

Mechanical, Vulcametric, and Thermal Properties of the Different 5-ethylidene 2-norbornene Content of Ethylene-Propylene-Diene-Monomer Vulcanized with Different Types and Compositions of Peroxides

Seda Çavdar, Tonguç Özdemir,* Ali Usanmaz

Departments of Chemistry and Polymer Science and Technology, Middle East Technical University, Ankara, Turkey

Received 30 April 2007; accepted 7 November 2008

DOI 10.1002/app.29688

Published online 11 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ethylene-propylene-diene-monomer (EPDM) rubber is an important commercial polymer. The vulcanization process significantly changes its thermal, mechanical, and vulcametric properties. This study was carried out to find optimum formulation of EPDM composite for a better application in automotive industry. Sixteen EPDM polymer samples having different 5-ethylidene 2-norbornene (ENB) and ethylene contents were vulcanized with different types and compositions of peroxide and coagents. The mechanical and vulcametric properties of these samples were measured and compared. The type of peroxide, coagent, and EPDM grade affected the mechanical, thermal, and vulcametric properties of the EPDM rubber to some extent. Use of aromatic peroxide and coagent increased the thermal

stability slightly. Mechanical properties were changed very slightly with the change of peroxide type for the same content of peroxide and coagent. Scorch time and cure time decreased with initial increase of the peroxide content. EPDM compound vulcanized with BBPIB peroxide and TAC/S coagent has higher cure time than EPDM compound vulcanized with DMBPha peroxide and TMPTMA coagent. Coran method was used for the modeling of experimental data. Velocity constant for the formation of peroxide radical and polymer radical were found for each case. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1891–1896, 2009

Key words: EPDM; vulcanization; mechanical properties; vulcametry; thermal properties

INTRODUCTION

Additives are used in the vulcanization process of ethylene-propylene-diene-monomer (EPDM) to achieve the compliance with the desired vulcametric, mechanical, and thermal properties. Peroxide vulcanization for EPDM is intensively investigated. Organic peroxides produce free radicals, which create the desired crosslinked networks in elastomers. The structure of peroxide affects its thermal and chemical stability, as well as the energy level of free radicals generated.¹ Duin and Dikland² reported that the peroxide crosslinking of EPDM proceed via two parallel pathways, that is the combination of two EPDM macro-radicals and/or addition of an EPDM macro-radical to the residual unsaturation.

Several factors including polymer type, peroxide type and content, and presence of other reactive species in the rubber formulation affects the vulcaniza-

tion process and the properties of rubber product. The nature of polymer has a profound effect on crosslinking, but coagents, antioxidants, oils, fillers, and the type and content of peroxide effect the crosslinking process.³

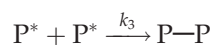
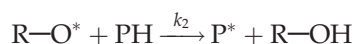
There have been extensive studies on the mechanical, viscoelastic, and vulcametric properties of the EPDM,^{4–9} which contains different additives. Ginic-Markovic et al.⁵ studied the viscoelastic behavior of filled and unfilled EPDM. The mechanism of triallylcyanurate as a coagent was investigated via IR spectroscopy and equilibrium swelling.⁹ The effect of the vulcanizing system on the mechanical properties of butyl rubber/EPDM and general purpose furnace black blends on static and dynamic mechanical properties were studied by Abd-El Salam et al.¹⁰ It was reported that the proper selection of the vulcanizing system and the type and content of carbon black is necessary for optimum performance of the rubber end product.¹⁰ Guriya et al.¹¹ studied the vulcametric properties of EPDM for gum and carbon black filled systems with variation of the blowing agent, extrusion temperature, and shear rate. The effect of oil and curing agent content on the mechanical behavior of thermoplastic vulcanizates, based on a polypropylene (PP) and EPDM was reported by Medintseva et al.¹²

*Present address: Turkish Atomic Energy Authority, 06530, Ankara, Turkey.

Correspondence to: A. Usanmaz (usanmaz@metu.edu.tr).

Naskar and Noordermeer¹³ studied the effects of different types of peroxides as curing agents on the properties of PP/EPDM thermoplastics vulcanizates, and it was shown that mechanical properties change significantly with the chemical nature of the peroxides.

In this study, it was intended to see the extent of any modification in mechanical, vulcanometric, and thermal properties of the EPDM compounds using a complex recipe for automotive industry applications, for which continuous improvement in the quality of EPDM rubber is aimed. EPDM polymer having different 5-ethylidene 2-norbornene (ENB) content was vulcanized with different type and content of peroxide and coagent. Mechanical and vulcanometric properties of 16 different vulcanized EPDM polymers were compared. Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) were carried out to understand the degree of change in thermal properties with the change of vulcanization agents. Coran¹⁴ postulated a simplified reaction scheme to explain the kinetics of delayed action sulfur vulcanization and this simplified scheme adequately accounted for the kinetics of crosslink formation. Although chemical mechanisms differ, vulcanization with other crosslinking systems may be explained in a similar way with Coran vulcanization scheme.¹⁵ Coran method was used for the interpretation of the experimental results. Simplified scheme for peroxide crosslinking is given below where P is polymer, R—O—O—R is peroxide, Z is k_1/k_2 , and * denotes free radical.



MATERIALS AND METHODS

The compositions of EPDM, peroxide, and coagent are given in Table I. Four different EPDM having different ethylene and ENB contents (5.0, 5.6, 7.5, and 8.9%) were used with two different peroxides with compositions of 3–5% and 5–7%. In total, mechanical and vulcanometric properties of 16 different vulcanized EPDM rubbers were compared. Other additives namely zinc oxide (5 phr), stearic acid (1 phr), carbon black filler (FEF N-550, 90 phr), and plasticizer (Tudalen 3909, Hansen & Rosenthal (Hamburg, Germany), 30 phr) were used with the same compositions for the each of the 16 EPDM rubbers. The peroxides used were 2,5-di(*t*-butylperoxy)-2,5-dimethyl hexane (DMBPHa) (Luperox 101XL45) and di(*tert*-butylperoxyisopropyl) benzene (BBPIB)

(Perkadox 14-40). Trimethylolpropane trimethacrylate (TMPTMA) was used as coagent with DMBPHa and triallylcyanurate [2,4,6-tris(allyloxy)-s-triazine] (TAC/S) as coagent with BBPIB.

The formulations were compounded as given in Table I in two stages, first by mixing equipment (two roll mills with friction ratio of 2 : 1) and subsequently cured by compression molding. MDR 2000 mark rheometer was used for vulcanometric studies. Vulcanometry tests were carried out both at 190°C with time flow of 3 min and 180°C with time flow of 10 min. Cure time and scorch time, which is the time required at a specified temperature to form incipient crosslinks,¹ were measured.

Tensile tests were carried out for the EPDM samples that were prepared in the form of dumbbell shaped tensile test specimens, cut from the sheet vulcanized in hydraulic press at 180°C for 10 min according to DIN 53,504. Hounsfield Tensometer with crosshead displacement rate of 500 mm/min was used for tensile tests and the result reported is the averages of the five specimens. Tests were done according to ASTM D412.¹⁶ Compression tests were carried out according to the ASTM D395.¹⁷ TGA were carried out on TA Instruments SDT Q600 under N₂ atmosphere with a heating rate of 10°C/min and the sample weight was about 10 mg. DSC thermograms of the polymers were taken on TA Instruments DSC 2010 under N₂ atmosphere with a heating rate of 10°C/min, aluminum pans were used and the temperature range for the analyses was 25–550°C.

RESULTS AND DISCUSSION

Vulcanometric properties

The vulcanometric test results are given in Figure 1. Scorch time decreased with the increase of the peroxide content in vulcanization system. Induction period (scorch delay, t_i) calculated according to Coran method affirmed that as peroxide content increases the induction period decreases and confirmed the experimental results. The rate of decrease is higher for the lower percentage of the peroxide that is probably due to relatively higher crosslink reaction rate with the initial increase of peroxide content. The EPDM vulcanized with BBPIB peroxide and TAC/S coagent has slightly lower scorch time when compared with EPDM vulcanized with DMBPHa peroxide and TMPTMA coagent [Fig. 1(a)], for the same content of peroxide and coagent, probably due to high energy radicals produced in the BBPIB used case that initiate crosslink reaction faster than the DMBPHa used case. Induction period (t_i) values calculated according to Coran method comply with the experimental results and are given in Table I. Moreover, velocity constant for the formation of peroxide

TABLE I
Different Types of EPDM Used and Alternative Vulcanization System

| | 1 (KELTAN 27) | | | | 2 (KELTAN 8340A) | | | | 3 (BUNA EP G 6850) | | | | 4 (KELTAN 4903Z) | | | |
|----------------------------------|---------------|------|------|------|------------------|------|------|------|--------------------|------|------|------|------------------|------|------|------|
| EPDM | 100 | | | | 100 | | | | 100 | | | | 100 | | | |
| % Ethylene | 50.8 | | | | 51.6 | | | | 52.9 | | | | 45.9 | | | |
| % ENB | 5.0 | | | | 5.6 | | | | 7.5 | | | | 8.9 | | | |
| Alternative vulcanization system | V1 | V2 | V3 | V4 | V1 | V2 | V3 | V4 | V1 | V2 | V3 | V4 | V1 | V2 | V3 | V4 |
| DMBPHa (phr) | 3 | 5 | – | – | 3 | 5 | – | – | 3 | 5 | – | – | 3 | 5 | – | – |
| TMPTMA (phr) | 2.5 | 2.5 | – | – | 2.5 | 2.5 | – | – | 2.5 | 2.5 | – | – | 2.5 | 2.5 | – | – |
| BBPIB (phr) | – | – | 5 | 7 | – | – | 5 | 7 | – | – | 5 | 7 | – | – | 5 | 7 |
| TAC/S (phr) | – | – | 2.5 | 2.5 | – | – | 2.5 | 2.5 | – | – | 2.5 | 2.5 | – | – | 2.5 | 2.5 |
| k_1 (min^{-1}) | 1.38 | 1.15 | 1.68 | 2.17 | 1.60 | 1.63 | 4.58 | 4.13 | 1.15 | 1.18 | 2.94 | 3.79 | 0.67 | 0.70 | 1.03 | 1.27 |
| k_2 (min^{-1}) | 0.99 | 1.53 | 1.40 | 1.76 | 1.07 | 1.55 | 1.17 | 1.21 | 1.01 | 1.54 | 1.23 | 1.30 | 1.27 | 1.46 | 1.25 | 1.26 |
| Z (k_1/k_2) | 1.39 | 0.76 | 1.20 | 1.23 | 1.49 | 1.05 | 3.91 | 3.41 | 1.14 | 0.77 | 2.39 | 2.92 | 0.53 | 0.48 | 0.83 | 1.01 |
| t_i (s) | 35.8 | 31.1 | 20.6 | 20.1 | 31.8 | 28.1 | 17.7 | 18.4 | 36.1 | 35.0 | 16.9 | 15.8 | 38.7 | 26.9 | 22.3 | 20.4 |
| t_{dis} (s) | 51.0 | 45 | 39 | 30.6 | 45.6 | 37.8 | 24.0 | 25.2 | 55.8 | 44.4 | 30.6 | 25.8 | 64.2 | 58.2 | 52.8 | 47.6 |

radical (k_1) values calculated according to Coran method showed that BBPIB peroxide and TAC/S coagent used case have higher k_1 values for the same content of DMBPHa peroxide and TMPTMA coagent, confirming that the experimental result of lower scorch time for the BBPIB peroxide and TAC/S coagent used case, the k_1 values are given in Table I.

The cure time (t_{90}), obtained at 190°C, is higher for the samples vulcanized with BBPIB and TAC/S when compared with the samples vulcanized with DMBPHa and TMPTMA [Fig. 1(b)] for the same content of peroxide and coagent. Cure time decreased with the increase of the peroxide content in vulcanization system. Velocity constant for the formation of polymer radical (k_2) calculated according to Coran method affirmed that as peroxide content increases (regardless of the type of peroxide) k_2 value increases confirming the experimental results of the decrease of cure time with the increase of peroxide content, the calculated k_2 values are given in Table I.

Velocity constant for the formation of polymer radical (k_2) value is higher for DMBPHa peroxide and TMPTMA coagent used case than BBPIB peroxide and TAC/S coagent used case having the same content of peroxide and coagent, confirming the experimental finding of cure time is higher for the BBPIB peroxide and TAC/S coagent used case compared with DMBPHa peroxide and TMPTMA coagent for the same content of peroxide and coagent.

Moreover, comparison of the DMBPHa used case with peroxide content of 3 and 5 phr showed that Z (inversely proportional with k_2) value is higher for the lower content of peroxide (3 phr), the calculated Z values are given in Table I. The time required for crosslinking to become unpertubed first order reaction (t_{dis}) calculated according to Coran method decreases as the content of peroxide increases due to

the increase of k_2 with peroxide content, the calculated t_{dis} values are given in Table I. The time required for crosslinking to become unpertubed first-order reaction (t_{dis}) value is lower for the BBPIB used case compared with DMBPHa used case for

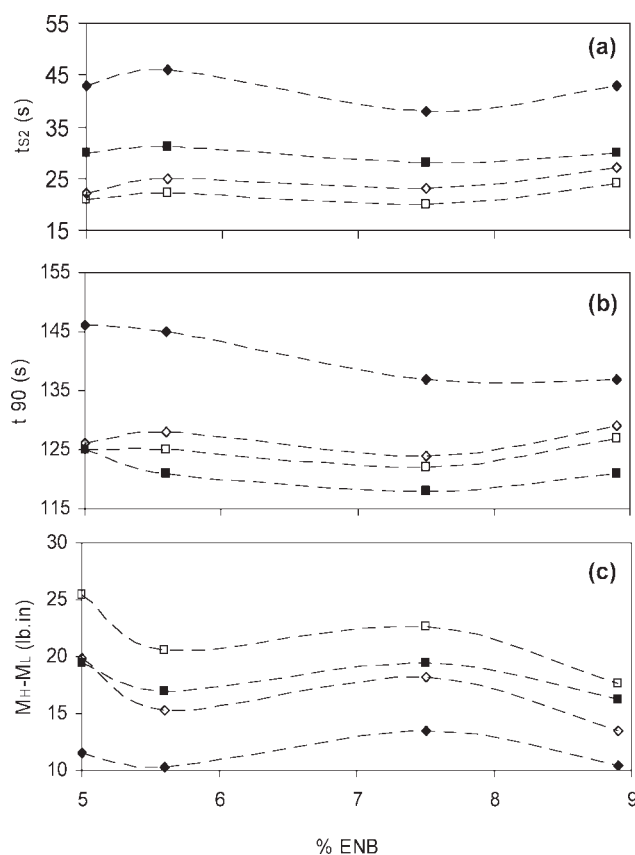


Figure 1 Change of vulcanometric properties with ENB content for different vulcanization systems, vulcanometric tests done at 190°C [DMBPHa (◆: 3 phr, ■: 5 phr) + TMPTMA, BBPIB (◇: 5 phr, □: 7 phr) + TAC/S].

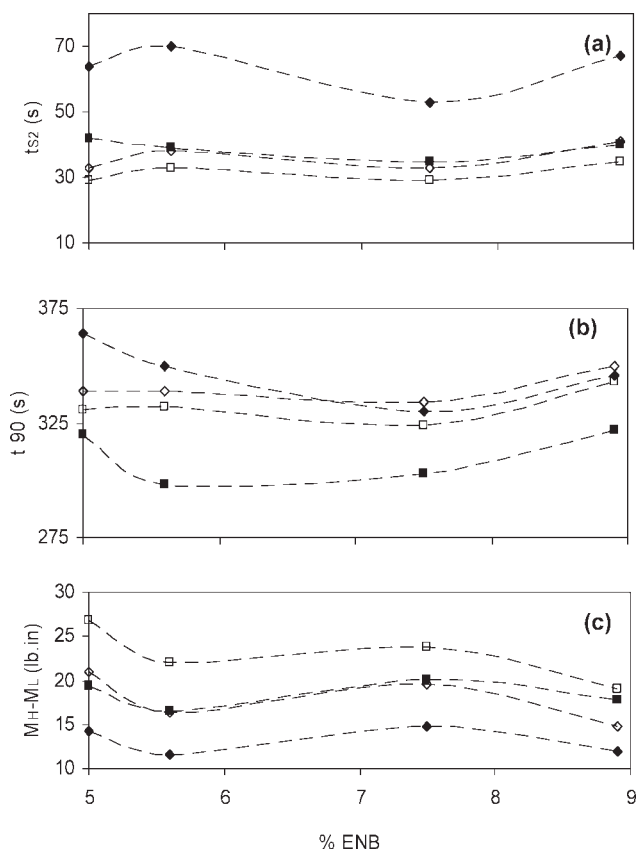


Figure 2 Change of vulcanometric properties with ENB content for different vulcanization systems, vulcanometric tests done at 180°C [DMBPHa (◆: 3 phr, ■: 5 phr) + TMPTMA, BBPIB (◇: 5 phr, □: 7 phr) + TAC/S].

the same content of peroxide used in the vulcanization, this is due to relatively higher scorch time in the DMBPHa used case.

Difference between maximum and minimum torque values, $M_H - M_L$, corresponds to the relative degree of crosslink.¹ The $M_H - M_L$ and relative degree of crosslink increased with the increase of peroxide content in vulcanization system [Fig. 1(c)].

The vulcanometric properties, obtained at 180°C, are given in Figure 2. The EPDM vulcanized with BBPIB peroxide and TAC/S coagent has very close scorch time with that of EPDM vulcanized with DMBPHa peroxide and TMPTMA coagent [Fig. 2(a)]. The cure time data, obtained at 180°C, is higher for the samples vulcanized with BBPIB and TAC/S when compared with samples vulcanized with DMBPHa and TMPTMA [Fig. 2(b)], for the same content of peroxide, this result complies with the data obtained at 190°C. This is probably due to that the allylic type coagents are reacting slower than the acrylate type coagent and that is why TAC/S coagent provides longer cure time.

Mechanical properties

Change of mechanical properties with ENB content for different vulcanization systems are given in

Figure 3. The elastic modulus for the EPDM polymers having the same peroxide content with different peroxide type have slightly different elastic modulus values as shown in Figure 3(a). Elastic modulus increased with the increase of peroxide content in vulcanization system. The elastic modulus is very close for the three of the EPDM polymer having 5.0, 5.6, and 7.5% ENB content and vulcanized with 7 phr BBPIB [Fig. 3(a)].

Ultimate stress at break has maxima for the ENB content of 7.5%. Thus, it can be stated that the optimum crosslink density is obtained when the ENB content is 7.5% [Fig. 3(b)]. Increase of the peroxide content in vulcanization system decreased the elongation at break significantly. The elongation at break data for the EPDMs having the same peroxide content with different peroxide type were slightly different as shown in Figure 3(c).

The change of the compression set values with the ENB content is shown in Figure 3(d). The compression set decreased as the peroxide content in vulcanization system increased. The rate of decrease is higher for relatively lower content of peroxide in vulcanization system. Compression set values

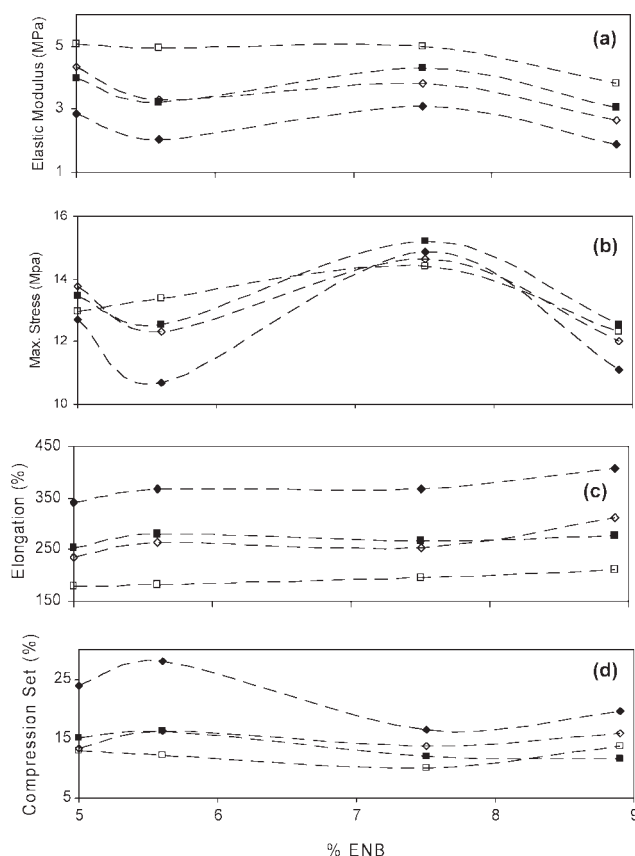


Figure 3 Change of mechanical properties with ENB content for different vulcanization systems (same annotations with Fig. 1).

became relatively low, that is mechanical properties improve positively, when the ENB content is 7.5%. This supported the idea of the optimum crosslink density occurrence at 7.5% ENB content.

Thermal investigation

The DSC thermograms for the samples, in the temperature range of 25–550°C, are given in Figure 4. The glass transition temperature is well below 0°C and therefore not observed in thermograms. Change of the ENB and ethylene content, peroxide, and coagent type and content changed the decomposition temperature range slightly. The EPDM having 5% ENB content vulcanized with 5 phr DMBPHA has a decomposition peak temperature at 465°C whereas EPDM having 5% ENB content vulcanized with 5 phr BBPIB has the peak temperature at 469.5°C. This result showed that the use of aromatic vulcanizing agent and coagent increased the thermal stability slightly.

TGA thermograms for the different ENB and ethylene content and/or peroxide used in the vulcanization system are given in Figure 5. Single step degradation was observed in the TGA thermograms. The mass loss in initial stage was relatively higher for the sample vulcanized with 5 phr DMBPHA peroxide having the 5.0% ENB content. The temperature at which 50% decomposition occurs (T_{50}) is generally considered as an index of thermal stability.¹⁸ T_{50} for thermogram (b) is 462°C (with max. weight loss at 457°C), for thermogram (c) is 464°C (with max. weight loss at 460°C) and for thermogram (a) is 466.5°C (with max. weight loss at 460.8°C). Comparison of thermograms (b) and (c) in Figure 5 shows that the aromatic peroxide (BBPIB) and coagent (TAC/S) used in vulcanization system slightly increased the thermal stability compared with the use of DMBPHA peroxide with TMPTMA coagent, reaffirming the results from the DSC study.

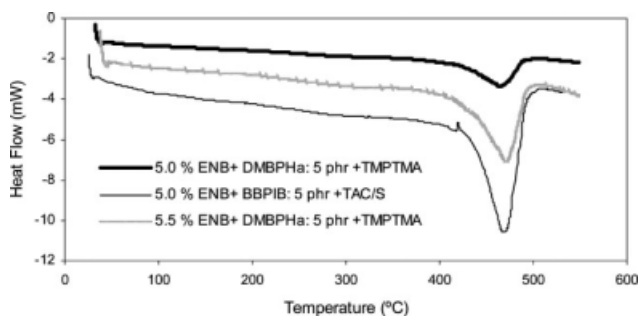


Figure 4 DSC thermograms for different ENB and vulcanizing agent contents of EPDM.

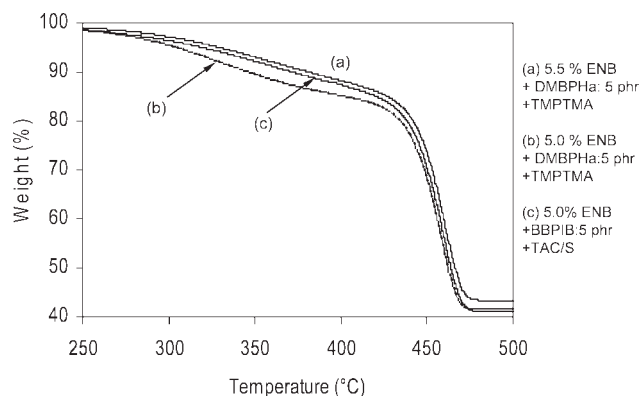


Figure 5 TGA thermograms for different ENB and peroxide contents.

CONCLUSIONS

The type and content of peroxide, coagent used in vulcanization system and ENB content changes the mechanical, thermal, and vulcanometric properties of the EPDM to some extent. Mechanical properties are very close for the same content of peroxide and coagent with different type of peroxide and coagent. Coran method were fitted well to the experimental data and experimental results were confirmed with the Coran model. Cure time data obtained at 180 and 190°C showed that the cure time is higher for the BBPIB peroxide and TAC/S coagent case compared with DMBPHA peroxide and TMPTMA coagent, probably due to the allylic type coagents are reacting slower than the acrylate type coagents and that is why TAC/S coagent provides longer cure time. Velocity constant for the formation of polymer radical (k_2) calculated according to Coran method affirmed that as peroxide content increases (regardless of the type of peroxide), k_2 value increases. Moreover, use of aromatic peroxide (BBPIB) and coagent (TAC/S) increases the thermal stability slightly.

References

- Palys, L. H. In *Rubber Technology: Compounding and Testing for Performance*; Dick, J. S., Ed.; Hanser Gardner Publications: Cincinnati, 2001.
- Duin, M.; Dikland, H. G. *Rubber Chem Technol* 2003, 76, 132.
- Dluzneski, P. R. *Rubber Chem Technol* 2001, 74, 451.
- Maity, A. K.; Xavier, S. F. *Eur Polym J* 1999, 35, 173.
- Ginic-Markovic, M.; Dutta, N. K.; Dimopoulos, M.; Roy Choudhury, N.; Matison, J. G. *Thermochim Acta* 2000, 211, 357.
- Osanaieye, G. J.; Adewale, K. P. *Polym Test* 2001, 20, 363.
- Prut, E.; Medintseva, T.; Dreval, V. *Macromol Symp* 2006, 233, 78.
- Goharpey, F.; Nazockdast, H.; Katbab, A. A. *Polym Eng Sci* 2005, 45, 84.
- Murgic, Z. H.; Jelencic, J.; Murgic, L. *Polym Eng Sci* 1998, 38, 689.

10. Abd-El Salam, F.; Abd-El Salam, M. H.; Mostafa, M. T.; Nagy, M. R.; Mohamed, M. I. *J Appl Polym Sci* 2003, 90, 1539.
11. Guriya, K. C.; Bhattachariya, A. K.; Tripathy, D. K. *Polymer* 1998, 39, 109.
12. Medintseva, T.; Erina, N.; Prut, E. *Macromol Symp* 2001, 176, 49.
13. Naskar, K.; Noordermeer, J. W. M. *Rubber Chem Technol* 2003, 76, 1001.
14. Coran, A. Y. *Rubber Chem Technol* 1964, 37, 689.
15. Trebar, M.; Susteric, Z.; Lotric, U. *Polymer* 2007, 48, 5340.
16. ASTM, 2006. Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension, ASTM D 412; ASTM: West Conshohocken, Pennsylvania.
17. ASTM, 2003. Standard Test Methods for Rubber Property—Compression Set, ASTM D 395; ASTM: West Conshohocken, Pennsylvania.
18. Abdel-Aziz, M. M.; Basfar, A. A. *Nucl Instrum Methods Phys Res B* 2001, 185, 346.