NR/PP Thermoplastic Vulcanizates: Selection of Optimal Peroxide Type and Concentration in Relation to Mixing Conditions

A. Thitithammawong,[1,2] C. Nakason,[1] K. Sahakaro,[1] J. W. M. Noordermeer[2]

[1]Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand
[2]Department of Rubber Technology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT: Thermoplastic vulcanizates (TPVs) from natural rubber (NR) and polypropylene (PP) were studied, prepared by dynamic vulcanization during melt mixing, using various peroxides to crosslink the rubber phase. The objective was to find a proper balance between degree of crosslinking of the rubber and degradation of the PP-phase, and the tendency of the peroxide to form smelly by-products, in particular acetophenone. Four types of peroxides were investigated: 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexyne-3 (DTBPHY), 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DTBPH), di(*tert*-butylperoxyisopropyl) benzene (DTBPIB), and dicumyl peroxide (DCP), at two mixing temperatures: 160 and 180°C for a 60/40 NR/PP TPV. 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 require a higher temperature of 180°C. The best mechanical properties, tensile strength, elongation at break and compression set are obtained at lower mixing temperature with DCP and DTBPIB, presumably due to less degradation of the NR and PP. Unfortunately, these two peroxides form more smelly by-products than 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 NR/PP TPVs. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2204–2209, 2007

Key words: thermoplastic vulcanizates; natural rubber; polypropylene; peroxide; mechanical properties

INTRODUCTION

Thermoplastic polyolefins (TPOs) and thermoplastic vulcanizates (TPVs) have wide industrial applications, where TPVs possess the required characteristics to substitute some thermoset rubbers used in automotive, household, and construction applications. A basic requirement for TPVs is the creation of crosslinks, which normally are formed *in situ* during melt mixing an elastomer with a thermoplastic polymer at elevated temperatures. The resulting blends consist of finely dispersed micrometer-sized elastomer particles of a high crosslink density embedded in a thermoplastic matrix.[1–3] They exhibit the elasticity characteristics of vulcanized rubber at room temperature, but provide thermoplastic processibility above their melting temperatures.[3,4]

Some studies on TPVs based on natural rubber (NR) and polypropylene (PP) have been reported.[5–12] The NR/PP TPVs, developed by the Malaysian Rubber Producers' Research Association (MRPRA), could replace vulcanized rubber in end products where high resilience and strength were not essential, especially impact resistance at low temperature.[13] They could also replace flexible plastics, such as plasticized PVC, ethylene vinyl acetate (EVA), and PP copolymers.[14,15] Various crosslinking systems were employed, peroxides and sulfur systems.[10,16–19]

The technique of crosslinking rubbers with peroxides has been known for long. 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.[20,21] 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.[22,23]

TABLE I
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	

Another selection criterion for the peroxide type is its tendency to decompose into smelly side-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. The aromatic nature of peroxides is related to the decomposition temperature of these peroxides, being lower the higher the aromatic content.

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

EXPERIMENTAL

Materials

Natural rubber (NR) (Air dried sheet; ADS) was received from Khuan Pun Tae Farmer Co-operation, Phattaluang, Thailand. PP 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 ob-

tained 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 I and II.

Mixing and preparation of samples

The formulations of the mixed compounds are given in Table III. To allow for a proper comparison between the peroxides, the amounts of peroxides

TABLE II
General Characteristics of the Peroxides Investigated[24]

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 III
Formulations of Mixed Compounds

Materials	Phr
NR	100.0
PP	65.0
Stabilizer	
I 1076	0.4
I 168	0.4
Peroxide	Varying dose (0.0–7.0)

in the range of 0.0–7.0 phr were recalculated on the basis of milli-equivalents (mequiv) of peroxide functionality per 100 g of pure NR rubber, as will be used later on. A blend without curatives (named ''CONTROL'') was also made. The NR/PP TPVs were mixed in a laboratory scale Brabender Plastic-Corder PL-2000 internal mixer, with a mixing chamber volume of 50 cm^3. 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 1 min later NR 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 TPV was immediately removed from the chamber and sheeted once through a cold two roll mill to obtain a sheet of about 2 mm thick. The TPVs were stored for 24 h at ~4°C before pressing. The samples were pressed for 5 min in a WLP 1600/5*4/3 Wickert laboratory compression molding 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 molded sheets in pararell to the original milling direction and kept at room temperature for 24 h before further testing.

Measurements

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 thick and 13 mm diameter. The set-tests were conducted at temperatures of 23 and 70°C for 24 h.

RESULTS AND DISCUSSION

The mixing torques of the blends with 10 mequiv of the various peroxides, at mixing temperatures of 160 and 180°C, respectively, are shown in Figures 1 and 2. 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. Figure 1 shows that 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. On increasing the mixing temperature to 180°C, as seen in Figure 2, the peaks of the blends with DCP or DTBPIB decrease a little bit relative to their height at 160°C. At 180°C, DTBPH or DTBPHY added into the TPVs increase the amount of crosslinking relative to 160°C, but they are still less pronounced than in the case of using DCP or DTBPIB. These results correlate well with the typical crosslinking temperature and crosslink efficiency of each peroxide, as shown in Table II. The typical crosslinking temperature is the temperature at which about 90% of crosslinking activity occurs within 12 min. DCP and DTBPIB have typical crosslinking temperatures of 160 and 170°C, respectively, and they also provide high crosslink efficiency; they show a good efficiency at 160°C. DTBPH and DTBPHY have typical crosslinking tem-
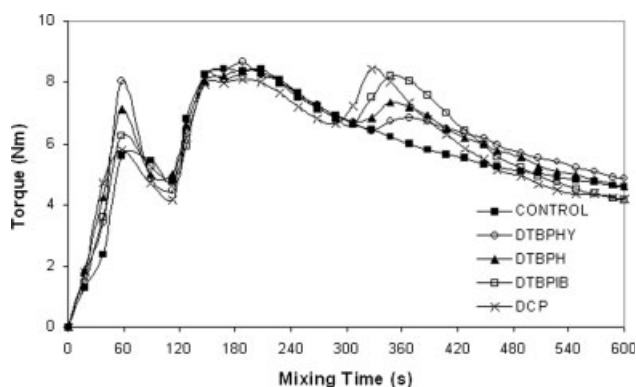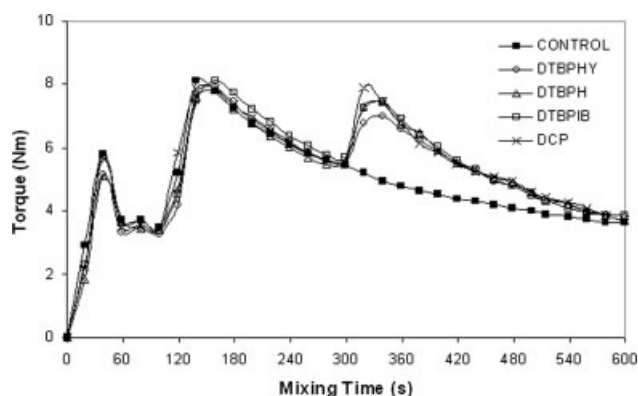

Figure 1 Mixing torque versus time for the NR/PP TPVs at mixing temperature of 160°C, with fixed concentration of peroxides of 10 mequiv peroxide functionalities.

Figure 2 Mixing torque versus time for the NR/PP TPVs at mixing temperature of 180°C, with fixed concentration of peroxides of 10 mequiv peroxide functionalities.

TABLE IV
Mixing Torques

	Types of peroxide (at 10 mequiv)				
	CONTROL	DTBPHY	DTBPH	DTBPIB	DCP
Mixing temperature 160°C					
Maximum torque after adding peroxide (N m)	–	6.88 ± 0.1	7.35 ± 0.0	8.49 ± 0.1	8.45 ± 0.0
Torque at the end of mixing (N m)	4.60 ± 0.0	4.85 ± 0.0	4.61 ± 0.0	4.15 ± 0.2	4.20 ± 0.1
Mixing temperature 180°C					
Maximum torque after adding peroxide (N m)	–	7.28 ± 0.0	7.89 ± 0.0	7.51 ± 0.1	7.91 ± 0.0
Torque at the end of mixing (N m)	3.50 ± 0.1	3.62 ± 0.0	3.91 ± 0.0	3.78 ± 0.0	3.75 ± 0.0

peratures of 170 and 180°C, respectively. This, combined with a lower crosslink efficiency than DCP and DTBPIB, accounts for the lower height of the peaks in Figure 2.

The mixing temperature, however, 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 IV. The degradation of the NR rubber molecules can best be seen in the blends without peroxide: the CONTROLs. The blend without peroxide, mixed at 180°C, has a torque at the end of mixing lower than the one mixed at 160°C. As discussed before, DCP and DTBPIB are good crosslinking agents at 160°C. However, at this temperature, some of their radicals also degrade the PP. Polypropylene degrades in the presence of peroxide through β chain-scission. This reaction results in a viscosity decrease of the PP. Apparently, at 160°C, the viscosity decrease of the PP due to chain scission overrules the viscosity increase due to crosslinking of the rubber phase, resulting in an overall effect of decreased end torque relative to the CONTROL. At 180°C, significant degradation of NR also comes into play, for the CONTROL as well as for the TPVs. The net result here is that all the ending torques are more or less

the same. It is well known that NR reaches the limits of stability at temperatures as high as 180°C.

The mechanical properties of the NR/PP TPVs cured with various types and concentrations of peroxides at different mixing temperatures are given in Figures 3–6. Figure 3 shows the tensile strength of the NR/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 curative provide superior tensile strength relative to the blends crosslinked with DTBPH or DTBPHY at all concentration levels. It is clear that the mixing temperature of 160°C is still too low relative to the decomposition temperatures for DTBPH and DTBPHY. Although at the mixing temperature of 180°C, apparently all peroxides are more or less equally reactive, the values of tensile strength for all levels of all peroxides are more or less comparable, but significantly below those for DCP and DTBPIB mixed at 160°C. Also the CONTROL without peroxide mixed at 180°C gives significantly lower tensile strength values than mixed at 160°C. In any case, the TPVs with 10 mequiv of DTBPIB show overall the highest tensile strengths for both mixing temperatures.
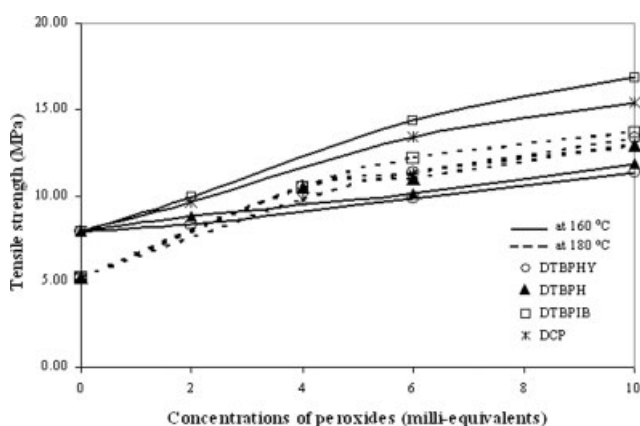

Figure 3 Tensile strength of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures.
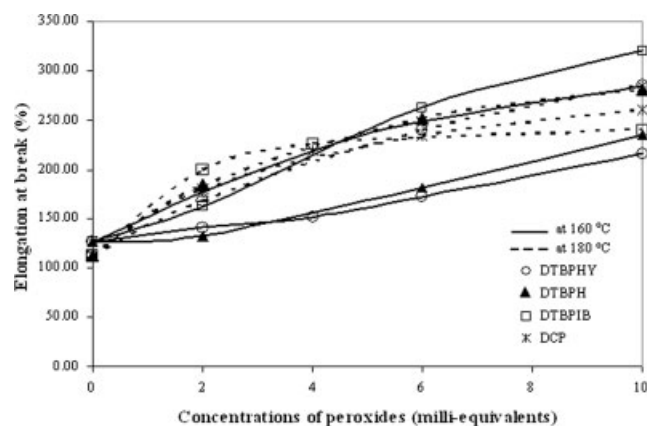

Figure 4 Elongation at break of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures.
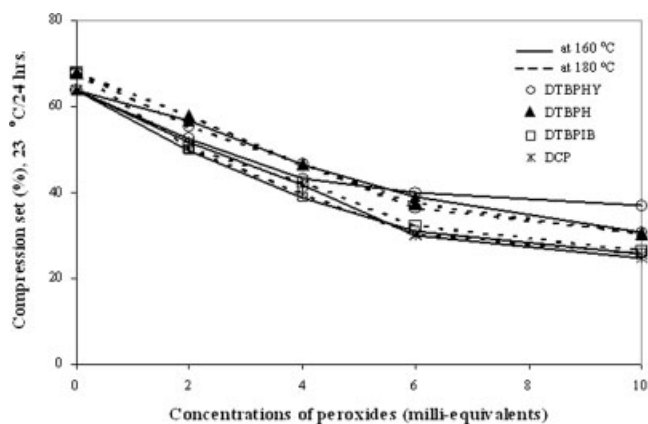
Figure 5 Compression set at 23°C/24 h of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures.

A plot of elongation at break versus concentration of peroxides is shown in Figure 4. The trends of elongation at break of the TPVs are in concord 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 for DTBPH and DTBPHY. Similarly, when the mixing temperature is increased to 180°C, the elongations at break of the TPVs are more or less merge for all peroxides used, but show some decrease relative to 160°C mixing temperature.

Compression set data at testing temperatures of 23 and 70°C for 24 h are plotted in Figures 5 and 6, respectively. The effect of mixing temperature combined with the selection of peroxide type shows little discrimination, apart from some better set values for DCP and DTBPIB at 160°C relative to the others. Apparently, the larger differences in tensile properties are not reproduced in the set-values.
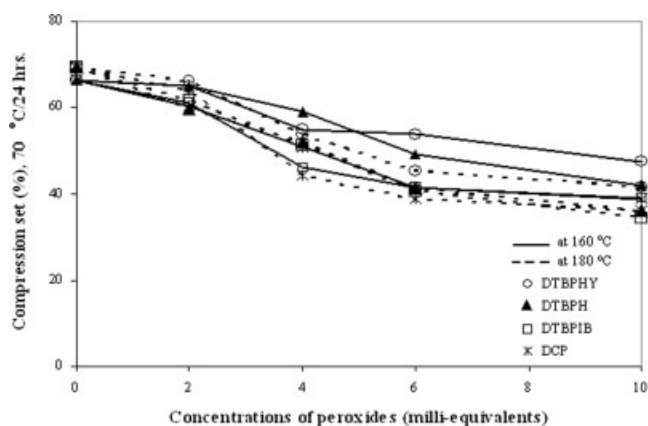

Figure 6 Compression set at 70°C/24 h of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides and mixing temperatures.

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 tensile properties obtained at 160°C for DCP and DTBPIB as a more optimal balance between the amount of crosslinking of the NR rubber phase, versus the degree of degradation of the PP and of the NR by radical scission of the molecular chains. Practically, a disadvantage is that the TPVs prepared with DCP and DTBPIB 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.

But even though DTBPH and DTBPHY are not as good for properties as DCP and DTBPIB, they do improve tensile and set properties for sufficiently high mixing temperature and do not result in a bad smell at the end. So selection of the proper peroxide for this application remains a matter of compromises.

CONCLUSIONS

Strong effects are seen of the types and concentrations of various peroxides, in combination with mixing temperatures, on the properties of 60/40 NR/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: tensile strength and elongation at break. 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 set-properties, this effect is less conspicuous. Irrespective of the mixing temperature and type of peroxide, the set properties generally improve to the same degree with increasing peroxide concentrations.

The results are interpreted in terms of the balance between crosslinking of the NR phase versus degradation of the PP and NR by radical scission of the molecular chains. The selection of the proper peroxide for NR/PP TPVs turns out to be a point of major consideration.

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