THE EFFECT OF ORGANIC PEROXIDES ON THE CURING BEHAVIOR OF EPDM ISOLATION MEDIUM VOLTAGE CABLES

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This work describes the influence of the concentration and type of peroxides on cure efficiency of various types of EPDMs (ethylene propylene diene monomer (M-class) rubber), [1][2][10]) with the various content of ethylene characterized by a wide range of applications. Rheology characteristics was investigated using the Monsanto Rheometer in the temperature range between 180 and 200 °C, with the data provided every 10 °C. Mechanical properties (tensile strength and elongation at break) was investigated using tensile tests according to standard ASTM D-412. The obtained results showed that peroxide (2,5-Dimethyl-2,5-Di (tert-butylperoxy) hexane (DTBPH) with the concentration of 7.5 phr (cure time 1.5 min) had a higher performance at the temperatures of 180 to 190 °C. At the higher peroxide level, there is the increase in the amount of residual peroxide, as well as the possibility of the formation of clusters due to the nonhomogeneous distribution of crosslinks. Peroxide cured EPDM with 45 wt% of the ethylene content gives the most effective mechanical properties for medium voltage cables. It is to be noted that t 100 for Dicumyl peroxide (DCP), Di (tert-butylperoxyisopropyl) benzene (DTBPIB), and (2,5-Dimethyl-2,5-Di (tert-butylperoxy) hexane (DTBPH) accounts for an average of 2 to 3 half-lives.

Keywords: crosslinking, kinetics, EPDM, organic peroxide, rheology

Introduction

One of the most diffused materials utilized for electric cable insulation is EPDM with the low unsaturation level and suitable dielectric properties, good aging resistance and good mechanical strength [1]. Rubber industry usually performs the curing characterization that will affect the processing physical, mechanical and dynamic properties. The study of the process of cure of EPDM rubbers in moving die rheometer (MDR) was studied by Rosca and Verghaud [2]. The reported cure time for a particular system is often inconsistent, this behavior of cure time results either in cure or excess residual peroxide (under-cured) in vulcanizates, both causing a reduction in mechanical properties. A wide range of peroxides for crosslinking of rubber is available on the market. Some of typically used peroxides are shown in Figure 1. Normally, relatively stable peroxides are selected for rubber vulcanisation, since they should be stable at the storage temperature and also compounding temperature, which can be rather high. However, they should be labile enough to quickly yield the radical species at the vulcanisation temperature, yet providing the proper scorch safety. The reactivity of peroxide is mainly determined by its molecular structure [3].

Figure 1. Example of commonly used peroxides for rubber crosslinking

Several authors agree with the fact that the following are very important factors to take into account in order to select a proper peroxide [3, 4, 5, 6, 7, 8] : Harmless decomposition products, the effect of additives on the

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efficiency on a stability, vulnerability to side reactions that lower the efficiency, non-volatility: to prevent loss during compounding and mixing, a possible generation of odour, safety: it should be non irritant and non-toxic (safe at the storage temperature, the processing temperature and at the increased production of decomposition products. A very important factor considered in peroxide selection is the nature of the radicals formed by its decomposition. Depending on the reactivity of these radicals, subsequent rearranging reactions take place leading to new radical species. These new radicals are sometimes reactive, but in other cases loose reactivity compared to the initial radical, and that will negatively reflect in the peroxide efficiency. For instance, when using DCP, one of the most used crosslinking peroxides are decomposition methyl radicals, see Figure 2 [6]. These radicals are still very reactive, and at the same time they are less sterically hindered than the initial cumyloxy radicals. Therefore, they will further easily react and provide good crosslink efficiency. The best radicals for peroxide crosslinking are those which are good abstractors, like for instance methyl and cumyloxy radicals, and poor in addition to double bonds. Figures 2-4 present main mechanisms of each peroxide to generate crosslinking.

For DCP, the actual crosslinking occurs by 2-phenylpropanoxy radicals and methyl radicals (Figure 2) while with DTBPIB decomposition products which can abstract hydrogen atoms they are tert butoxy, methyl and di-(hydroxy-i-propyl) benzen radicals shown in Figure 3.

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 [9]. The aromatic nature of peroxides is related to the decomposition temperature of the peroxides being lower with the higher aromatic content.

Figure 2. Decomposition mechanism of Dicumyl peroxide (DCP)

The first step of crosslinking is the homolytic scission of DCP molecules to form two alkoxy radicals. The kinetic parameters of this reaction depend solely on temperature and the concentration of DCP and are independent of any other species in the system. In the next step, the β cleavage of cumyloxy radicals leads to the formation of acetophenone molecules. Acetophenone is volatile and leaves the system during crosslinking. The side products of the acetophenone formation is methyl radical which, based on the proposed mechanism, holds the same kinetic parameters as acetophenone. Cumyloxy radical can also directly attack hydrocarbon chains and abstract a hydrogen atom from a cumylalcohol molecule and macroradicals. Methyl radicals resulting from β -scission of cumyloxy can whether abstract a hydrogen atom to form methane molecule and a macroradical, or combine with another methyl radical to form an ethane molecule. These two molecules are highly volatile and can easily evaporate out of the system. The formation ratio between these two products was determined, but regarding the low concentration of methyl radical it is easy to conclude that the concentration of methane would be higher than of ethane. The consumption of ENB double bond is the result of a radical attack of previously formed macroradicals. The addition of macroradical onto an ENB double bond creates a macroradical and a crosslink. This latter can also be created by the combination of secondary radicals formed from ethylene units. Therefore, the total number of crosslinks can be calculated by summing up these two contributions. A kinetic approach for the lifetime determination of DCP is possible considering the first-order decomposition reaction of DCP. In the literature, the activation energy equal to 140 KJ.mol⁻¹ and a pre-exponential factor equal to 1.85 x10¹⁴ is found [9]. With these data, we obtain a half-life of 2 minutes for DCP at 170 °C. Consequently, the conversion of DCP after 15 minutes at 170 °C is higher than 99%. It is important to precise that the residual value is not capable of giving any quantitative information about the concentration of consumed residual peroxide, and reveals only the time needed for the total consumption of DCP molecules.

The total crosslinking enthalpy remains constant per mole of peroxide for the concentrations inferior to 10 phr. Beyond this concentration, the total enthalpy per mole of peroxide decreases. This deviation has been previously reported in the work of Schwartz, where it was shown that deviation occurs for butyl rubber and nitrile butadiene rubber for the concentrations above 5 phr of peroxide [10]. The deviation from linearity beyond 10 phr of DCP is related to dispersion state of peroxide in the matrix. In fact, at low concentrations the peroxide molecules are homogeneously dispersed among polymer chains. However, as the concentration increases, the DCP molecules get closer and form clusters. General characteristics of peroxides are given in Table 1.

Figure 3 Decomposition mechanism of Di (tert-butylperoxyisopropyl) benzene (DTBPIB)

Figure 4 Decomposition mechanism of (2,5-Dimethyl-2,5-Di (tert-butylperoxy) hexane (DTBPH)

Table 1. General characteristics of peroxides (investigated) [11]

Peroxides	M _w	Temperature(°C) t _{1/2} =1 min	Typical Crosslinking Temperature(°C)	Crosslink efficiency* (%)
DTBPH	290	183	170	
DTBPIB	338	185	170	52
DCP	270	189	160	50

* Crosslink efficiency of pure grades

The rank of cure rates for these peroxides follows: DTBPH<DCP<DTBPIB [11]. The typical crosslinking temperature is the temperature at which about 90% of the crosslinking activity occurs within 12 min [5].

Vulcanization Kinetics

The general equation for the kinetics of the first-order

chemical reaction is:

$$\ln(a-x) = kt + \ln a \quad (1)$$

where, (a) -initial peroxide concentration, [phr]

(x) -reacted quantity at time t, [phr]

(k) -first-order reaction rate constant

for typical peroxides ($t_{1/2}$) drops to about 1/3 of its value for each 10 °C increase of the temperature. The half-life is obtained as:

$$t_{1/2} = \ln 2/k \quad (2)$$

The larger the value of the first-order rate constant k, the faster the reaction.

Determination of Curing Rate

Cure time tc_{90} and tc_{10} and cure rate index were calculated following equations (3) and (4) respectively:

$$tc_x = (x/100)(M_H - M_L) + M_L \quad (3)$$

$$\dots\dots\dots(4)$$

where, (M_L) - minimum torque [d.Nm],

(M_H) - maximum torque [d.Nm],

(x) - present state of cure [%],

(tc_x) - time to a given percent (x) state to produce torque [min.]

High cure rate means fast vulcanisation. The best processing conditions are achieved when ts_2 (scorch time) has a high value.

The scorch time ts_2 is taken at the time to reach 2% of the delta torque above minimum [12]. The increase in torque may take place very rapidly. If this occurs the partially crosslinked polymer cannot properly flow anymore, it is called premature scorch and is related to low ts_2 values. Also, the amount of residual peroxide can be calculated theoretically from the equation (5):

$$((a-x)/a) \times 100 \quad (5)$$

where, (a) - is the initial concentration of peroxide ($M_H - M_L$)

(x) - reacted quantity of peroxide at time t ($M_t - M_L$)

Experimental

Materials and Method

EPDM for the study was Keltan 2470 (ethylene content 75 wt%), Keltan 2450 (ethylene content 45 wt%) and Keltan 5469Q (ethylene content 59wt %) from Lanxess Bayer AG, Cologne, Germany. Peroxides from this study were Perkadox BC (Dicumyl peroxide (DCP), Perkadox 14/40 (Di (tert-butylperoxyisopropyl) benzene (DTBPIB)) and Trigonox 29/40 (2,5-Dimethyl-2,5-Di (tert-butylperoxy) hexane(DTBPH)) from Akzo Nobel N.V Amsterdam, the Netherlands. Besides EPDM and the peroxide, the present invention consists of other compounds such as: zinc oxide (IsoQure ZnO 25 CC) (ZnO coating min. 93%)

supplied by Isochem Kautschuk-GmbH (Frankfurt), medium particle size calcined clay for anti blocking (Polestar 200 R) supplied by Imerys minerals, Cornwall (England) and Silane DSC supplied by Hexpol Compounding, Eupen (Belgium), antioxidant Vulkanox MB (4,5-Methylbenzimidazole-2-thiol) and cross linking activator for peroxide curing Rhenofit TAC/S (70 % of triallyl cyanurate and 30 % of silica) supplied by Lanxess Bayer AG, Cologne (Germany).

Preparation of compounds

The formulation used is given in Tables 2, 3 and 4. At the beginning, the weighted amount of EPDM was fed into the laboratory mixer at 50 °C - 60 °C (Francis Shaw MK3, Manchester, England). Then ZnO powder with Vulkanox MB, Polestar 200 R, silane DSC and TAC/S (70%) were added to the compound and the milling process continued for 10 min. The curing agent peroxide was subsequently added to the mixture and the whole formulation was milled for additional 5 min. To prepare the samples for further investigations, the resultant compounds were prepared on a two-roll mixing mill Berstroff, Hamburg as per ASTM D 3162-07. Determination of Mechanical Properties

Mechanical properties: tensile strength and elongation at break were determined using dumbbell-shaped specimens and measured according to ASTM D 412 by the testing machine OTTO Wolpert EZR-30, Germany. After preparing in a two-roll mixing mill, test specimens were pressed at 175 °C for 20 minutes by the press Burkle Robert model LA 100, Germany and were cut from plates 150mm x 150 mm x 2 mm by means of an automatic punching die.

Crosslinking Characteristic Measurement

The crosslinking characteristics were measured by Monsanto Moving Die Rheometer (MDR 2000 model, Alpha Technologies, USA) according to the test method ASTM D 5289-97.

About 4 g samples of the respective compounds were tested at the temperatures ranging from 180 °C to 200 °C with the measuring time of 15 min.

Table 2. Formulation of mixes with Perkadox BC

	A ₁	B ₁	C ₁	D ₁	E ₁	F ₁	G ₁	I ₁	J ₁
Formulation	Keltan 2470			Keltan 5469 Q			Keltan 2450		
EPDM, phr*	100	100	100	100	100	100	100	100	100
DCP, phr	7.5	10	12.5	7.5	10	12.5	7.5	10	12.5
Ethylene content in EPDM, wt %	75	75	75	59	59	59	45	45	45
Zinc oxide, phr	5	5	5	5	5	5	5	15	15
Vulkanox MB, phr	2	2	2	2	2	2	2	2	2
Polestar 200 R, phr	100	100	100	100	100	100	100	100	100
Silane DSC, phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TAC/S (70%), phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

* phr- parts per hundred

Table 3. Formulation of mixes with Perkadox 14/40

	A ₂	B ₂	C ₂	D ₂	E ₂	F ₂	G ₂	I ₂	J ₂
Formulation	Keltan 2470			Keltan 5469 Q			Keltan 2450		
EPDM, phr*	100	100	100	10	10	100	100	100	100
DTBPIB, phr	7.5	10	12.	7.5	10	12.	7.5	10	12.
Ethylene content in EPDM, wt %	75	75	75	59	59	59	45	45	45
Zinc oxide, phr	5	5	5	5	5	5	5	15	15
Vulkanox MB, phr	2	2	2	2	2	2	2	2	2
Polestar 200 R, phr	100	100	100	1	1	100	100	100	100
Silane DSC, phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TAC/S (70%), phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

* phr- parts per hundred

Table 4. Formulation of mixes with Trigonox 29/40

	A ₃	D ₃	E ₃	F ₃	G ₃	I ₃	J ₃
Formulation	Keltan 2470		Keltan 5469 Q		Keltan 2450		
EPDM, phr*	100	100	100	100	100	100	100
DTBPH, phr	7.5	7.5	10	12.5	7.5	10	12.5
Ethylene content in EPDM, wt %	75	59	59	59	45	45	45
Zinc oxide, phr	5	5	5	5	5	15	15
Vulkanox MB, phr	2	2	2	2	2	2	2
Polestar 200 R, phr	100	100	100	100	100	100	100
Silane DSC, phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TAC/S (70%), phr	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Results and discussion

The experimental cure curves of various peroxides used for the vulcanization of EPDM are presented in Figure 5. Rheographs were recorded at 180 °C, 190 °C and 200 °C.

Figure 5. Rheometric curves of DCP cured EPDM at 180 °C, 190 °C, 200 °C mix A₁, A₂, A₃

According to the results presented in Figure 5, it can be seen that as the temperature increases, there is a non-significant increase in torque. Hence, the maximum torque depends on the temperature with the temperatures lower than 180 °C, where the rate of cure increases with the temperature increase, which leads to a high torque [13]. At 180 °C, the optimum cure is reached, and it would take a minimum 11 min. to complete the consumption of the DCP in the vulcanizate. The curve (at 180 °C) converges to a point and at 190 °C, (t_{100}) remains almost constant. At 200 °C, the role of decomposition of peroxides is high and it is consumed in a limited time, hence the lower t_{100} value. The cure parameter drawn from rheographs is given in Tables 5, 6 and 7.

Table 5. Rheometric properties of vulcanizates (mix A1, 7.5 phr DCP loading)

Temperature °C	M_H d.Nm	$M_H - M_L$ d.Nm	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	78.0	62.5	4.27	5.30	11.0	0.8
190	77.7	61.8	2.48	3.12	5.02	0.5
200	75.9	60.4	1.48	2.09	3.03	0.5

Table 6. Rheometric properties of vulcanizates (mix A2, 7.5 phr DTBPIB loading)

Temperature °C	M_H d.Nm	$M_H - M_L$ d.Nm	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	92.0	77.1	8.12	14.0	24.0	0.8
190	89.9	72.4	3.36	4.45	8.30	0.6
200	88.8	70.3	2.18	3.03	4.48	0.5

Table 7. Rheometric properties of vulcanizates (mix A3, 7.5 phr DTBPH loading)

Temperature °C	M_H d.Nm	$M_H - M_L$ d.Nm	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	60.9	27.0	2.48	3.30	10.0	0.9
190	62.5	28.6	1.54	3.30	4.39	0.5
200	60.0	25.4	1.06	1.12	2.30	0.4

According to the results presented in Tables 5, 6 and 7, optimum cure times of peroxides t_{90} at the temperature 190 °C has the highest influence on the curing efficiency. The experimental cure curves of various peroxides used for the vulcanization of EPDM are presented in Figure 6. It can be seen from rheometer curves that the torque dramatically increases and reaches the equilibrium state within 2.48 to 3 min. The highest influence has been noted at peroxide DTBPH with the lowest value of t_{90} for EPDM. Thus, peroxide DTBPH gained the fastest and complete curing reaction. This parameter is used to describe the ability of peroxide to quickly decompose and generate free radicals. Compounds with different concentrations of peroxides are cured at 180 °C for 15 min., as it is shown in Figure 6. At the start of curing, there are non-significant changes in torque differences at peroxides DCP, DTBPIB rheometric curves, at vari-

ous concentrations (7.5 phr, 10 phr and 12.5 phr) (Figure 6). After 1 min. of vulcanization, the torque of peroxide DTBPH at all concentrations significantly increased reached an optimum cure. Peroxides DCP and DTBPIB reached maximum torque at the concentration of 12.5 phr and peroxide DTBPH has maximum torque at the concentration of 10 phr. According to the results presented in Figure 6, there are non-significant differences between the values of maximum torque at other concentrations of peroxides. These concentrations at which the maximum torque is reached may generate an excess of radicals for the crosslinking reaction much more than in other concentrations. In Figure 7, the effect of a different content of ethylene in EPDM with the peroxide concentration (7.5 phr) on the curing behavior of EPDM is shown. The results indicate that EPDM with peroxide DTBPIB applied in the concentration of (7.5 phr) and with the ethylene content of 59%, can be cured faster than in other blends, M_H was much higher than in the concentration (12.5 phr) (Figure 6).

Figure 6. Rheometric curves of cured EPDM mix D1, E1, F1, B3, E3, F3, D2, E2, F2 with various concentrations and types of peroxides at 180 °C

Figure 7. Rheometric curves of cured EPDM mix A2, D2, G2 at 180 °C, with various contents of ethylene

Vulcanization kinetics

As it can be seen in Figure 8, the reaction of crosslinking of EPDM with peroxide follows the first-order kinetics at all temperatures. The value of the rate constant can be derived from a relative measure of the reactant concentration with time. The change of the moment of crosslinking with the time is directly proportional to the density of the network. The linear dependence of the $\ln(M_\infty - M_t)$ function from the time of crosslinking indicates that the overall EPDM network reaction follows the first-order kinetics. The rate of the EPDM networking reaction rate can be determined from the slope of this linear dependence. With increasing the temperature, the chemical reaction rate constant increases (Table 8 and 10).

Figure 8. Variation of $\log(a-x)$ with time for DCP cured EPDM at 180 °C, 190 °C, 200 °C, mix A₁

The half-life, the time required for half of the peroxide in the formulation to thermally decompose decreases with the increased temperature. Half-lives completed at t_{90} , t_{95} , t_{100} are also given in Tables 8, 9 and 10.

Table 8. Variation of the rate constant and $t_{1/2}$ completed half-life with temperature (mix A₃)

Temperature °C	$t_{1/2}$ min ⁻¹	k min ⁻¹	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	2.57	0.2689	1.27	2.07	3.89	0.9
190	1.59	0.4340	0.78	1.35	2.77	0.5
200	0.83	0.8380	0.57	1.28	2.76	0.4

Table 9. Variation of the rate constant and $t_{1/2}$ completed half-life with temperature (mix A₂)

Temperature °C	$t_{1/2}$ min ⁻¹	k min ⁻¹	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	8.20	0.0845	1.00	1.71	2.92	0.8
190	4.57	0.1514	0.73	0.97	1.82	0.6
200	3.62	0.1912	0.6	0.84	1.23	0.5

Table 10. Variation of the rate constant and $t_{1/2}$ completed half-life with temperature (mix A₁)

Temperature °C	$t_{1/2}$ min ⁻¹	k min ⁻¹	t_{90} min	t_{95} min	t_{100} min	ts_2 min
180	5.08	0.2364	0.84	1.04	2.16	0.8
190	3.39	0.2036	0.73	0.92	1.47	0.5
200	3.26	0.2128	0.45	0.64	0.92	0.5

After the first half-life, 87.2% of DCP, 87.1% DBTPIB and 87.5% of DTBPH decompose. The process continues and theoretically never reaches 100% of decomposition/consumption. After two half-lives 97.5% DCP, 93.6% of DTBPIB and 98.2% of DTBPH decompose. It is to be noted that t_{100} for DCP, DTBPIB, and DTBPH accounts for an average of 2 to 3 half-lives. Figure 9 shows the effect of temperature on the cure rate index (CRI) and delta torque. The torque differences of peroxide DCP extend significantly more with the cure temperature than those of other compounds (Figure 8). For DCP at 180 °C, the cure rate index (CRI) which indicates the efficiency of peroxide is the same as for DTBPIB at 190 °C, while for peroxide DTBPH the values of CRI were two times higher than for other two peroxides at 180 °C. Cure times (t_{90}) in EPDM were compared in Figure 10. It can be seen that cure time decreases with increasing the temperature. Peroxide DTBPH has a slow curing time up to 9 min. at 180 °C and dramatical values of curing times decrease 3 times at 190 °C and 200 °C. Peroxides DCP and DTBPIB clearly had fast cure times which indicates that DBTPH could achieve faster curing: about 3 times faster than other peroxides at 180 °C and about 2 times faster by increasing the cure temperature up to 10 °C. This could be one of the reasons to use DTBPH at curing temperatures lower than 180 °C in order to avoid thermal degradation, while the other peroxides cannot reach the same cure level below 180 °C. Figure 9 shows the cure rate index (CRI) where the efficiency of DCP at 180 °C is the same as DBTPIB at 190 °C.

Figure 9. Effect of temperature on torque differences (—MH-ML) and the index of the cure rate (---CRI) of (mix A₁, A₂, A₃)

Figure 10. Effect of curing temperature on t_{c90} of (mix A1, A2, A3)

Mechanical properties

The variation of the tensile strength with the concentration of peroxide and the content of ethylene in EPDM is shown in Figure 11. The tensile strength increased with the increase of the concentration of peroxide up to an optimum level and then decreased, but in EPDM with 59% of ethylene, the tensile strength stays much more constant at all peroxides when the optimum concentration is reached. At peroxide DTBPIB crosslinked with EPDM (ethylene content 45% and 75%) the values of the tensile strength at the concentration of 10 phr and at higher concentrations were almost the same. Opposite to these trends, after the treatment with peroxide DCP, the values of the tensile strength were the same at the concentration of 10 phr in EPDM (with the ethylene content 45% and 75%) but at higher concentration values of the tensile strength they decreased. This could be attributed to the fact that at the higher peroxide level, there is the increase in the amount of residual peroxide, as well as the possibility of the formation of clusters due to the non-homogeneous distribution of crosslinks [14, 15]. It can be seen from Figure 12 that the value of the tensile strength of peroxide DTBPH at the concentration of 12.5 phr is the highest with the ethylene content of 45%, even higher than the tensile strength of peroxide DCP and DTBPIB at the same concentration (12.5 phr) and with 75% of the ethylene content in EPDM.

It can be seen from Figure 12 that elongation at break increases with increasing the concentration of peroxide up to an optimum level (10 phr), and then decreased with increasing the concentration of peroxide. Opposite to this trend, the values of elongation at break decreases with increasing the content of ethylene in EPDM, which is not the case with peroxide DCP where the content of ethylene does not influence the values of elongation at break. The values of elongation at break of peroxide DTBPH are the highest with the concentration of 10 phr and the ethylene content of 45%. Even at the lower concentration of peroxide DTBPH, the value of elongation at break was the highest.

Figure 11. Variation of the tensile strength as a function of the concentration of peroxides and the ethylene content in EPDM

Figure 12. Variation of elongation at break as a function of the concentration and type of peroxides and the ethylene content in EPDM

Conclusions

Considering the fact that peroxide vulcanization of EPDM is one of the most widely used methods in the cable industry, the producers in the world are trying to achieve better production while they are dealing with different factors that will influence the final properties of the product. In this study three most common peroxides and their influence on properties of EPDM with various contents of ethylene were used. It was found that Peroxide DCP is good for curing at temperatures in the range of 180 °C to 190 °C which accomplished an ultimate cure within 11 to 5 minutes. More over, DTBPH has higher performance, which decreased the optimum cure time to 1.5 minutes. Peroxide DBTPH could achieve faster curing: about 3 times faster than other peroxides at 180 °C and about 2 times faster by increasing the cure temperature up to 10 °C. The crosslinking efficiency of peroxide depends on the number of completed half-lives. In order to avoid thermal degradation, peroxide could be used at

temperatures lower than 180 °C. While other peroxides cannot reach the same cure level below 180 °C. After two half-lives decompose 97.5% DCP, 93.6% of DTBPIB and 98.2% of DTBPH is decomposed. Besides the peroxide concentration which is the dominant factor at the temperatures lower than 180 °C, the important factor for peroxide vulcanization is also the content of ethylene in EPDM. The values of elongation at break and the tensile strength of peroxide DTBPH is the highest with the concentration of 7.5 phr and the ethylene content of 45%. DCP and DTBPIB peroxides show excellent mechanical properties at the concentration of 10 phr and with EPDM which consists of 45% of ethylene. The interplay between key variables in the formulation was important for evaluating final mechanical properties of the final product, in this case, a medium voltage cable.

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Izvod

UTICAJ PEROKSIDA NA PROCES UMREŽAVANJA EPDM IZOLACIJE KABLOVA SREDNJEG NAPONA

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Ovaj rad opisuje uticaj koncentracije i vrste peroksida na efikasnost umrežavanja različitih tipova EPDM-a (etilen propilen dien monomer (M-klase) gumu), [1] [2] [10] sa različitim sadržajem etilena koji se koristi u širokom spektru aplikacija. Reološke karakteristike su ispitane korišćenjem Monsanto reometra sa temperaturnim režimom u opsegu između 180 i 200 °C, gde se mere parametri reometarskih krivi na svakih 10 °C. Mehaničke osobine: zatezna čvrstoća i prekidno izduženje su ispitani sa testom zatezanja u skladu sa standardom ASTM D-412. Dobijeni rezultati ukazuju da peroksid DTBPH sa koncentracijom 7.5 phr daje najbolje rezultate (vreme umrežavanja 1,5 min.) na temperaturi od 180 do 190 °C. Pri većoj koncentraciji peroksida, prilikom umrežavanja ostaje veća količina rezidvalnog peroksida, koji povećava mogućnost preumrežavanja i nastajanja nehomogene umrežene strukture. Peroksidno umreženi EPDM sa 45% sadržaja etilena daje najefikasnije mehaničke osobine izolacije srednje naponskih kablova. Značajno je pomenuti da vreme koje je potrebno za potpuno 100% umrežavanje EPDM-a (t100) za perokside dikumil peroksid (DCP), di (tert-butil peroksi izopropil) benzen (DTBPIB), and (2,5-di metil-2,5-di (tert-butilperoksi) heksan (DTBPH) u proseku odgovara za 2-3 njihova poluvremena raspada.

Ključne reči: Umrežavanje, kinetika, EPDM, organski peroksid, reološke karakteristike.