-products in relation to their chemical composition will be considered.

2. Experimental

2.1. Materials

A twenty mole percent epoxide of epoxidized natural rubber (ENR) was synthesized on lab-scale by using a chemical reactor at Prince of Songkla University, Pattani campus, Thailand [21,22]. The polypropylene used in this study was Stamylan P 11E10 with a Melt Flow Index (MFI) of 0.3 g/10 min, measured at 230 °C and 2.16 kg, as obtained from DSM Polypropylenes B.V., the Netherlands. The stabilizers, Irganox® 1076 and Irgafos® 168 were obtained from Ciba Geigy, Switzerland. Four types of peroxides were obtained from Akzo Nobel Polymer Chemicals, the Netherlands. The chemical and commercial names, structures and some general characteristics are given in Tables 1 and 2.

2.2. Mixing and preparation of samples

The formulations of the mixed compounds are given in Table 3. In order to allow for a proper comparison between the peroxides, the amounts of peroxides in the range of 0.0–7.0 phr. were recalculated on the basis of milli-equivalents (meq) of peroxide functionality per 100 g of pure ENR, as will be used furtheron. A blend without curatives (named "CONTROL") was also made. The ENR/PP TPVs were mixed in a laboratory scale Brabender Plastic-Corder PL-2000 internal mixer, with a mixing chamber volume of 50 cm³. The batch size ranged between 38 and 40 g. The mixer was operated at a constant rotor speed of 80 rpm. The temperature setting of the mixer was 160 or 180 °C. The mixing for each batch took 10 min: PP was first added into the mixing chamber and mixed for 1 min; then the stabilizers were fed to the molten PP and one minute later the ENR was added to the mixer; after another 3 min of mixing, the peroxide was added and the mixing continued for another 5 min to complete the dynamic vulcanization process. The produced

Table 1
Chemical/commercial names and structures of the peroxides investigated

Chemical/commercial name	Chemical structure
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (DTBPHY)/Trigonox 145-45B	
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH)/Trigonox 101-40B	
di(tert-butylperoxyisopropyl)benzene (DTBPIB)/Perkadox 14-40B	
Dicumyl peroxide (DCP)/Perkadox BC-40B	

Table 2
General characteristics of the peroxides investigated [30]

Coding	M_w	Temperature (°C) $t_{1/2} = 1$ min	Typical crosslinking temperature (°C)	Crosslink efficiency[a] (%)
DTBPHY	286	194	180	30
DTBPH	290	183	170	41
DTBPIB	338	185	170	52
DCP	270	179	160	50

[a] Crosslink efficiency of the pure grades.

Table 3
Formulations of mixed compounds

Materials		Phr
ENR		100.0
PP		65.0
Stabilizer	11076	0.4
	1168	0.4
Peroxide		Varying dose (0.0–7.0)

TPV was immediately removed from the chamber and sheeted once through a cold two roll mill to obtain a sheet of about 2 mm thickness. The TPVs were stored for 24 h at approximately 4 °C before pressing. The samples were pressed for 5 min in a WLP 1600/5*4/3 Wickert laboratory compression moulding press at a temperature of 190 °C and at a pressure of 12.5 MPa. Subsequently, the samples were cooled down under pressure to room temperature. Dumbbell shaped test specimens were die-cut from the moulded sheets in parallel to the original milling direction and kept at room temperature for 24 h before further testing.

2.3. Mechanical properties

Tensile tests were carried out according to ISO 37 on type 2 dumbbell specimen using a Zwick tensile testing machine ZO2O at a constant cross-head speed of 500 mm/min. Compression sets were tested according to ISO 815 on samples of 6 mm thickness and 13 mm diameter. The set-tests were conducted at temperatures of 23 and 70 °C for 24 h.

2.4. Oil resistance

Oil resistance of ENR/PP TPVs was tested according to ASTM D471 using IRM 903 oil (which is similar to the former ASTM Oil no. 3). Specimens in the form of rectangular having dimensions of $20 \times 20 \times 2$ mm were immersed in the oil at a temperature of 100 °C for 70 h. The test specimens were then removed from the oil, wiped with tissue paper to remove excess oil from the surface, and weighed. The percentage mass swell was calculated as follows:

$$\text{Change in mass } (\%) = [(W_2 - W_1)/W_1] \times 100 \ (\%) \quad (1)$$

where W_1 is initial mass of specimen (g), W_2 is mass of specimen after immersion (g).

3. Results and discussion

3.1. Mixing torques

Figs. 1 and 2 show the mixing torques of the 60/40 ENR/PP TPVs with 10 meq's of the various peroxides, at mixing temperatures of 160 and 180 °C, respectively. They clearly show an effect of the different types of peroxide in relation to the mixing temperatures on the mixing curves of the blends. With respect to the peaks in the torque after adding the peroxides at 300 s, the height of these peaks is related to the amount of crosslinks formed in the rubber phase. A peak does not show in case of the blend without peroxide: CONTROL. The blends with DCP or DTBPIB as curing agents give a stronger effect of crosslinking at 160 °C than the blends

with DTBPH or DTBPHY. The peak for DTBPIB is most pronounced while the blend with DTBPHY shows the lowest peak. On increasing the mixing temperature to 180 °C, the peaks for the blends with DCP or DTBPIB marginally decrease relative to their height at 160 °C and come close to the peaks for the blends with DTBPH or DTBPHY, which in turn are a bit increasing relative to mixing at 160 °C (Fig. 2). In addition, different rates of cure for different types of peroxides can be explained in terms of the half-life time of the corresponding peroxides. That is, the half-life decreases with increasing the mixing temperature. The half-life of peroxides used in this work was reported by Naskar [29] that is in a range from 0.45 to 2.00 min at 160 and 180 °C. Therefore, because of the half-life aspect together with other criterions for peroxide
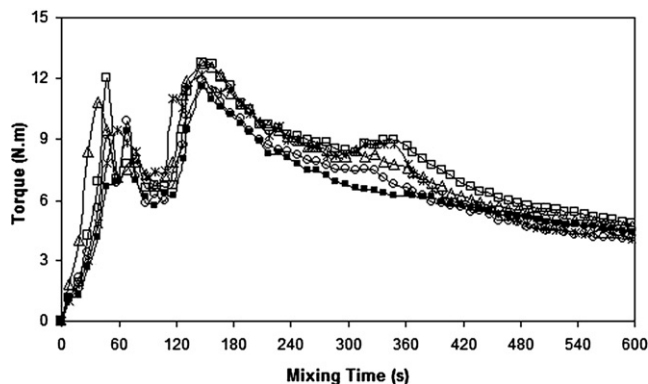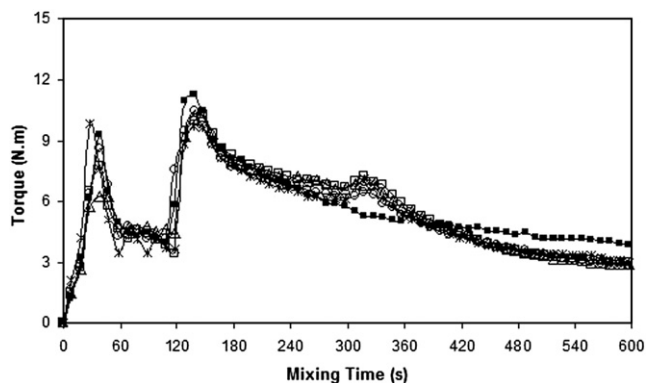

Fig. 1. Mixing torque vs. time for the ENR/PP TPVs at mixing temperature of 160 °C, with fixed concentration of peroxides of 10 milliequivalents peroxide functionalities, including Control without peroxide; —■—: CONTROL; —◇—: DTBPHY; —△—: DTBPH; —□—: DTBPIB; —✕—: DCP.

Fig. 2. Mixing torque vs. time for the ENR/PP TPVs at mixing temperature of 180 °C, with fixed concentration of peroxides of 10 milliequivalents peroxide functionalities, including Control without peroxide; —■—: CONTROL; —◇—: DTBPHY; —△—: DTBPH; —□—: DTBPIB; —✕—: DCP.
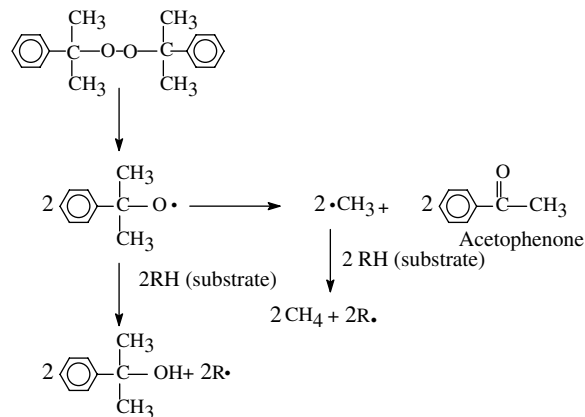
crosslinking resulted in all peroxides decomposed and reached the maximum torque within 1 min of mixing. Also the rate of crosslinking of TPVs at 180 °C is definite faster than those at 160 °C due to the shorter half-life times of the peroxides. Time dependency of the torque using various types of peroxides is another significant parameter. It is seen that the TPV with DTBPHY reaches the maximum value with the shortest time (i.e., less than 30 s). The time used to obtain the maximum torque for various types of TPVs is ordered as follows: DTBPHY < DTBPH < DCP < DTBPIB. This corresponds to the rank of the cure rate indices (CRI) of these types of peroxides cured EPDM vulcanizates [29]. It is therefore concluded that the peroxide with higher rate of cure exhibits shorter time to approach the maximum torque. These results correlate well with the typical crosslinking temperatures and crosslink efficiencies of each peroxide and also agree with the relative amounts of decomposition products, as shown in Tables 2 and 4. The typical crosslinking

Table 4
Relative amounts of decomposition products from various peroxides in pentadecane

Name of peroxide	Experimental temperature (°C)	Decomposition products	Relative amount (mol/mol peroxide)
DTBPHY	180	Methane	0.57
		Carbon dioxide	0.02
		Acetone	0.57
		Tert-butanol	1.39
		2,5-Dimethyl-2,5 dihydroxyhexyne-3	0.79
DTBPH	145	Methane	0.31
		Ethane	0.40
		Acetone	1.62
		Tert-butanol	1.65
		Tert-amylalcohol	0.23
DTBPIB	155	Tert-butanol	1.83
		Acetone	0.13
		Methane	1.10
		Di-(hydroxy-i-propyl) Benzene	0.30
		Acetyl hydroxy-i-propyl Benzene	0.54
		Diacetyl benzene	0.14
DCP	160	Methane	0.91
		Acetophenone	0.91
		2-Phenylpropanol-2	1.06
		α-Methyl styrene	0.01
		Water	0.01

temperature is the temperature at which about 90% of crosslinking activity occurs within 12 min [30]. The relative amounts of decomposition products refer to the chemical compounds formed after decomposition under high temperature. Not all of the decomposition products from a peroxide can cause crosslinking by abstraction of hydrogen atoms from a polymer chain, but only some of them can do. Schemes 1–4 present the main mechanisms of each peroxide to generate crosslinking. For DCP, for example, the actual crosslinking occurs by 2-phenylpropanoxy radicals and even mainly by methyl radicals: Scheme 1, while for DTBPIB as seen in Scheme 2, the decomposition products which can abstract hydrogen atoms are tert-butoxy, methyl, and di-(hydroxy-i-propyl) benzene radicals. With higher amounts of decomposition products, the blend-type peroxides provide a higher crosslink density. DCP and DTBPIB have typical crosslinking temperatures of 160 and 170 °C, respectively, provide a high crosslink efficiency, but also lead to relatively high amounts of decomposition products. On the other hand DTBPH and DTBPHY have typical crosslinking temperatures of 170 and 180 °C, respectively. This combined with a lower crosslink efficiency and lower relative amount of decomposition crosslinking products than DCP and DTBPIB, accounts for the lower height of the peaks as seen in Figs. 1 and 2.
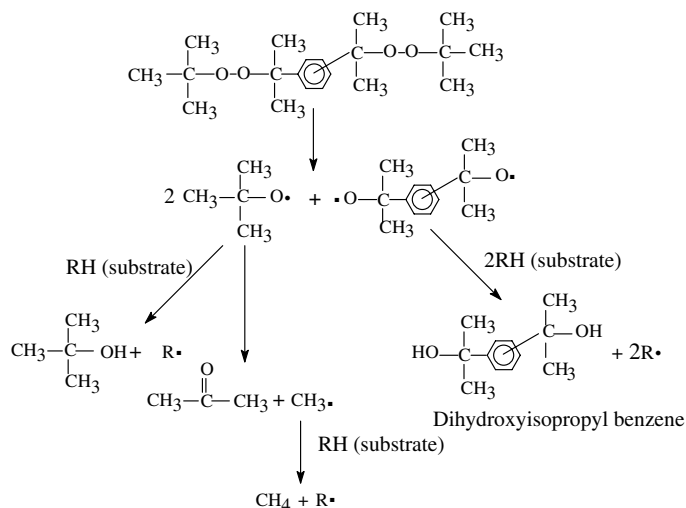
The mixing temperature not only affects the amount of crosslinking, but also enhances degradation of the polymers. The maximum torques after adding the peroxides, and the torques at the end of mixing cycles for the different mixing temperatures are given in Table 5. Polypropylene can easily degrade in the presence of peroxide through β

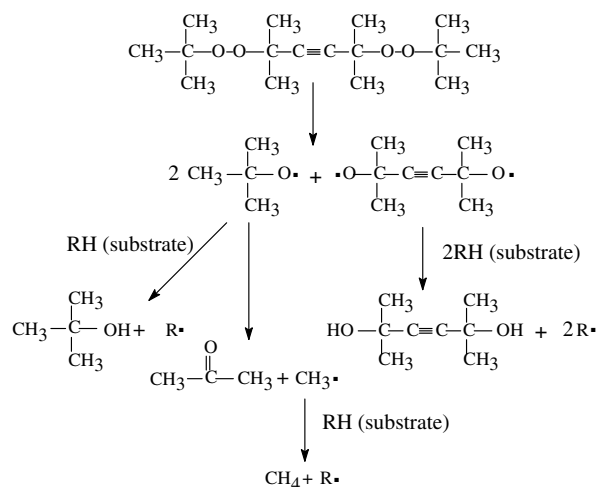Scheme 1. Decomposition mechanism of DCP.

Scheme 2. Decomposition mechanism of DTBPIB.
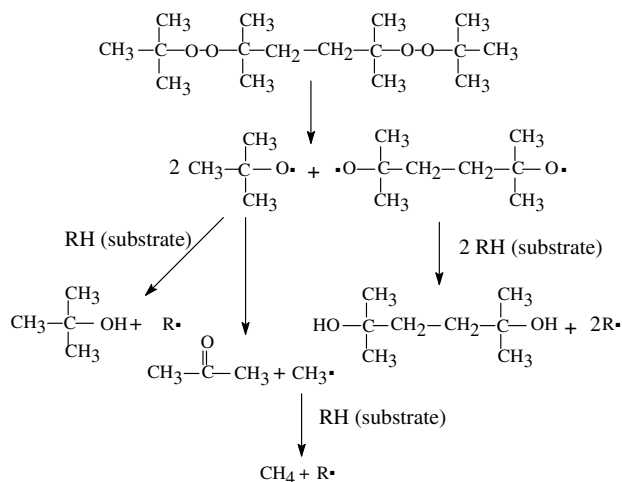
Scheme 3. Decomposition mechanism of DTBPH.

chain-scission. The chain-scission mechanism is shown in Scheme 5. This reaction results in a viscosity decrease of the polypropylene. Similarly, it is well known that NR starts to degrade substantially if temperatures of 180 °C and higher are reached. It is noted that the stabilizers are used to prevent the degradation of polymers and to effectively extend the useful lifetime of polymers. In general, the use of stabilizers in combination with a peroxide curing system needs special care because stabilizers are free radical scavengers and they can also interfere with peroxide vulcanization chemistry. They typically donate very active hydrogen atoms to the chain-propagating peroxy, alkoxy and hydroxyl radicals

of peroxides, resulting in a reduced crosslinking efficiency of the peroxide. However, combination of Irganox® 1076 (i.e., hindered phenol type) and Irgafos® 168 (i.e., phosphate type) stabilizers used in this work was the good stabilizer package, since it provided the optimum protection against oxidation and had little effect on the peroxide cure according to the works of Dluzneski [29] and Naskar [29]. For the stabilizer present in the PP (i.e., Stamylan), the hindered phenol type antioxidant or synergistic antioxidant blend are used to ensure thermal and processing stability during storage, processing and end-use. The contained stabilizer in the PP protected the PP from peroxide induced chain-scission

Scheme 4. Decomposition mechanism of DTBPHY.

reaction. Therefore, it has a little affect on peroxide vulcanization of the TPVs. The degradation of the ENR and PP can therefore best be seen at the mixing temperature of 180 °C. For all TPVs, irrespective of the type of peroxide used, the ending torques are well below the one for the CONTROL, indicative of a significantly lower viscosity. A closer look at the ending torques obtained at 160 °C mixing temperature in Table 5 does not show this

decrease to a significant degree. DCP gives a marginally lower ending torque than the CONTROL, and DTBPIB even a somewhat higher value. As there is no reason to suspect a significantly higher amount of β-scission of PP relative to the crosslinking of ENR by the peroxides due to a different partitioning over the ENR- or PP-phases, the lower ending torques relative to the CONTROL at 180 °C must be the result of disproportionally more degradation of the ENR and PP by the high mixing temperature in combination with the presence of the peroxides.

3.2. Mechanical properties

The mechanical properties of the ENR/PP TPVs cured with various types and concentrations of peroxides at different mixing temperatures are given in Figs. 3–6. Fig 3 shows the tensile strength of the ENR/PP blends as a function of concentration of peroxides. There is a clear trend of increasing tensile strength when the concentration of crosslinking agents increases at both mixing temperatures. At 160 °C the TPVs prepared using DCP or DTBPIB as curatives provide superior tensile strength relative to the blends crosslinked with DTBPH or DTB-PHY at all concentrations. It is clear, that the

Table 5
Mixing torques

| | Types of peroxide (at 10 milli-equivalents) | | | | |
	CONTROL	DTBPHY	DTBPH	DTBPIB	DCP
Mixing Temperature 160 °C					
Maximum Torque after adding peroxide (Nm)	–	7.50	8.26	8.95	8.78
Torque at the end of mixing (Nm)	4.40	4.10	4.61	4.86	4.13
Mixing Temperature 180 °C					
Maximum Torque after adding peroxide (Nm)	–	6.48	6.85	7.26	7.13
Torque at the end of mixing (Nm)	3.86	2.84	2.90	3.03	3.04
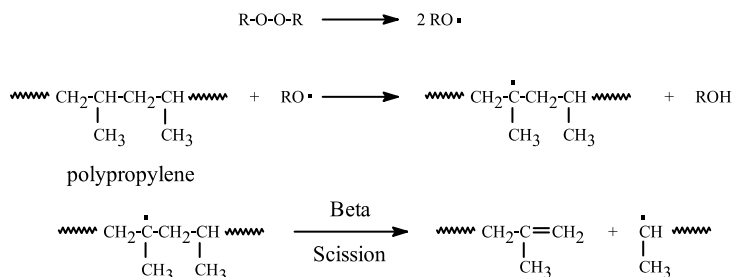
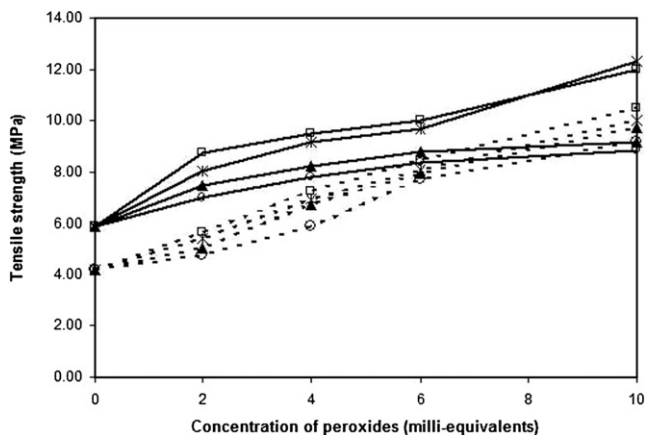Scheme 5. Simplified reaction scheme for peroxide degradation of PP by β-scission.

Fig. 3. Tensile strength of ENR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures, (○): DTBPHY; (▲): DTBPH; (□): DTBPIB; (×): DCP; —: 160 °C; ----: 180 °C.
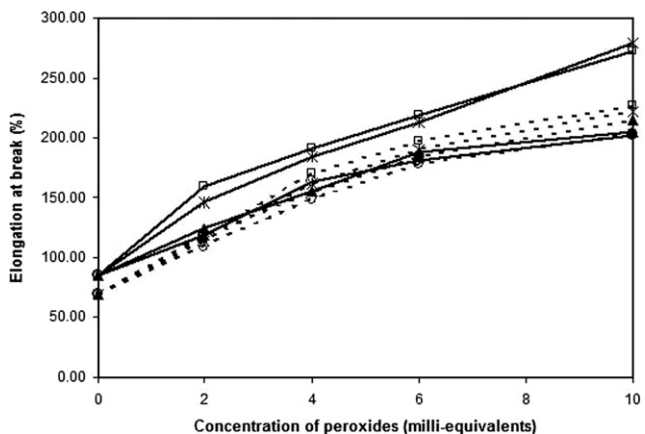

Fig. 4. Elongation at break of ENR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures, (○): DTBPHY; (▲): DTBPH; (□): DTBPIB; (×): DCP; DCP; —: 160 °C; ----: 180 °C.
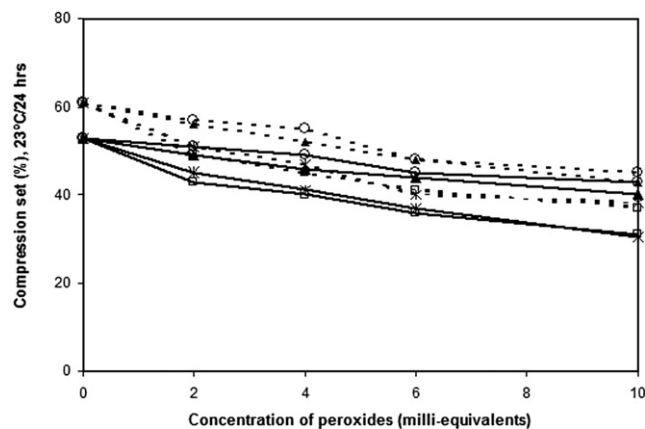

Fig. 5. Compression set at 23 °C/24 hrs of ENR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures, (○): DTBPHY; (▲): DTBPH; (□): DTBPIB; (×): DCP; DCP; —: 160 °C; ----: 180 °C.
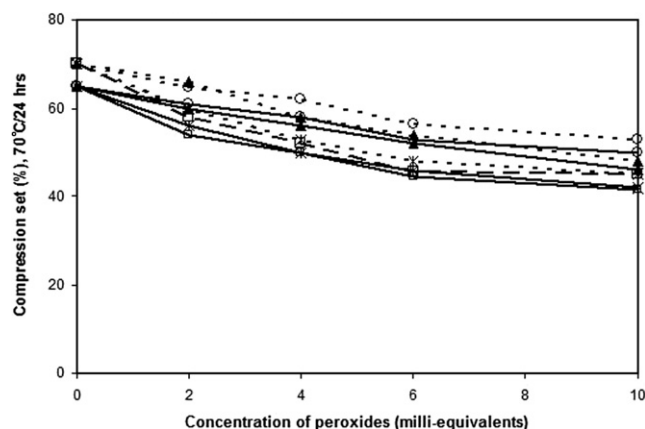
Fig. 6. Compression set at 70 °C/24 hrs of ENR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures, (○): DTBPHY; (▲): DTBPH; (□): DTBPIB; (×): DCP; DCP; —: 160 °C; ----: 180 °C.

mixing temperature of 160 °C is still too low relative to the decomposition temperatures for DTBPH and DTBPHY. At the mixing temperature of 180 °C the blends with DTBPH and DTBPHY also increase in tensile strength and come close to the results for DCP and DTBPIB. The tensile strength for all levels of all peroxides are more or less comparable, but significantly lower than those of the DCP and DTBPIB mixed at 160 °C. Also the CONTROL without peroxide, mixed at 180 °C gives significantly lower tensile strength than that of the TPVs mixed at 160 °C. In any case, the TPVs with 10 meq's of DTBPIB show overall the highest tensile strengths for both mixing temperatures.

A plot of elongation at break versus concentration of peroxides is shown in Fig. 4. The trends of elongation at break of the TPVs agree with the trends in tensile strength. The elongation at break of all TPVs increases with increasing concentrations of peroxide. At the mixing temperature of 160 °C the TPVs prepared with DCP and DTBPIB show a higher elongation at break than the TPVs prepared using DTBPH and DTBPHY. Similarly, when the mixing temperature is increased to 180 °C, the elongation at break of all TPVs more or less merge for all peroxides used, but show some decrease relative to 160 °C mixing temperature. The TPVs with 10 meq's of DTBPIB again show overall the highest elongation at break for both mixing temperatures.

Compression set data at testing temperatures of 23 and 70 °C for 24 h are plotted in Figs. 5 and 6, respectively. The effect of mixing temperature combined with the selection of the peroxide type shows some discrimination. The blends with DCP or

DTBPIB show better set values at both mixing temperatures than the blends with DTBPH or DTBPHY, which corresponds with the trend of tensile strength.

3.3. Oil resistance

The effect of peroxide loading on mass swell of the TPVs in IRM 903 oil are shown in Fig. 7. Presence of crosslinks in TPVs decreases the percent of change in mass swell. DCP and DTBPIB, which give the highest amounts of crosslinks, show indeed the best oil resistance.

According to all results, DTBPIB shows the best overall balance of the crosslinking agents on properties of the TPVs, while DTBPHY is the worst. It should be noted, that the optimal processing temperature of DCP and DTBPIB is 160 °C. We tend to interpret the better physical properties obtained at 160 °C for DCP and DTBPIB as a more optimal balance between the amount of crosslinking of the ENR rubber phase, versus the degree of degradation of the PP and of the ENR by radical scission of the molecular chains. Practically, a disadvantage is that the TPVs prepared with DCP give a bad smell of acetophenone in the end product. This smell is due to the decomposition of peroxides with an aromatic ring in the structure. On the other hand, the TPVs prepared with DTBPIB lead to blooming phenomena due to the formation of dihydroxy isopropyl benzene, because of its limited solubility in the rubber matrix.

The TPVs prepared using DTBPH and DTBPHY are not as good for properties as prepared using DCP and DTBPIB. However, the first two
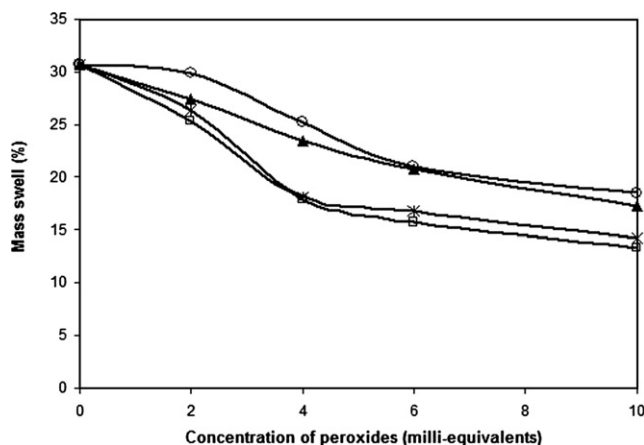
Fig. 7. Oil resistance of ENR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures, ─⊕─: DTBPHY; ▲: DTBPH; ─□─: DTBPIB; ─×─: DCP.

types of peroxides do improve tensile and set properties for sufficiently high mixing temperature and do not result in a bad smell and blooming phenomena at the end. Therefore, a selection of the proper peroxide for this application remains a matter of compromises.

4. Conclusions

Strong effects are seen of the types and concentrations of various peroxides, in combination with mixing temperatures, on the properties of the 60/40 ENR/PP TPVs. Out of the selection of four peroxides, the two showing a significant decomposition in time at a mixing temperature of 160 °C result in the best tensile properties. Increasing the mixing temperature to 180 °C makes all peroxides react equally well, however at the cost of a decrease in tensile properties, for all peroxide levels employed. A synergistic effect between type and concentration of the various peroxides and mixing temperature is clearly observed for all properties investigated. The results are interpreted in terms of the balance between crosslinking of the ENR phase, versus degradation of the PP and ENR by radical scission of the molecular chains. The selection of the proper peroxide for the ENR/PP TPVs turns out to be a point of major consideration.

Acknowledgements

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