Material Properties

Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends

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Abstract

Influences of various types and concentrations of peroxides on the properties of thermoplastic vulcanizates based on natural rubber/polypropylene (PP) blends were investigated. The objective was to find a proper balance between the influences of degree of crosslinking of the rubber and degradation of the PP phase on the rheological, mechanical, and morphological properties. The typical crosslinking temperature and crosslink efficiency and also relative amounts of decomposition products of each peroxide play an important role in the properties of the TPVs. In this work, the TPVs prepared with DCP or DTBPIB give a superior overall balance of properties relative to the TPVs crosslinked with DTBPH or DTBPHY.
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1. Introduction

Thermoplastic vulcanizates (TPVs) have become a very useful class of thermoplastic elastomers since their introduction in 1981. These materials have the processing characteristics of a thermoplastic and the functional performance of a conventional thermoset rubber. The 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], Coran and Patel [6], and Coran et al. [7]. The process was further advanced by Abdou-Sabet and Fath [8] and Ousa et al. [9] through the use of preferred curing agents to achieve improvement in elastomeric properties and flow characteristics, which led to successful commercialization of dynamic vulcanization technology.

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Some studies on TPVs based on natural rubber (NR) and polypropylene (PP) have been reported [10–19]. 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 but good low-temperature performance was needed [20]. They could also replace flexible plastics, such as plasticized PVC, ethylene vinyl acetate (EVA) and PP copolymers [21]. Various crosslinking systems such as peroxides and sulfur systems were employed [15,21–24].

The technique of crosslinking rubbers with peroxides has been known for long. The general advantages of peroxide-based crosslinks are good high-temperature aging resistance, good elastic behavior, in particular compression set, and no discoloration of the finished products [25,26]. 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. An appropriate peroxide should therefore be selected on the basis of its decomposition rate at the approximate processing temperature [27].

The aim of this present work is to study the effect of different types and concentrations of peroxides as crosslinking agents on the properties of a 60/40 NR/PP TPVs. The influence of each peroxide on

rheological, mechanical, and morphological properties is investigated.

2. Experimental

2.1. Materials

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 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 and structures and some general characteristics are given in Tables 1 and 2.

2.2. Preparation of TPVs

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 NR rubber, as will be used later on. A blend without curatives (named "CONTROL") was also made.

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 45% on carrier	
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH)/Trigonox 101–40B 40% on carrier	
Di(tert-butylperoxyisopropyl)benzene (DTBPIB)/Perkadox 14–40B 40% on carrier	
Dicumyl peroxide (DCP)/Perkadox BC-40B 40% on carrier	

Table 2
General characteristics of the peroxides investigated [26]

Coding	Mw. $t_{1/2} = 1\,min$	Temperature (°C) (°C)	Typical crosslinking temperature (%)	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
NR	100.0
PP	65.0
Stabilizer	
I 1076	0.4
I 168	0.4
Peroxide	Varying dose (0.0–7.0)

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 and the temperature setting was 160 °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 TPV was immediately removed from the chamber and sheeted once through a cold two-roll mill to obtain a sheet about 2 mm thick. The TPVs were stored for 24 h at approximately 4 °C before use. The mixing torque of the Brabender Plastic-Corder was captured using an external data acquisition system and the relationship between mixing torque and time was plotted for each type of blend.

2.3. Rheological characterization

A capillary rheometer (model 8052, Kayeness INC., Pennsylvania, USA) was used to study the shear flow properties of the TPVs. The experiment was carried out using a wide range of shear rates from 5 to $2500\,s^{-1}$ at 190 °C. Dimensions of the capillary die used were 2 mm diameter, 32 mm length, and 90 °C entry angle with aspect ratio (L/D) of 16/1. The TPVs were brought into the barrel of the rheometer and preheated for 3 min. The test was carried out at a series of shear rates, programmed via a microprocessor. The pressure drop across the capillary channel and melt temperature were captured via a data acquisition system during the test. The apparent shear stress, shear rate and shear viscosity were calculated using the derivation of Poiseuille's law.

2.4. Mechanical testing

The mixed 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. Tensile tests were carried out according to ISO 37 on type 2 dumbbell specimen using a Zwick tensile testing machine ZO2O at a constant crosshead 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.

2.5. Morphological studies

Morphological studies were carried out using a high-resolution scanning electron microscope (HR-SEM), model 1550 (Leo Co. Ltd., UK.). Molded sampled of the NR/PP TPVs were cryogenically fractured in liquid nitrogen to avoid any possibility of phase deformation during the fracture process. The PP phase was preferentially extracted by immersing the fractured surface into xylene at 110 °C for 30 min. The samples were later dried in a vacuum oven at 40 °C for 12 h to eliminate

contamination of the solvent. The dried surfaces were gold-coated before scanning.

3. Results and discussion

3.1. Mixing torques

The effect of dynamic vulcanization on the mixing torque–time curves of the TPVs prepared from the 60/40 NR/PP blends with various types of peroxides at fixed concentration of 10 meqs of each peroxide is shown in Fig. 1. It clearly shows an effect of the different types of peroxide 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. It does not appear in the case of the blend without peroxide: CONTROL. The blends with DCP or DTBPIB as curing agent show a stronger effect of crosslinking than the blends with DTBPH or DTBPHY. Among the four types of peroxides used, the blend with DTBPIB shows the most pronounced and the blend with DTBPHY the least effect, with the TPVs with DCP or DTBPH being intermediate. These results correlate well with the typical crosslinking temperatures and crosslink efficiencies of each peroxide, and also agree with relative amounts of decomposition products, as shown in Tables 2 and 4. The typical crosslinking temperature is the temperature at which about 90% of crosslinking

occurs within 12 min [28]. The relative amounts of decomposition products refer to the chemical compounds formed after decomposition under high temperature. Not all of these decomposition products from a peroxide can cause crosslinking by abstraction of hydrogen atoms from a polymer chain. The main mechanisms of each peroxide to generate crosslinking are shown in Schemes 1–4. For DCP, as seen in Scheme 1, actual crosslinking occurs mainly by methyl-radicals and some 2-phenylpropanoxy-radicals, while for DTBPIB, as seen in Scheme 2, the decomposition products which can abstract hydrogen atoms are tert-butanoxy-, methyl-, and di-(hydroxy-i-propyl)-benzene-radicals. With higher amounts of relative decomposition products, the blend-type peroxides provide a higher crosslink density. DCP and DTBPIB having typical crosslinking temperatures of 160 and 170 °C, respectively, provide relatively high amounts of decomposition crosslinking products and, consequently, have a high crosslink efficiency. DTBPH and DTBPHY have typical crosslinking temperatures of 170 and 180 °C, respectively. This, combined with a lower relative amount of decomposition crosslinking products than DCP and DTBPIB, and consequently lower crosslink efficiency, accounts for the decreased height of the torque peaks during mixing.

The final mixing torque also shows some information about the blends. As seen in Fig. 1, the final mixing torques of the blends with DCP or DTBPIB
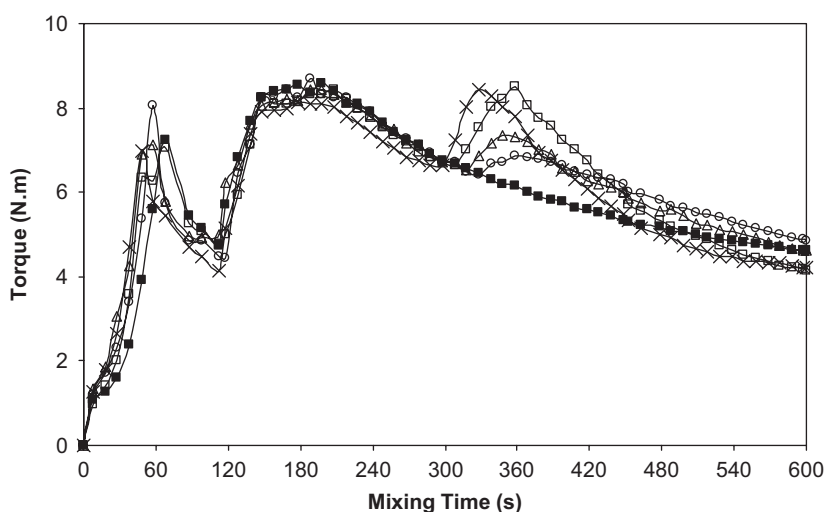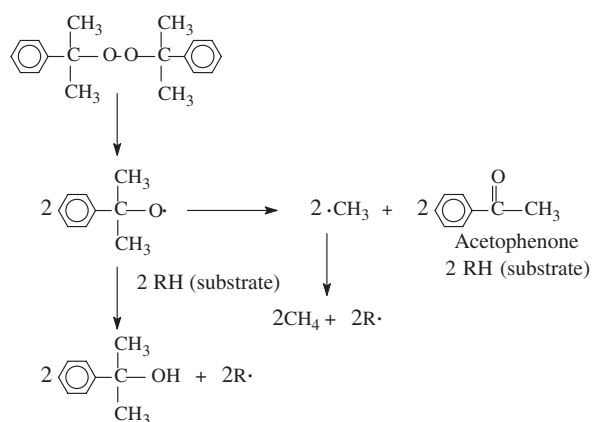

Fig. 1. Mixing torque vs. time for the NR/PP TPVs at mixing temperature of 160 °C, with fixed concentration of peroxides of 10 meq peroxide functionalities; including CONTROL without peroxide; (—■—): CONTROL; (—○—): DTBPHY; (—△—): DTBPH; (—□—): DTBPIB; (—✕—): DCP.

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-2,5dihydroxyhexyne-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
		a-Methylstyrene	0.01
		Water	0.01

Scheme 1. Decomposition mechanism of DCP.

are lower than of the CONTROL and the blends with DTBPH or DTBPHY. In the presence of peroxy-radicals at high temperature, polyopopylene can degrade through β chain-scission. The chain

scission mechanism is shown in Scheme 5 [29]. This reaction results in a viscosity decrease of the PP. High reactive radicals generated from DCP or DTBPIB not only give high amount of crosslinking, but also some degradation of the PP molecules. Apparently, 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 final mixing torque of the blends with DCP or DTBPIB, relative to the other blends.

3.2. Rheological properties

Plots of apparent shear stress versus shear rate (i.e. flow curves) and apparent shear viscosity versus shear rate (i.e. viscosity curves) of the TPVs are shown in Figs. 2 and 3, respectively. The shear stress and shear viscosity of all blends with peroxides at a given shear rate are higher than the CONTROL. The increase in shear stress and shear viscosity is the result of the crosslinking of the rubber molecules. However, chain scission of the PP molecules causes a decrease in stress and viscosity of the blends, and is the main competing effect over crosslinking, especially in the case of the highly reactive radicals forming peroxides: DCP or DTBPIB. Among the four different types of peroxides, the TPVs prepared with DCP or DTBPIB show both shear stress and shear viscosity lower than for the blends with DTBPH and DTBPHY, and close to the CONTROL. These trends in shear stress and viscosity correspond with the trends seen already in the mixing torque–time curves in Fig. 1.

3.3. Mechanical properties

The mechanical properties of the NR/PP TPVs cured with the various types and concentrations of peroxide are given in Figs. 4–7. In Fig. 4, there is a clear trend of increasing tensile strength when the concentration of crosslinking agents increases. The TPVs prepared using DCP or DTBPIB as curatives provide superior tensile strength relative to the blends crosslinked with DTBPH or DTBPHY at all concentration levels. The TPV with 10 meqs of DTBPIB shows overall the highest tensile strength.

A plot of elongation at break versus concentration of peroxides is shown in Fig. 5. The trends of elongation at break are in concordance with the trends in tensile strength. The elongations at break of all TPVs increase with increasing concentration
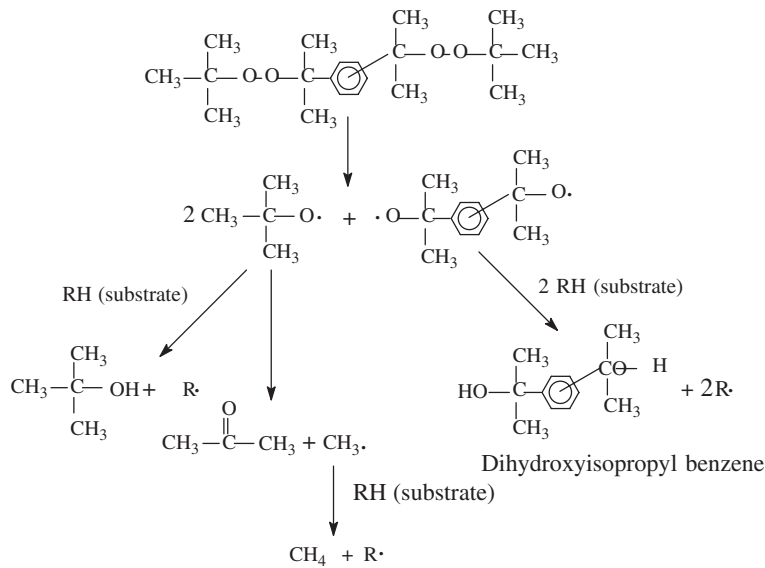
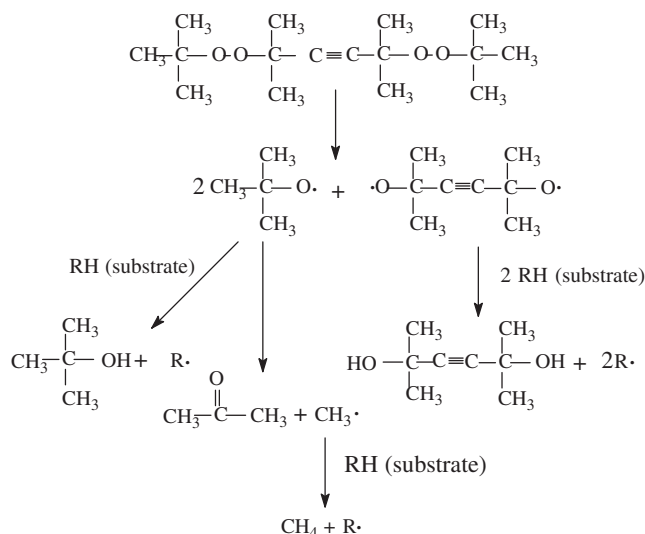Scheme 2. Decomposition mechanism of DTBPIB.
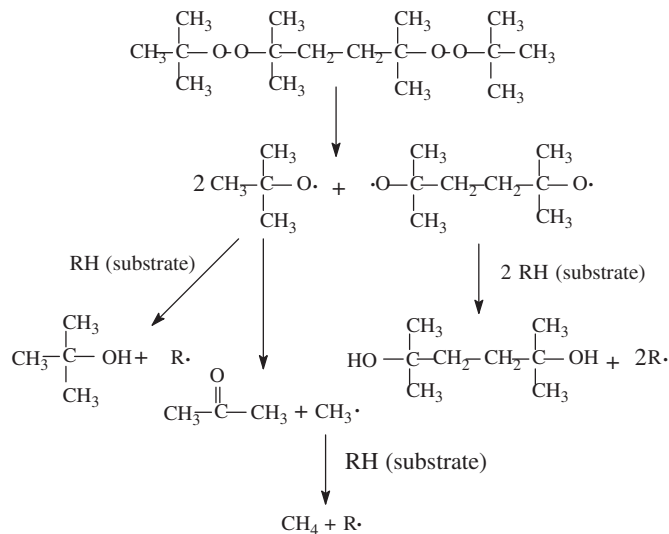
Scheme 3. Decomposition mechanism of DTBPH.

of peroxide. Also, the TPVs prepared with DCP and DTBPIB show a higher elongation at break than DTBPH and DTBPHY.

Compression set data at testing temperatures of 23 and 70 °C for 24 h are plotted in Figs. 6 and 7, respectively. The effect of various types of peroxides shows relatively little discrimination at low peroxide concentrations but larger differences in set-values are found with increased peroxide concentration.

These differences in mechanical properties must be attributed to influences of peroxide type and PP degradation. DCP and DTBPIB have typical crosslinking temperatures close to the mixing temperature, high crosslink efficiency and provide highly reactive radicals as discussed in 3.1, so they can easily provide a high amount of crosslinking in the rubber molecules. Moreover, in spite of the decreasing viscosity of PP via PP degradation, the blends with DCP or DTBPIB still give superior overall mechanical properties relative to the case of using DTBPH or DTBPHY as curatives.

Scheme 4. Decomposition mechanism of DTBPHY.
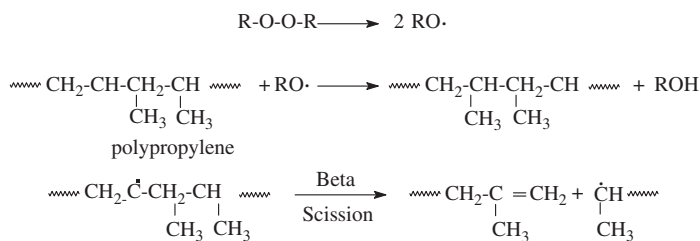
Scheme 5. Simplified reaction scheme for peroxide degradation of PP by β-scission.
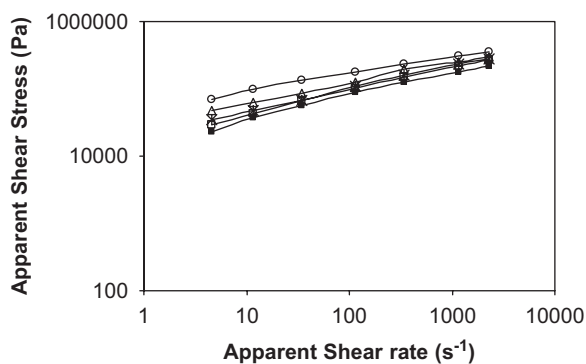

Fig. 2. Relationship between apparent shear stress and shear rate of the TPVs using various peroxides; (—■—): CONTROL; (—○—): DTBPHY; (—△—): DTBPH; (—□—): DTBPIB; (—✕—): DCP.
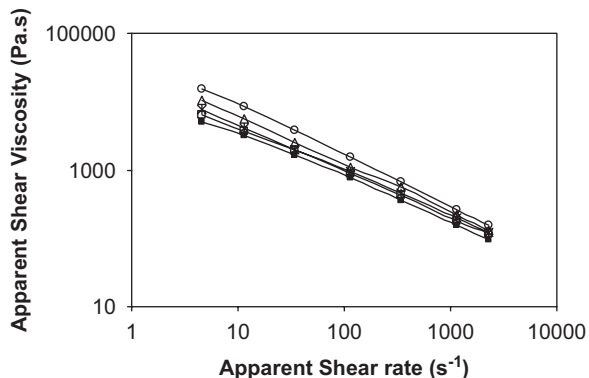

Fig. 3. Relationship between apparent shear viscosity and shear rate of the TPVs using various peroxides; (—■—): CONTROL; (—○—): DTBPHY; (—△—): DTBPH; (—□—): DTBPIB; (—✕—): DCP.

3.4. Morphologies

The high-resolution SEM micrographs of the TPVs are shown in Fig. 8. The hot xylene-etched

fracture surfaces after extraction of the PP phase were measured. The morphology of the TPVs is obviously improved when adding peroxide into the
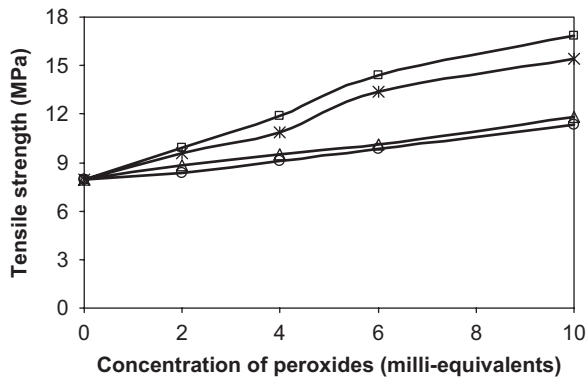
Fig. 4. Tensile strength of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides; (—⊖—): DTBPHY; (—▵—): DTBPH; (—☐—): DTBPIB; (—✳—): DCP.
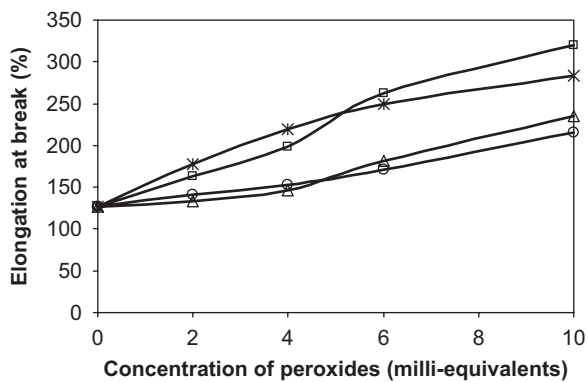

Fig. 5. Elongation at break of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides; (—⊖—): DTBPHY; (—▵—): DTBPH; (—☐—): DTBPIB; (—✳—): DCP.
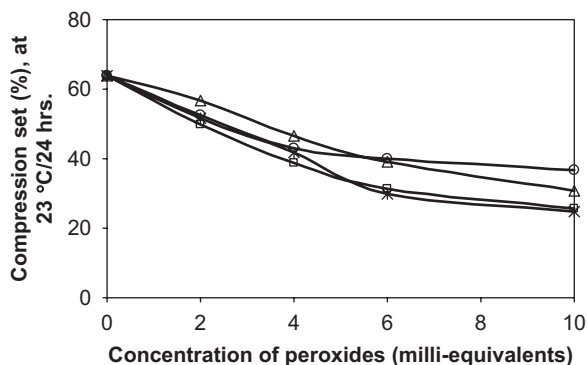

Fig. 6. Compression set at 23 °C/24 h of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides; (—⊖—): DTBPHY; (—▵—): DTBPH; (—☐—): DTBPIB; (—✳—): DCP.
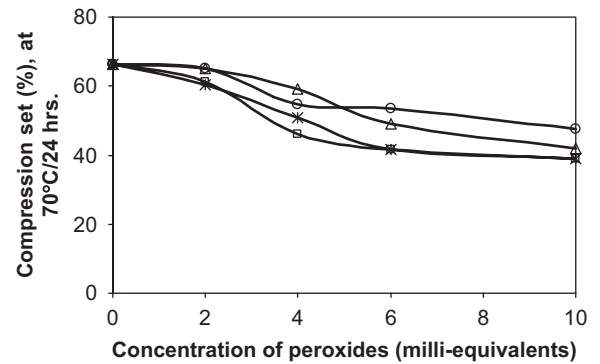

Fig. 7. Compression set at 70 °C/24 h of NR/PP TPVs as a function of concentration of peroxides for different types of peroxides; (—⊖—): DTBPHY; (—▵—): DTBPH; (—☐—): DTBPIB; (—✳—): DCP.

system. The TPV without peroxide: CONTROL (A) shows large size and non-uniform rubber particles, whilst the other 4 dynamically vulcanized TPVs show smaller and finely dispersed rubber particle morphology. Among the four different types of peroxides, the efficiency of each peroxide apparently has an important effect on the morphology of the TPVs. These results correspond to the rheological and mechanical properties. DTBPH and DTBPHY do not fully vulcanize the rubber phase and do not provide a high degree of crosslinking, as do DCP and DTBPIB. It can be seen that some rubber phase particles coalesce together and do not show very good dispersion, even though they already show some signs of a small size rubber phase. The most uniform morphologies are observed with DCP or DTBPIB as crosslinking agents. In this study, DTBPIB provides the very best morphology, which corresponds with the superior mechanical properties obtained with this peroxide.

4. Conclusions

The effect of various types and concentrations of peroxides on the rheological, mechanical and morphological properties of a 60/40 NR/PP TPVs were investigated. The main factors that influenced the properties of the TPVs are: the typical cross-linking temperature, the crosslink efficiency and the relative amounts of decomposition products of each peroxide, in combination with the degradation of PP in the presence of peroxide. DCP and DTBPIB have typical crosslinking temperatures close to the mixing temperature, provide high crosslink efficiency, and highly reactive radicals. They provide
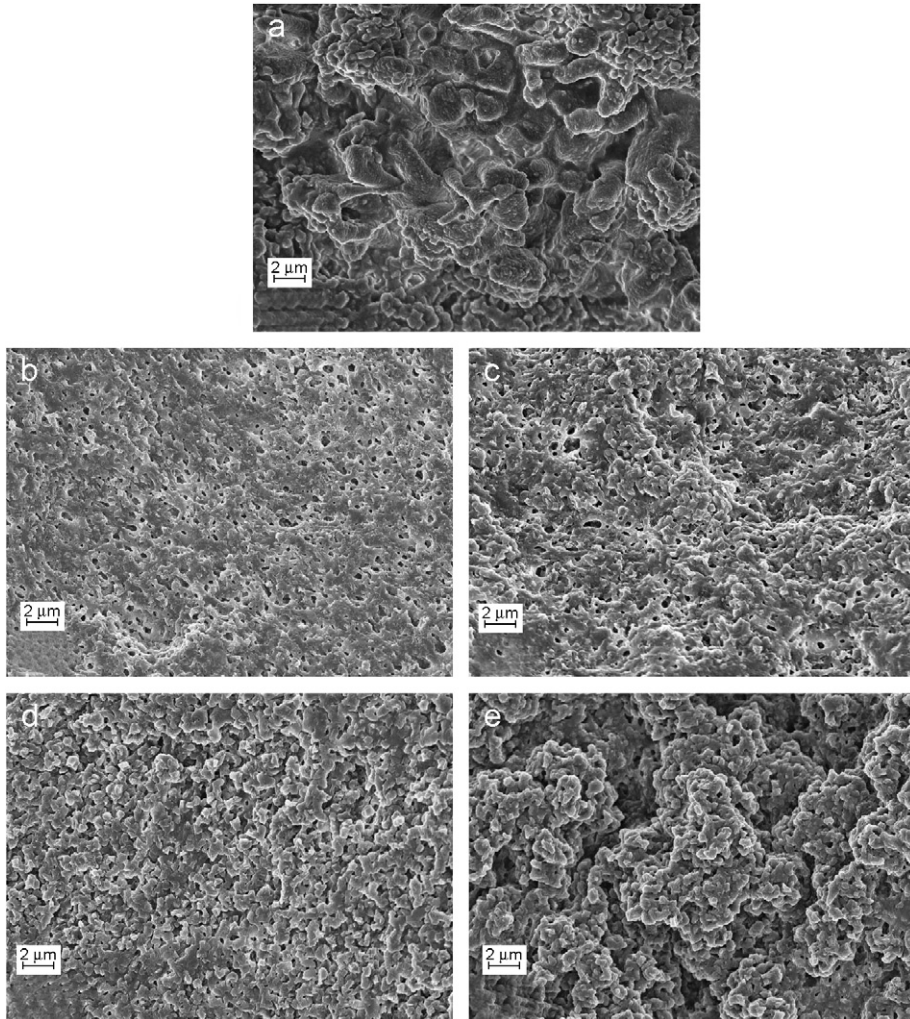
Fig. 8. SEM micrographs of the 60/40 NR/PP TPVs with and without 10 meq's of various types of peroxides; (a): CONTROL; (b): DTBPHY; (c): DTBPH; (d): DTBPIB; (e): DCP.

high amounts of crosslinks in the rubber molecules. Moreover, in relation to decreasing viscosity of the PP via the PP degradation mechanism, the TPVs with DCP or DTBPIB give superior overall properties relative to DTBPH or DTBPHY as curatives.

Acknowledgements

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