

Multifunctional Peroxide as Alternative Crosslink Agents for Dynamically Vulcanized Epoxidized Natural Rubber/Polypropylene Blends

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ABSTRACT: Commonly used dicumyl peroxide (DCP) in combination with coagent, triallyl cyanurate (TAC), as a crosslinking agent is well acceptable for dynamically vulcanized rubber phase of thermoplastic vulcanizates (TPVs). However, it generally produces volatile decomposition products, which cause a typical unpleasant smell and a blooming phenomenon. In this work, influence of two types of multifunctional peroxides: 2,4-diallyloxy-6-*tert*-butylperoxy-1,3,5-triazine (DTBT) and 1-(2-*tert*-butylperoxyisopropyl)-3-isopropenyl benzene (TBIB), on properties of TPVs based on epoxidized natural rubber (ENR)/polypropylene (PP) blends were investigated. The conventional peroxide/coagent combinations, i.e., DCP/TAC and *tert*-butyl cumyl peroxide (TBCP)/ α -methyl styrene (α -MeS) were also used to prepare the TPVs for a comparison purpose. The TPVs with multifunctional peroxide, DTBT,

provided good mechanical properties and phase morphology of small dispersed vulcanized rubber domains in the PP matrix which were comparable with the DCP/TAC cured TPVs. However, the TPVs with TBIB/ α -MeS and TBCP/ α -MeS showed comparatively low values of the tensile properties as well as rather large phase morphology. The results were interpreted by three main factors: the kinetic aspects of the various peroxides, solubility parameters of respective peroxide/coagent combinations in the ENR and PP phases, and the tendency to form unpleasantly smelling byproducts. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 819–825, 2009

Key words: thermoplastic vulcanizate; multifunctional peroxides; coagent; epoxidized natural rubber; polypropylene

INTRODUCTION

Polymer blend and thermoplastic vulcanizates (TPVs) have been prepared using a wide variety of commercially available rubbers and thermoplastics. Epoxidized natural rubber (ENR) is a chemically modified natural rubber. The presence of the polar oxirane groups in the rubber chain provides some excellent properties such as oil resistance, low gas permeability, good wet grip, and high damping characteristics.¹ TPVs based on dynamically cured ENR blended with several types of thermoplastics have been extensively investigated by using sulfur-based system, mixed system (i.e., sulfur and peroxide), phenolic resin, and peroxides.^{2–10}

There are some commercially available TPVs that crosslinked with peroxides. The general advantages of peroxide-based crosslinking are good high temperature resistance, good elastic behavior in particular compression set, and no discoloration of the finished products.^{11,12} However, tendency of peroxide to show a blooming effect and decompose into smelly byproducts are main disadvantages. In particular, the formation of acetophenone byproduct from aromatic moieties contained in the peroxide molecular structure has been well known to cause the notorious smell.^{7,9,13} Multifunctional peroxides, containing unsaturated functional groups in addition to a peroxide functionality, were recently developed to overcome the afore-mentioned drawbacks and applied to vulcanize TPVs, especially the TPVs based on EPDM/PP. In this manner, part of the decomposition products is no longer volatile nor will give rise to smell or blooming phenomena.^{14,15}

In this work, efficiency of multifunctional peroxides as curing agents for dynamic vulcanized ENR for preparation of ENR/PP TPVs is focused to limit the formation of unpleasant or smelly byproducts from the decomposition of conventional peroxides.

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EXPERIMENTAL

Materials

An ENR with 20 mole percent epoxides (ENR-20) was synthesized on lab-scale by using a chemical reactor at Prince of Songkla University, Pattani campus, Thailand. The PP used was Stamylan P 11E10 with a MFI of 0.3 g/10 min, measured at 230°C/2.16 kg, obtained from DSM PPs B.V., the Netherlands. The stabilizers, Irganox[®] 1076 and Irgafos[®]

168 were obtained from Ciba Geigy, Switzerland. Four types of peroxides investigated were obtained from Akzo Nobel Polymer Chemicals, the Netherlands as detailed in Table I. The first two types of multifunctional peroxides, i.e., 2,4-diallyloxy-6-*tert*-butylperoxy-1,3,5-triazine (DTBT) and 1-(2-*tert*-butylperoxyisopropyl)-3-isopropenyl benzene (TBIB), combine peroxide and coagent functionalities in a single molecule. Other two conventional peroxides, i.e., dicumyl peroxide (DCP) and *tert*-butyl cumyl

TABLE I
Chemical/Commercial Names and Structures of Peroxides and Coagents Investigated

Chemical/commercial name	Chemical structure
Peroxides	
2,4-Diallyloxy-6- <i>tert</i> -butylperoxy-1,3,5-triazine (DTBT) (95%) multifunctional	
1-(2- <i>Tert</i> -butylperoxyisopropyl)-3-isopropenyl benzene (TBIB) (71%) multifunctional	
Dicumyl peroxide (DCP) (Perkadox BC-40B) (40%)	
<i>Tert</i> -butyl cumyl peroxide (TBCP) (Trigonox T) (50%)	
Coagents	
Triallyl cyanurate (TAC) (50%)	
α -Methyl styrene (α -MeS) (99%)	

TABLE II
ENR/PP TPV Compositions

Component	Compositions, phr ^a											
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12
ENR-20	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
PP	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0
Peroxide												
DTBT	1.2(4)	1.8(6)	3.0(10)	–	–	–	–	–	–	–	–	–
TBIB	–	–	–	1.4(4)	2.1(6)	3.5(10)	–	–	–	–	–	–
DCP	–	–	–	–	–	–	2.7(4)	4.1(6)	6.8(10)	–	–	–
TBCP	–	–	–	–	–	–	–	–	–	1.7(4)	2.5(6)	4.2(10)
Coagent												
TAC	–	–	–	–	–	–	1.3(8)	2.0(12)	3.3(20)	–	–	–
α -MeS	–	–	–	0.5(4)	0.7(6)	1.2(10)	–	–	–	1.0(8)	1.4(12)	2.4(20)
Stabilizers												
I 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
I 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

^a Numbers in the bracket represent milliequivalents of peroxide and coagent per 100 parts of ENR.

peroxide (TBCP), were employed as references due to their structural similarity with the multifunctional peroxides. In this study, triallyl cyanurate (TAC), 50% and α -methyl styrene (α -MeS), 99% were used as references for correction a lack of the coagent functionalities in recipes. For DCP, TAC was used as coagent because of the structural similarity with DTBT, whereas for TBCP, α -MeS was applied as coagent due to the structural similarity with TBIB.

Mixing and preparation of samples

The 60/40 ENR/PP TPVs were mixed in an internal mixer at 160°C with a rotor speed of 80 rpm for 10 min. The compositions of the mixed compounds are given in Table II. To make a comparison among the various peroxides, care has to be taken, that with equal amounts of peroxides added per 100 g of pure ENR but the amounts of the coagent functionality per 100 g of pure ENR differ. They depend on the amount of coagent functionality provided by the peroxide itself. For example, if 10 milliequivalents (meqs) of peroxide were used, DTBT by its nature having two pendent allylic groups, provides 20 meqs of coagent functionality. This level of 20 meqs of coagent functionality was then taken as reference, and a correction was applied to make up the lack of coagent functionality in the other recipes by add-

ing either TAC or α -MeS, as shown in Table III. Properties of the prepared TPVs were later investigated.

Mechanical testing

The mixed samples were pressed for 5 min in a WLP 1600/5*4/3 Wickert laboratory compression molding 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 Z020 at a constant crosshead speed of 500 mm/min.

Morphological studies

Morphological studies were carried out using a high-resolution scanning electron microscope (HR-SEM), model 1550 (Leo Co., Ltd, UK). Molded samples 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

TABLE III
Correction of Coagent Functionality

Peroxide	Amount of peroxide (mmol)	Peroxide functionality (meqs)	Coagent functionality (meqs)	Coagent added extra (meqs)
DTBT	10	10	20	–
TBIB	10	10	10	10 (α -MeS)
DCP	10	10	–	20 (TAC)
TBCP	10	10	–	20 (α -MeS)

the solvent. The dried surfaces were gold coated before scanning.

Curing characterization

A rubber process analyzer, RPA-2000 (Alpha Technologies) was used to measure curing characteristics of the different types of peroxide/coagent combinations in pure ENR-20 compounds at 180°C according to ISO 6502. The samples were prepared by mixing the ENR-20 with chemicals at room temperature on a two-roll mill. The concentration of the different crosslinking agents was set at 10 meqs peroxides/20 meqs of coagent functionalities per 100 g of ENR-20.

RESULTS AND DISCUSSIONS

Influence of different types and concentrations of crosslink agents on the mechanical properties of 60/40 ENR-20/PP TPVs

The mechanical properties in terms of tensile strength, elongation at break, and Young's modulus of the ENR-20/PP TPVs dynamically cured with various crosslinking agents at different concentrations are shown in Figures 1–3, respectively. From these figures, there was a clear trend of increasing tensile strength, elongation at break, and Young's modulus with more concentration of crosslinking agent added in all recipes, except for TBIB/ α -MeS. The latter case showed an increasing trends of tensile strength and Young's modulus, when crosslinking agent increased from 4 till 6 meqs. After that, decreasing trend of those properties was observed for the system with higher content of TBIB than 6 meqs. Although elongation at break of TBIB cured ENR/PP also showed an increasing trend at all concentrations. The TPVs with TAC-assisted DCP exhibited the best combination of mechanical properties. On the other hand, the multifunctional peroxide DTBT provided properties which came close to the

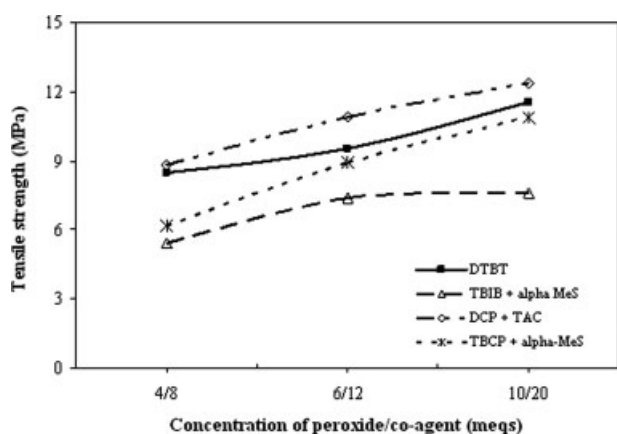


Figure 1 Tensile strength of ENR/PP TPVs as a function of crosslinking agents.

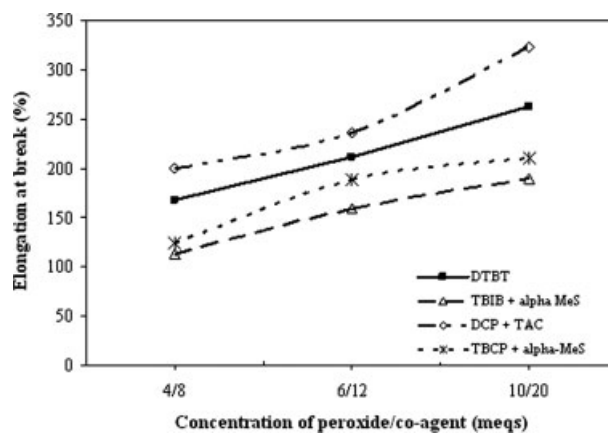


Figure 2 Elongation at break of ENR/PP TPVs as a function of crosslinking agents.

DCP/TAC, whereas TBCP/ α -MeS and TBIB/ α -MeS gave comparatively low values.

Effect of peroxides on morphological properties of 60/40 ENR-20/PP TPVs

Morphological properties of peroxide dynamically vulcanized ENR/PP TPVs at fixed concentration of 10 meqs peroxides/20 meqs of coagents are shown in Figure 4. It is clear that a well-defined small spherical shape of vulcanized ENR particles dispersed in PP matrix was observed. Furthermore, it is seen that the TPVs vulcanized by DCP/TAC gave the smallest size of vulcanized rubber domains. The TPVs with DTBT showed slight larger rubber domain than that of the TPVs with DCP/TAC. The size of vulcanized rubber domains can be ranked as followed: TPVs with DCP/TAC < DTBT < TBCP/ α -MeS < TBIB/ α -MeS, respectively.

The differences in mechanical and morphological properties of the ENR/PP TPVs dynamically cured with various peroxide/coagent combinations are discussed in terms of kinetic aspects of the various

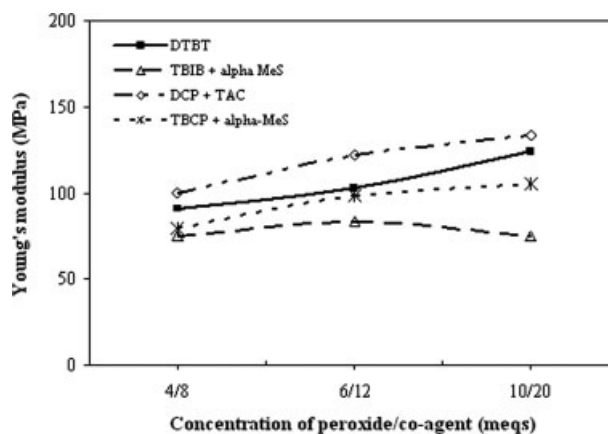
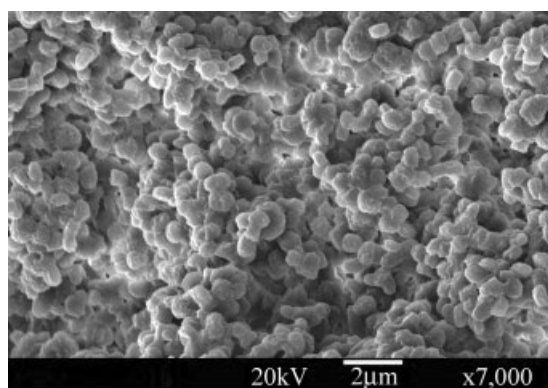
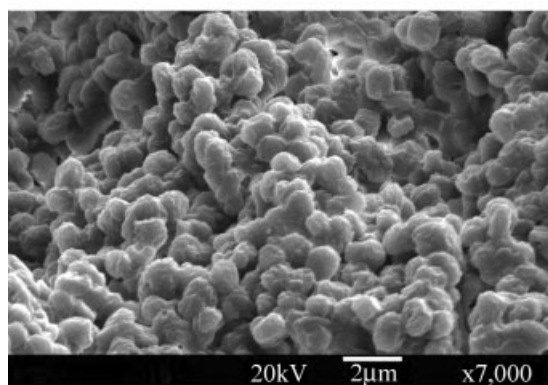


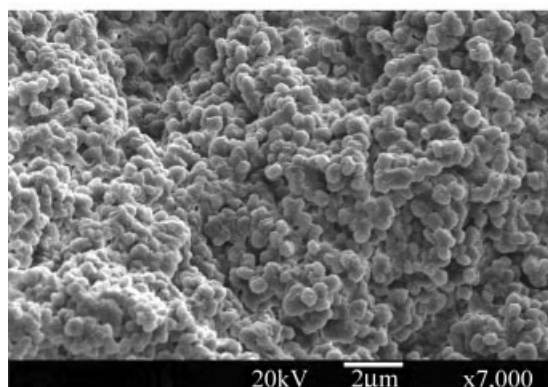
Figure 3 Young's modulus of ENR/PP TPVs as a function of crosslinking agents.



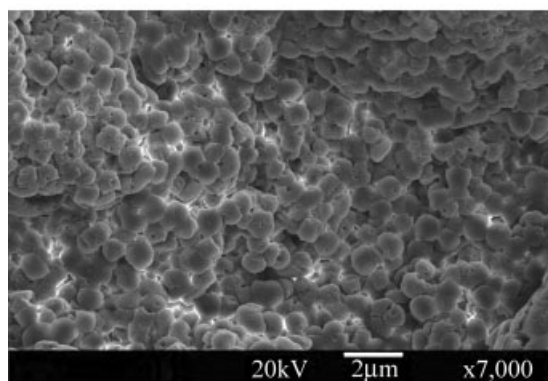
A: ENR/PP with DTBT



B: ENR/PP with TBIB/α-MeS



C: ENR/PP with DCP/TAC



D: ENR/PP with TBBCP/α-MeS

Figure 4 SEM micrograph of ENR/PP TPVs dynamically vulcanized with various types of peroxides.

peroxides, solubility parameters of respective curing agents in the ENR and PP phases, and the tendency to form unpleasantly smelling byproducts.

Kinetic aspects

Curing characteristics of the peroxide/coagent combinations in pure ENR-20 gum compounds, with the omitted PP are shown in Figure 5. It was found that DCP/TAC gave the fastest rate of cure, following by DCP without TAC. DTBT showed the cure rate index close to DCP with and without TAC, whereas TBIB/α-MeS clearly showed the slowest rate of cure. The data of cure rate index corresponded to the delta torque obtained. High values of the delta torque were achieved for the TPVs with DCP with and without TAC. The delta torque of DTBT came close to that of the DCP without TAC and was better than those of TBIB and TBCP assisted by α-MeS. This can be implied to the extent of crosslink occurred in the ENR phase. Therefore, the DCP/TAC gave the highest degree of crosslinking, following by DCP without TAC, DTBT, TBCP/α-MeS, and TBIB/α-MeS, respectively. As a consequence, the ENR/PP TPVs vulcanized by DCP/TAC provided superior mechanical properties. Furthermore, higher rate of cure and delta torque caused faster rate of vulcanization of the rubber phase with higher viscosity. This was a reason for severe break up of the vulcanizing rubber phase to be smaller particles dispersed in the molten PP phase under high-shear conditions. Therefore, this system with high rate of cure and viscosity (i.e., DCP/TAC) provided smaller vulcanized rubber domains. The TPVs with TBIB/α-MeS which showed the lowest cure rate and delta torque (in Fig. 5) exhibited the worst mechanical properties. Also, the largest vulcanized rubber domains were also observed. In the case of the multifunctional peroxide

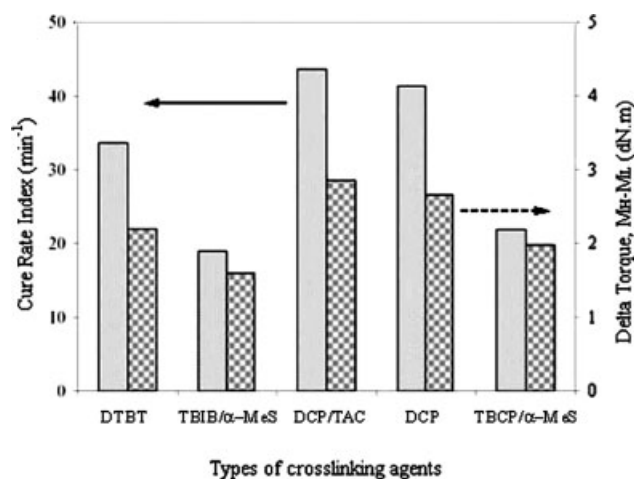


Figure 5 Cure rate index and torque difference for peroxide-cured pure ENR vulcanizates.

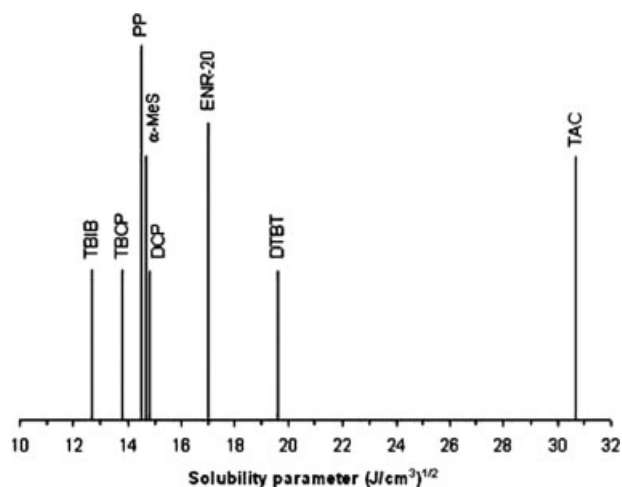
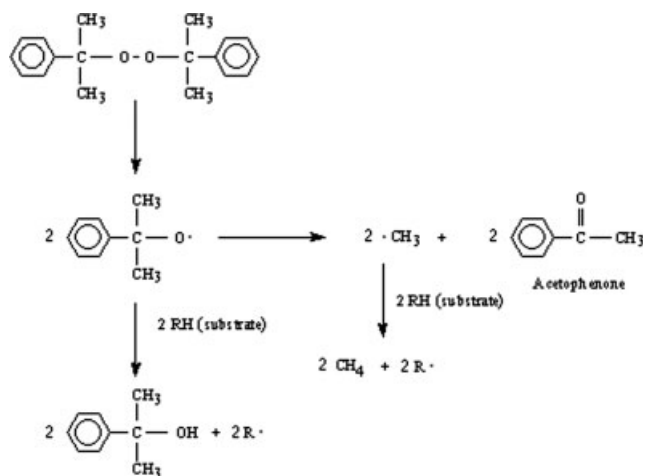


Figure 6 Relative ranking of solubility parameters of various components.

DTBT cured TPVs, they showed a comparable performance to that of DCP without TAC, and a better performance compared with those of coagent assisted TBCP and TBIB. This proved that the DTBT performed the best as peroxide and as coagent in a same molecule in the TPVs investigated.

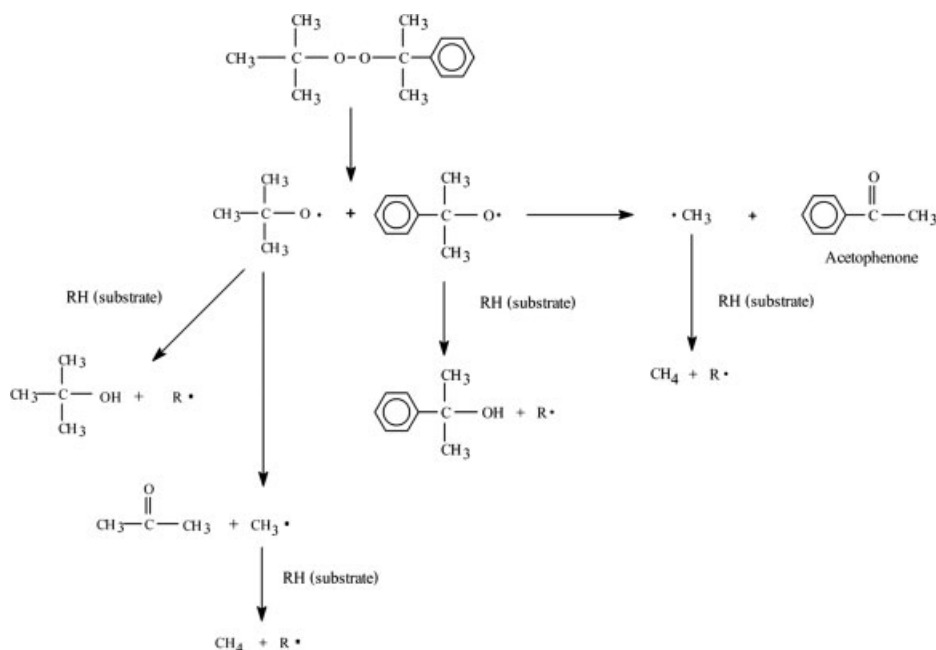
Solubility parameters

The solubility parameters (δ) at the mixing temperature of 180°C calculated using the Hildebrand equation¹⁶ for each component are graphically depicted in Figure 6. It can be deduced that there was a tendency for TBIB, TBCP, and DCP to preferably partition toward the PP phase because their δ values are



Scheme 1 Decomposition mechanism of dicumyl peroxide.

close to the δ value of the PP. However, in the case of the DTBT, it shows a preference toward the ENR phase. Among the three former peroxides, DCP has δ value closest to the ENR in combination with very high cure rate index and delta torque. Therefore, DCP relatively transferred to the ENR phase. This resulted in a higher degree of crosslinking in the ENR phase. Added TAC as a coagent to DCP, a very high- δ value of TAC caused radicals generated preferably moved into the ENR phase. Therefore, the degree of crosslink in the ENR phase by DCP was enhanced due to synergistic effect between activity of DCP and TAC. This was seen in large effect on tensile properties (i.e., tensile strength and Young's modulus) and morphology with small size



Scheme 2 Decomposition mechanism of *tert*-butyl cumyl peroxide.

of vulcanized ENR particles. For TBIB, TBCP, and coagent, α -MeS, their δ values are very close to the δ value of the PP, so that they preferred partition toward the PP phase. This resulted in the comparatively low values of mechanical properties regarding to the small amounts of crosslinking in the ENR phase. Unsurprisingly, by further addition TBIB/ α -MeS from 6 to 10 meqs, the leveling off of tensile strength and Young's modulus was observed. However, the increasing of elongation at break in TBIB which differed from other two properties was possibly due to a degradation of PP in the presence of TBIB. The multifunctional peroxide DTBT, because its high δ value on the ENR side, preferably ended up in the ENR phase to perform its proper role as a crosslink agent yielding in the mechanical properties closed to the TPVs with DCP/TAC, and small rubber particles distributed in the PP matrix.

Tendency to form unpleasantly smelling byproducts

The multifunctional peroxides DTBT and TBIB did not provide the TPVs with the best overall properties than the TPVs with conventional peroxides (i.e., DCP/TAC and TBCP/ α -MeS, respectively). However, the molecular structures of the former peroxides do not contain aromatic rings which can be decomposed to cumyloxy radicals. Therefore, there is no possibility in those two multifunctional peroxides to form acetophenone byproduct. Unlike DCP and TBCP, their molecular structures (as shown in Schemes 1 and 2) contain aromatic rings. They primarily generated cumyloxy radicals, which further decomposed into highly reactive methyl radicals and acetophenone which having a typical unpleasant smell.

CONCLUSIONS

It is well established that the multifunctional peroxides especially DTBT provided the ENR/PP TPVs with properties were more or less comparable to those obtained by using the conventional coagent assisted peroxides DCP/TAC system. It was also found that the properties of ENR/PP TPVs with

DCP/TAC and DTBT multifunctional peroxide were superior than those of the TPVs with TBIB/ α -MeS and TBCP/ α -MeS, respectively. However, the decomposition products of DCP normally give the badly smell of acetophenone byproduct. Therefore, an alternative selection of multifunctional peroxides (such as DTBT) as a curing agent is another approach for a preparation of the ENR/PP TPVs with proper mechanical and morphological properties without unpleasant smell. It was also found that the δ value of DTBT is close to the δ value of the ENR. This causes the movement of DTBT toward the ENR phase during mixing operation. As a consequence, the coagent functionalities in DTBT molecules contributed to an improvement of the crosslink efficiency of the ENR/PP TPVs. Moreover, the TPVs with DTBT did not provide unpleasant smell byproducts after decomposition unlike in the case of TPVs with DCP and TBCP.

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