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RESEARCH ARTICLE

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Identification of temperature scanning stress relaxation behaviors of new grade ethylene propylene diene elastomers

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Abstract

Natural rubber is the most common material for dynamic applications. Its limited service temperature leads to search alternative elastomeric materials for related areas. In this study, natural rubber, traditional ethylene propylene diene rubber (EPDM), and a new grade EPDM with modified structural properties have been evaluated by means of tensile properties, characteristic temperatures, cross-link density, isothermal and nonisothermal relaxation behaviors with temperature scanning stress relaxation (TSSR) method. Linear molecular structure of the alternative EPDM elastomers provided improved tensile strength and isothermal stress relaxation behavior. Small amount of process oil addition also improved their service temperatures due to better processing conditions. Annealing study showed that strain-induced crystallization is one of the important factors controlling service conditions of EPDM. Besides, TSSR technique was concluded to be a fast and powerful technique for measuring cross-link density and for predicting service temperatures of natural rubber and EPDM elastomers.

KEYWORDS

annealing, cross-link density, elastomers, relaxation, temperature scanning stress relaxation

1 | INTRODUCTION

Natural Rubber (NR) has been used in dynamic applications for many years. NR has satisfactory resilience, vibration, and fatigue properties.[1,2] Besides all these good properties, NR has quite poor aging resistance; also, its service temperature is limited to about 90°C.[3] Improving aging and relaxation characteristics of NR is a common problem for both rubber industry and academy. Nowadays, especially automotive industry has been focused on thermally resistant static and dynamic rubber-based materials in new-generation automobiles because of current strict emission regulations. There are a lot of attempts to improve service conditions of NR. However, results are not comparable with alternative saturated rubbers such as ethylene propylene diene rubber (EPDM).

Attempts for improving both aging and dynamic properties of NR focus on adjusting curing system and main chain modification. In the past, Stratton and Ferry investigated effect of various vulcanization systems on dynamic mechanical properties of NR.[4] They studied peroxide vulcanization, γ-radiation, vulcanization by tetramethyl thiuram disulfide (TMTD) as sulfur donor, and various sulfur/accelerator ratios in sulfur vulcanization, comparatively. Reversion behavior and dynamic mechanical properties of gum and carbon black filled NR vulcanizates were studied by Fan et al.[5] Conventional (CV), semi-efficient (semi-EV), and efficient (EV) vulcanization systems were evaluated for the same cross-link densities. Higher glass transition temperatures (T_g) and higher damping ratio (tan δ) values were obtained for carbon black-filled NR vulcanizates in case of CV system. It

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was concluded that reversion had a major effect on dynamic properties of NR. Simma et al.[6] tried to improve thermal stability and aging resistance of a model NR skim compound by hydrogenation in latex form via diimide reduction. Peroxide, zinc oxide, stearic acid, and organic accelerators containing a curing system were evaluated. Hydrogenated NR compounds could exhibit moderate thermal stability when compared to NR and EPDM. Hydrogenated NR could also retain its mechanical properties after aging. Besides, its ozone resistance was significantly higher than that of NR. Low molecular weight of an epoxidized natural rubber (ENR) was also considered to improve thermal properties of NR compounds.[7] It was concluded that increasing saturation in the rubber matrix improved aging behavior of NR based materials, as expected. Higher ENR incorporation gave enhanced thermal resistance.

Temperature scanning stress relaxation (TSSR) is a new method, which can be used for all plastics, thermoplastic elastomers (TPEs), and elastomers; mainly provides valuable information about stress relaxation behaviors and cross-link density, as well as about characteristic temperatures of the materials.[8–13] There are limited number of studies in the literature conducted on TSSR applications. Sirinivasan et al.[9] studied relaxation behavior of carbon black-filled EPDM compounds to find effect of filler–filler and polymer–filler interactions on relaxation behavior of the vulcanizates. They focused on investigating physical interactions between the mentioned matrices. Vennemann et al.[11] investigated cross-link density and network structure of unfilled NR vulcanizates cured by various sulfur curing systems, by means of TSSR. They found that sulfur/accelerator ratio had a strong impact on the shape of the relaxation spectrum, deduced from the significant peaks related to polysulfidic cross-link cleavage in the relaxation spectrum. Nobari-Azar and Şen[12] studied effects of accelerator type on stress relaxation behavior and network structure of aged natural rubber/chloroprene rubber (NR/CR) vulcanizates. They found that there was a strong interdependence between accelerator type and stress relaxation behavior, network structure, and cross-link density of the NR/CR vulcanizates. TSSR studies of uncross-linked and radiation cross-linked shape memory polymer blends of ethylene octane copolymer (ECO) and EPDM have been carried out by Chatterjee et al.[13] over a certain temperature range. Cross-link density measurements and TSSR index (or RI values) calculations were performed using TSSR instrument. Elasticity and shape recovery behavior of the blends were successfully correlated with TSSR test results.

In this study, new formulations based on a high ethylene content, linear chain structure, high molecular weight, and narrow molecular weight distribution of an EPDM have been evaluated by means of stress relaxation behavior, cross-link density, and characteristic service temperatures using TSSR test method. Indeed, new EPDM compounds have been suggested for dynamic applications. However, in this study, it was aimed to reveal the consistency between relaxation behavior and tensile properties of the vulcanizates.

2 | EXPERIMENTAL

2.1 | Materials

Natural rubber (CV 60) was supplied from Baria Rubber Co. (Vietnam) with 60 ± 5 MU of Mooney viscosity (@100°C ML(1 + 8)), 82 of plasticity retention index, and 0.019% of dirt content. Butadiene rubber (BR) was supplied from Voronezh (Russia) having 44 ± 5 MU of Mooney viscosity (@100°C ML(1 + 4)). Alternative EPDM (Keltan 9565Q) was obtained from Lanxess (USA). Conventional (reference) EPDM (KEP 2380) having similar ENB with alternative one were obtained from Kumho (Korea). KEP 2380 has 82 ± 5 of Mooney viscosity (@125°C ML(1 + 8)), 53.5%–57.5% ethylene content, and 5.2%–6.2% ENB content. Properties those of Keltan 9565Q (alternative) were 67 MU (@150°C ML(1 + 8)), 62%, and 5.5%, respectively. Keltan 9565Q has also 50 phr extender oil to provide satisfactory process conditions. Carbon black FEF550 (DBP: 121 ± 6 mg 100 L^{-1}) and surface area (39 ± 6 m^2/g) obtained from OMSK (Russia) was used as filler. Heavy paraffinic oil and naphthenic oil were obtained from Shell (Turkey) and Petroyağ (Turkey), respectively. Paraffinic oil has 487 mm^2/s of viscosity (@40°C) and 906.3 kg/m^3 of density, whereas naphthenic oil has 22 mm^2/s of viscosity and 902 kg/m^3 of density. The other compound ingredients were commercially used chemicals for rubber and tire industries and supplied from various companies.

2.2 | Method

Rubber compounds were prepared in a 1.5 L internal mixer (Werner & Pfleider) and a two-roll mill, subsequently. Main compound containing rubber(s), reinforcing filler, process oil, activators, and stabilizers was prepared in the internal mixer. Compound was dropped at 120°C. After 1 min wrapping on two-roll mill, curatives were added; compounding continued for further 2 min at various mill gaps.

Optimum cure times were obtained using a moving die rheometer (MDR, Alpha Technologies MDR 2000) at 165°C according to ISO 6502. Vulcanization and molding were carried out on a hydraulic hot press (Panstone) at 165°C for their respective optimum cure times obtained from rheometer curves. Test specimens were cut from the molded sheets into required dimensions by standard blades. Tensile properties were measured according to ISO 37 using universal tensile tester (Zwick/Roell 2.5 kN).

Molecular weight (MW) and molecular weight distribution (MWD) of both raw EPDMs have been compared using

rubber process analyzer (RPA, Montech RPA 3000) for validating their specifications declared by the manufacturers. Loss modulus values measured from time sweep test, which was performed at 100°C, 1 Hz frequency, and 10% strain conditions, were evaluated to compare MW of raw EPDMs. Frequency sweep test for evaluating MWD was performed for 0.1–100 rads^{-1} frequency range at 100°C and 10% strain amplitude.

Temperature scanning stress relaxation tests have been performed using TSSR instrument obtained from Brabender (Germany) using dumbbell-shaped samples defined in ASTM G154-05 and applying 2 hr of isothermal relaxation accompanied by heating step. The TSSR instrument consists of an electrical heating chamber where the sample, an S2 testing rod, is placed between two clamps. The clamps are connected to a linear drive unit to apply a certain uniaxial extension to the sample. A high-quality signal amplifier in combination with a high-resolution AD converter is used to detect and digitize the analogue signals of the high-resolution force transducer and the thermocouple.[8]

The conventional TSSR test method (CS) is a two-step procedure. First step is the application of initial stress at 23°C. To minimize the influence of thermal expansion, TSSR experiments should be performed at initial strains (E_0) not below 50%. The second step, which is called isothermal relaxation, starts immediately after the first step and continues for 2 hr. Then, the heating step starts at the rate of $\beta = 2$ K/min until the complete relaxation or rupture of the sample. In this study, during the TSSR test, called classical TSSR, a constant tensile strain of 50% was applied to a dumbbell test specimen (type 5A, ISO 527). After extension was applied, the sample was preconditioned for isothermal relaxation at 23°C for 2 hr without heating. Subsequently, the sample was heated at a rate of 2°C/min up to 300°C, until the stress relaxation was fully complete.

Additionally, single and double annealing effects were investigated for finding information about possible crystallization process for NR, conventional and alternative EPDM vulcanizates. In the single annealing study (SA), there were three steps. In the first step, conventional isothermal TSSR procedure was performed (extension ratio is 50% and relaxation time is 2 hr). In the second step, sample heated up to 130°C and annealing at this temperature for 10 min and cooling it again 25°C. In the third step, conventional TSSR test procedure was performed (up to 300°C), and relaxation curve was recorded for the comparative evaluation.

In the double annealing procedure (DA), there were five steps. The first three steps were completely as same as single annealing procedure. The fourth step was repetition of the first two steps. In the fifth step, conventional TSSR test procedure was performed. Classical heating, single and double annealing TSSR procedures have been defined schematically in Figure 1.

Cross-link density of thermoplastic vulcanizates (TPVs) and conventional elastomers can be identified from TSSR curves according to classical rubber elasticity theory. Assuming an ideal rubber network, the mechanical stress is simply proportional to the absolute temperature. If the stress relaxation test is performed for a constant elongation, slope of the temperature–stress curve, in other words, the derivative of stress with respect to temperature is assigned as temperature coefficient κ as depicted in Equation (1). For a linear relation, cross-link density can be calculated multiplying κ and absolute temperature and given Equation (2).[8]

$$\kappa = (\partial\sigma/\partial T)_{\lambda} \tag{1}$$

According to the well-known theory of rubber elasticity, the mechanical stress σ is proportional to the absolute temperature T [12,13] and can be expressed by Equation (2).

$$\sigma = (\rho RT/M_c)(\lambda - \lambda^{-2}) \tag{2}$$

where ρ is the mass density; $\lambda = l/l_{o,}$ the strain ratio of the sample, and R, the universal gas constant. M_c is defined as the average molar mass between cross-links, which is proportional to the reciprocal value of the cross-link density ν of the network. At constant strain the slope of the stress versus temperature plot reveals the cross-link density. From Equation (3), obtained by a combination of Equations (1) and (2), the cross-link density ν can be easily calculated from the experimentally obtained value of the temperature coefficient κ for an ideal network. Indeed, filled elastomers are not really elastic as assumed in Equation (1). There will be some absolute error between the real and calculated cross-link densities.[14] However, in this study, all EPDM formulations were prepared using the same amount of filler, therefore relative error in cross-link density calculations was tried to be kept in equal approximation.

$$\nu = \kappa/R(\lambda - \lambda^{-2}) \tag{3}$$

where,

$$\nu = \rho/M_c \tag{4}$$

An HECUS system with Kratky optic and line collimation was used to measure wide angle X-ray scattering (WAXS) data. The scattering profile was obtained with the Cu Kα = 1.54 Å, V = 50 kV, I = 40 mA conditions of the sealed X-ray tube and then the linear gas detector with 1,024 channels was calibrated. Thin film sample holder was used to measure the rubber samples with the size of 8 × 4 × 2 mm. Measurement time and temperature for each sample was 400 s and 22°C. The graphics were plotted according to scattering intensity (I (q)) and the magnitude of the scattering vector ($q = 2\pi/d$).

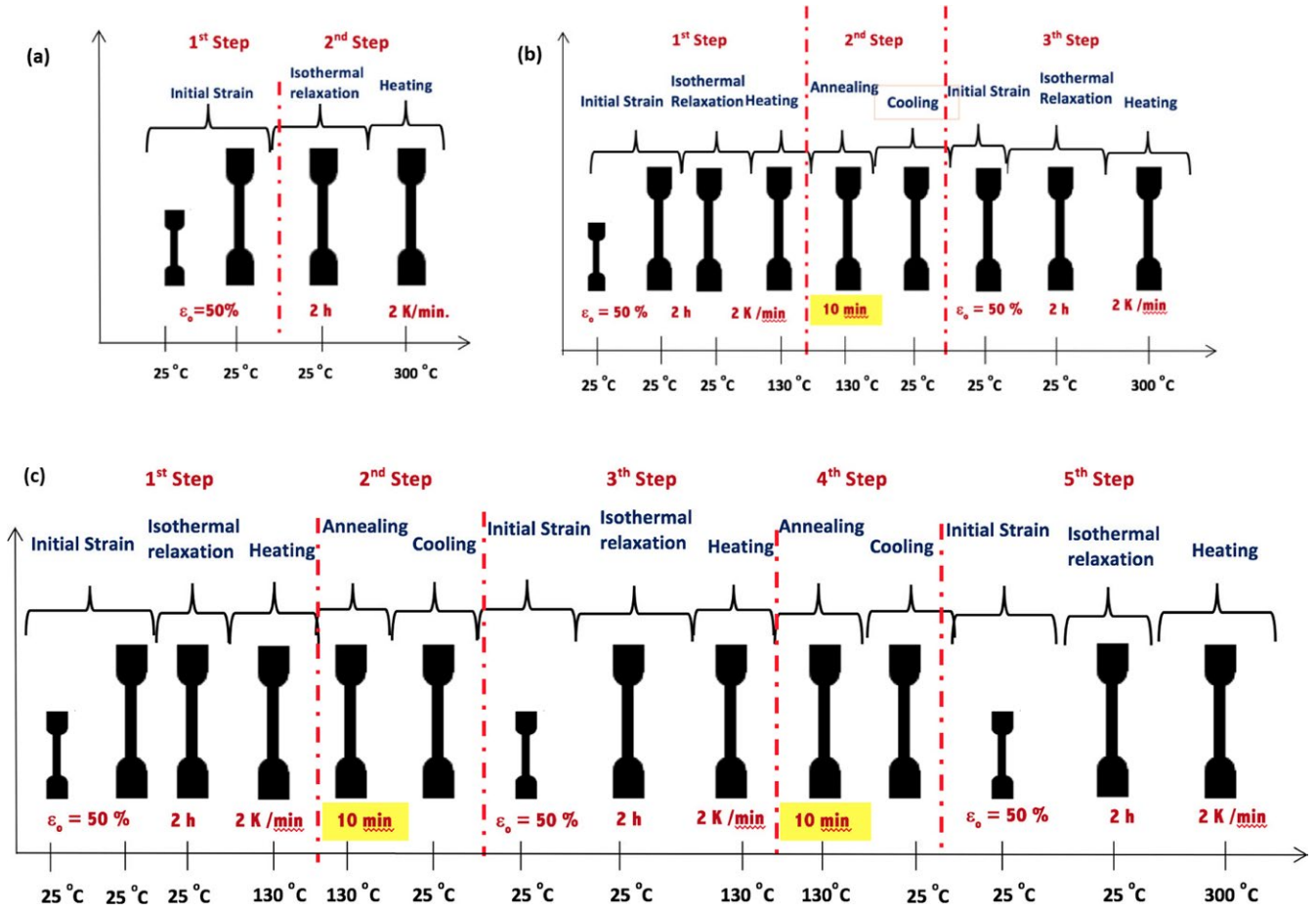


FIGURE 1 (a) Conventional temperature scanning stress relaxation, (b) single-annealing and (c) double-annealing procedures

3 | RESULTS AND DISCUSSION

Help to evaluate stress relaxation properties of EPDM based vulcanizates, NR/BR-based reference compound and two different grades of EPDM were compared in detail. All the compound formulations are given in Table 1. NR represents a reference formulation used in traditional dynamic applications. The formulation was designed considering similar modulus relative to EPDM based compounds. EPDM-0 formulation is based on KEP 2380 (conventional EPDM) which has similar ENB content of Keltan 9565Q (alternative EPDM). EPDM-A formulations are based on Keltan 9565Q and likewise, it contains 50 phr extender oil. This is the reason that rubber matrix of EPDM-A formulations is defined as 150 phr, and also EPDM-0 formulation contains 50 phr process oil whereas EPDM-As do not. EPDM-A5, EPDM-A10, EPDM-A20, and EPDM-A30 formulations contain additional paraffinic process oil to overcome poor processability and to investigate the effects of this solution on the mechanical and stress relaxation properties. The other compounding ingredients were kept as same for studying their own unique contributions of the selected variables.

3.1 | Tensile properties

As it is well-known, traditional EPDM-based vulcanizates have quite poor mechanical properties relative to NR, besides limited dynamic properties. One of the main factors of this is low crystallization ability of traditional EPDMs. Increasing the chain linearity is intuitively thought to be a good solution for providing stronger vulcanizates. Tensile test results of all the vulcanizates are given in Figure 2.

From the figure, it could be stated that EPDM-A formulation has significantly higher tensile strength relative to EPDM-0. There is only about 15% deviation from NR-based reference formulation. This can be attributed to linear molecular structure of alternative EPDM. Oil incorporation deteriorates tensile properties of EPDM-A, as expected; EPDM-A5 has comparable strength, while 10 phr or more oil content exhibit inappropriate ones for usual applications instead of NR.

3.2 | Dynamic properties (RPA study)

It is well known that loss modulus represents viscous part of the material and it can be related to viscosity and molecular

TABLE 1 Compound formulations

Compound	NR-60	EPDM-0	EPDM-A	EPDM-A5	EPDM-A10	EPDM-A20	EPDM-A30
Composition (phr)							
EPDM		100	150	150	150	150	150
NR	70						
BR	30						
Carbon black	54	80	80	80	80	80	80
Process oil		50	0	5	10	20	30
Zinc oxide	10	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
IPPD	3						
TMQ	2						
Wax	2						
CBS	1	2	2	2	2	2	2
ZBEC		1.5	1.5	1.5	1.5	1.5	1.5
ZTDP		2.5	2.5	2.5	2.5	2.5	2.5
MBT		1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	2.5	1.75	1.75	1.75	1.75	1.75	1.75

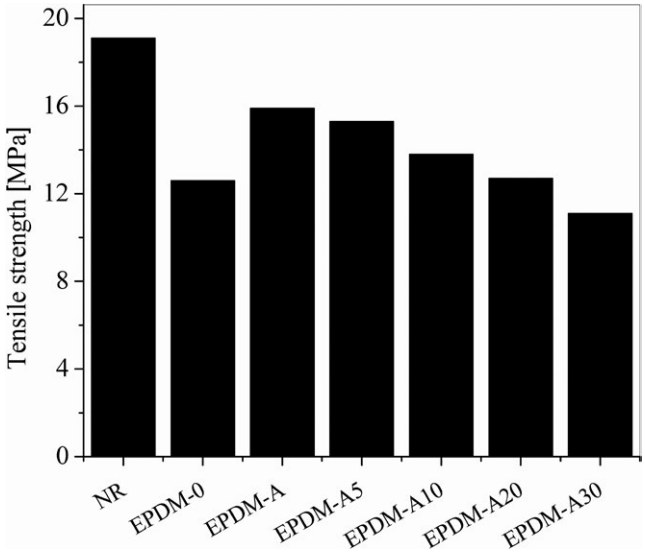


FIGURE 2 Tensile strength values of the vulcanizates

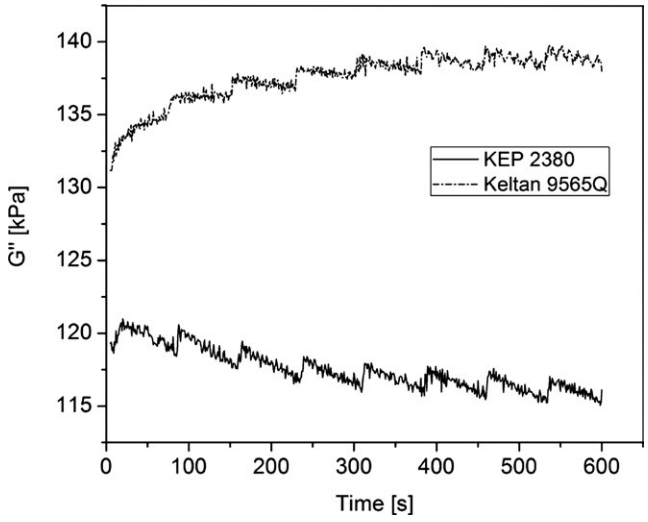


FIGURE 3 Loss modulus values for traditional and alternative EPDMs

weight of rubber materials.[15–17] Here, loss modulus values obtained from RPA time sweep measurements were evaluated to compare MW of raw EPDMs and given in Figure 3. As it is clearly seen from Figure, alternative EPDM (Keltan 9565Q) has quite higher MW than traditional EPDM (KEP 2380) as the manufacturers declare.

Tan delta obtained from frequency sweep measurement can be used for comparing MWD of raw rubbers.[16,18] Highly branched molecules exhibit low damping coefficient (tan delta) at low frequencies due to their less Newtonian or more elastic character. Besides, reducing effect of branching on tan delta values significantly compensated due to insufficient time to change molecular conformation. Difference between tan delta values at low and high frequencies is a good indicator of MWD of the rubber. However, especially at high frequencies, tan delta values are also influenced by the average molecular weight of the polymer, resulting overlapped dynamic response. Practically, normalized frequency sweep data, which is obtained by dividing tan delta by loss modulus, give more suggestive results for MWD evaluation. Figure 4 represents viscosity normalized tan delta values versus angular frequency for both EPDM types. It is clearly seen from

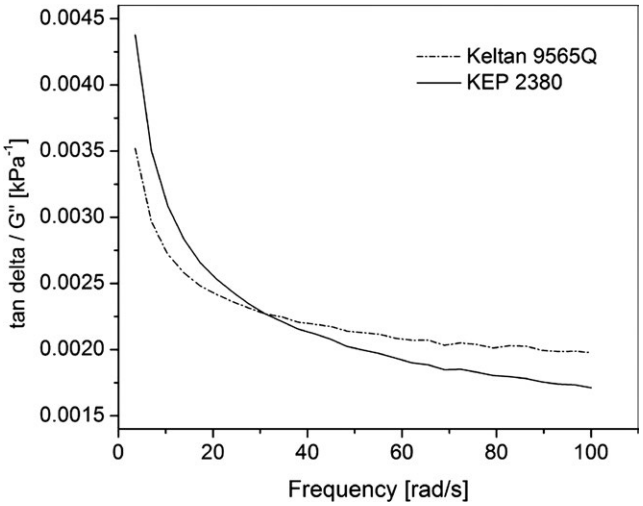


FIGURE 4 Normalized tan delta values for traditional and alternative EPDMs

the Figure that alternative EPDM has significantly narrower MWD than the traditional one.

3.3 | Temperature scanning stress relaxation measurements

3.3.1 | Isothermal relaxation behavior of NR and EPDM

Temperature scanning stress relaxation experiments consist of two steps; isothermal relaxation and nonisothermal relaxation. Isothermal relaxation after straining of the sample is executed for the elimination of negative contribution of stress relaxation. Isothermal relaxation test results for NR and EPDM at ambient temperature after 50% strain are given in Figure 5. Figure 5a represents absolute isothermal relaxation, and Figure 5b represents normalized stress versus time relaxation curve. It is better to compare relaxation behavior using the normalized one.

As it is seen from the figures, relaxation rate of NR is significantly higher than that of both EPDMs. If we compare two EPDM types (EPDM-0 and EPDM-A), relaxation rate is clearly seen to be related to molecular weight distribution of the polymeric matrix. EPDM-A, which has narrow molecular weight distribution, exhibits slower drop in stress. Furthermore, total relaxation is quite lower for narrow molecular weight an EPDM. It was concluded that isothermal relaxation behavior could be improved using alternative (high and low molecular weight distributed) EPDM.

3.3.2 | Nonisothermal relaxation behavior of NR and EPDM

Nonisothermal temperature scanning relaxation behavior of the reference vulcanizates, NR, EPDM-0, and EPDM-A

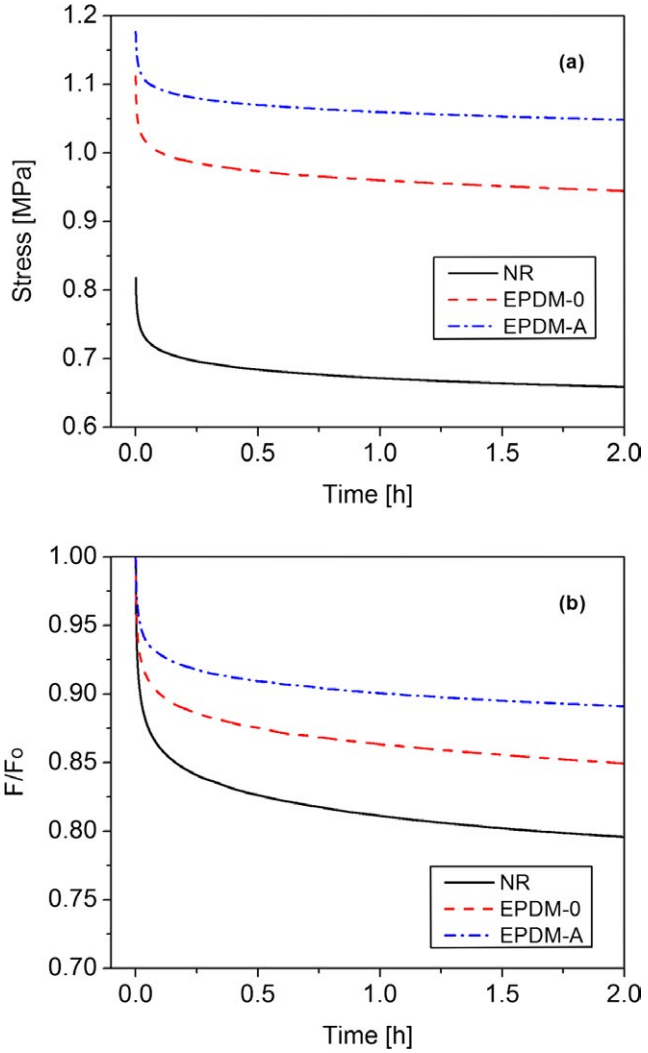


FIGURE 5 (a) Absolute isothermal relaxation curve, (b) Normalized isothermal relaxation curve for natural rubber, EPDM-0, and EPDM-A

have been compared in Figure 6. When the relaxation curves were evaluated, it has been observed that NR had a temperature T_{90} around 200°C. This property was higher when the polymer type changed. For EPDM-0, it was about 300°C; T_{90} was also not present if the relaxation test was performed up to 300°C. In this case, only T_{50} characteristic temperature could be determined. Indeed, T_{90} is related to molecular structure for the same polymer. The significant shift of T_{90} to the higher temperatures can be attributed to higher molecular weight and linearity of EPDM-A than that of EPDM-0. Here, it was concluded that TSSR could be a powerful technique for characterizing the linearity of the rubber-based materials. However, more detailed comparative analyses must be performed using TSSR and other relevant techniques to identify this relationship.

The recent studies performed on the application of TSSR was showed that this technique is fast and easy technique for the determination of cross-link density of elastomers

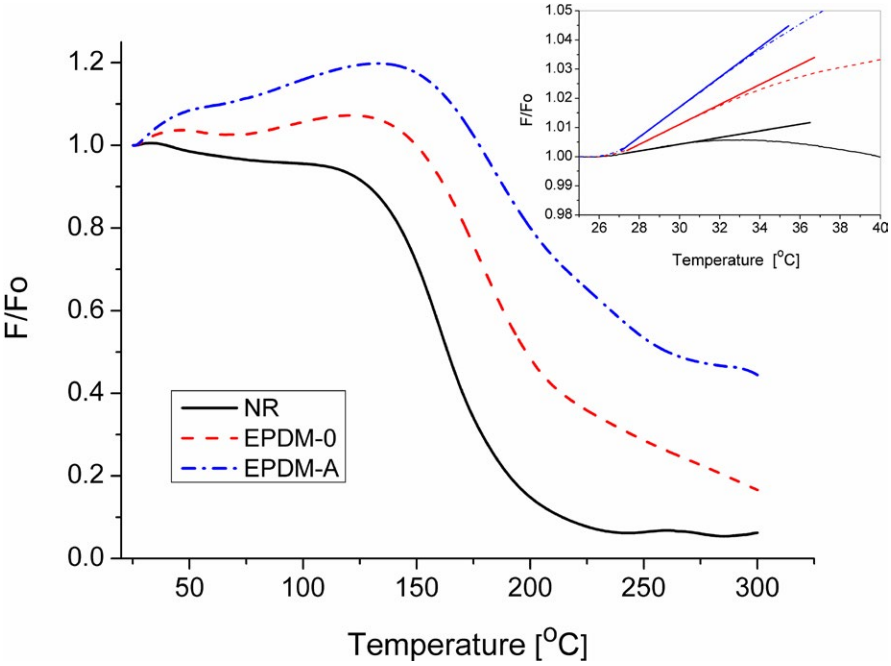


FIGURE 6 Nonisothermal relaxation curves for natural rubber and EPDMs

TABLE 2 Cross-link densities and molecular weights between cross-links for all the vulcanizates

Sample	κ (Pa/K)	Density (g/cm^3)	$\lambda - \lambda^{-2}$	M_c (g/mol)	Cross-link density (mol/m^3)
NR	700	1.167	1.0555	14,630	79.8
EPDM-0	2,800	1.104	1.0556	3,460	319.0
EPDM-A	4,800	1.077	1.0556	1,969	546.9
EPDM-A5	4,200	1.079	1.0556	2,254	478.6
EPDM-A10	3,800	1.088	1.0556	2,512	433.0
EPDM-A20	3,700	1.062	1.0556	2,518	421.6
EPDM-A30	2,700	1.043	1.0556	3,390	307.7

and TPVs.[8,13] Initial part of the stress–temperature curves obtained was used to calculate the temperature coefficient κ by numerical differentiation according to Equation (1). κ and cross-link density calculation step in stress–temperature curves has been given for NR and EPDM-A in Figure 6. Cross-link densities and molecular weights between cross-links (M_c) have been given for all vulcanizates in Table 2.

As it is seen from the table that molecular weight between cross-links were considerably higher for NR, representing lower cross-link density. For EPDMs, EPDM-A had twice more mole number of cross-links in one cubic meter of polymer compared with EPDM-0. This could be attributed to high cross-linking ability of linear EPDM chains in EPDM-A. EPDM is a polymer, which can constitute cross-links via ethylidiene norbornene (ENB) on the side groups. For highly branched and broad MWD an EPDM, such as EPDM-0, ENB groups are intuitively hindered by the other main EPDM chains and exhibit lower cure extent. Intramolecular interactions are more dominant than that of narrow MWD an EPDM. Linearity may set the ENB groups free for interact with vulcanization agents to create more cross-links as it coincides with related Monte Carlo simulations.[19,20] This is thought to be why more cross-links were in EPDM-A.

3.3.3 | Effect of oil content on EPDM's isothermal and nonisothermal relaxation

In this part, oil addition effect has been studied by means of both isothermal and nonisothermal relaxation behavior of EPDM-A vulcanizates (Figure 7a,b). As clearly seen from the Figure 7a, isothermal relaxation rate was higher for more oil content. Total relaxation was also more than EPDM-A, for all oil containing vulcanizates. However, it was not possible to say the variation was linear with respect to the oil ratio.

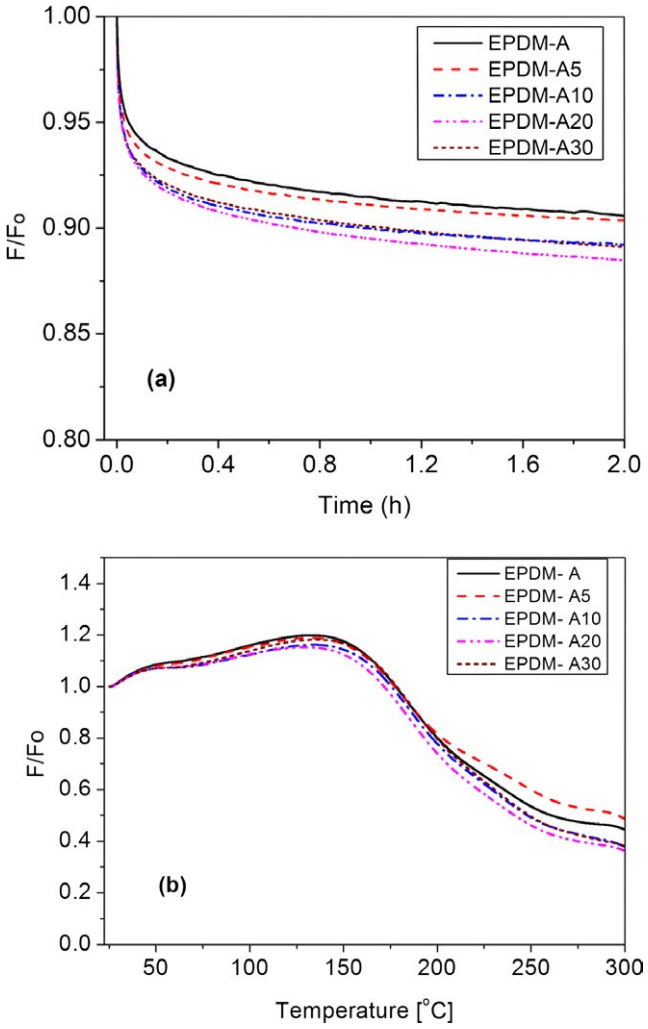


FIGURE 7 (a) Isothermal, (b) nonisothermal relaxation curves for EPDM-A vulcanizates

Oil addition has much more clear effect when we consider the nonisothermal relaxation curves. T_{10} was quite closed for all the vulcanizates; however, T_{50} and T_{90} temperatures were considerably lower for oil containing vulcanizates. This means faster property loss at higher temperatures. There was an interesting finding for EPDM-A5 that characteristic temperatures (T_{50} and T_{90}) shifted to right on temperature scale. This finding also coincides with the tensile test results, which the tensile deterioration could be neglectable for the same vulcanizate when compared to the other oil containing ones. Indeed, alternative linear EPDM was quite difficult to prepare homogeneous compounds. Small amount of process oil addition could improve processability in compounding step. Interesting nonisothermal relaxation behavior and so better high temperature properties have been attributed to satisfactory dispersion of EPDM-A5 compound.

The third output of nonisothermal relaxation study given above is highlighting the high temperature crystallization phenomena, which is realized from the second hill of the increasing stress region. Here, we can say that EPDM-A tends to crystallize, much more than EPDM-0. For the following of

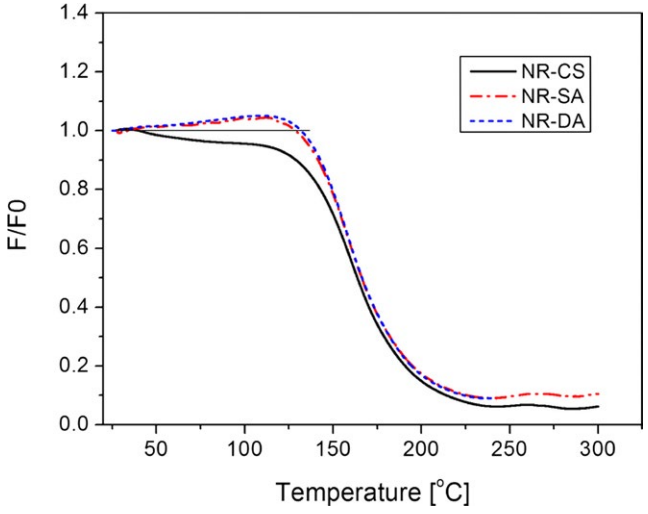


FIGURE 8 Normalized temperature scanning stress relaxation relaxation curves of natural rubber (NR). NR-CS, without annealing; NR-SA, single annealing; NR-DA, double annealing

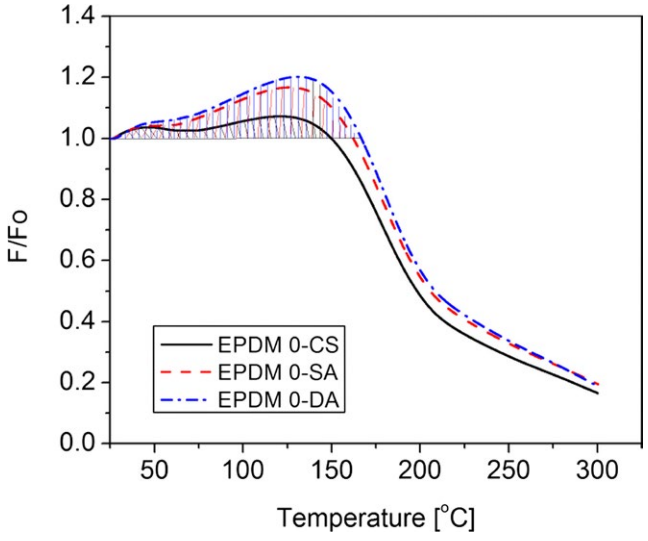


FIGURE 9 Normalized temperature scanning stress relaxation relaxation curves of EPDM-0. EPDM-0-CS, without annealing, EPDM-0-SA, single annealing, EPDM-0-DA, double annealing

crystallization phenomena in EPDMs, the isothermal crystallization or annealing experiments were followed by applying different heating and cooling steps in TSSR instruments.

3.4 | Effect of annealing on the crystallization and service temperature of the EPDM's

For the identification of strain-induced crystallization in EPDM's, the annealing experiments were performed by modified heating and isothermal steps in TSSR given in experimental section, the last part of TSSR studies. Method is applying more

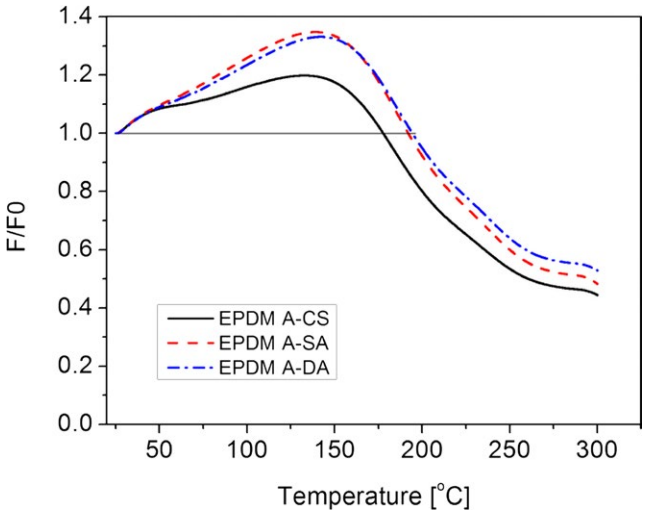


FIGURE 10 Normalized temperature scanning stress relaxation relaxation curves of EPDM-A. EPDM-A-CS, without annealing; EPDM-A-SA, single annealing; EPDM-A-DA, double annealing

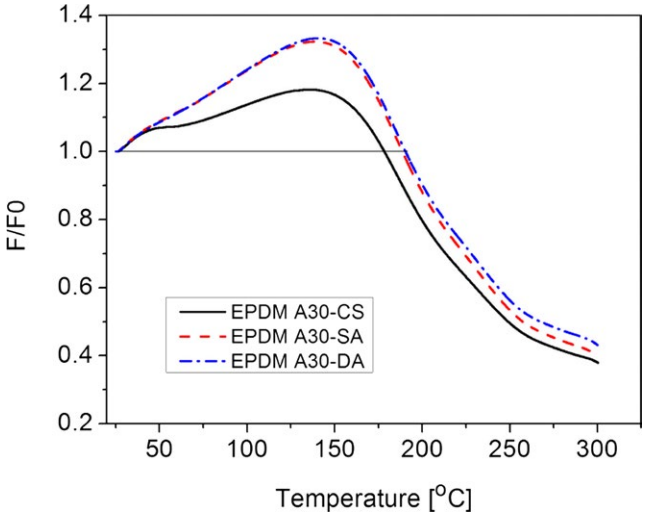


FIGURE 11 Normalized temperature scanning stress relaxation relaxation curves of EPDM-A30. EPDM-A30-CS, without annealing; EPDM-A30-SA, single annealing; EPDM-A30-DA, double annealing

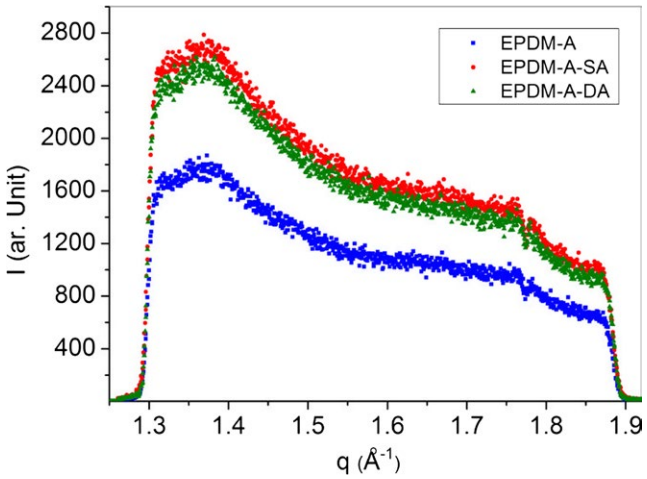


FIGURE 12 Effect of annealing on ethylene propylene diene rubber wide angle X-ray scattering profiles

than one run on relaxation tests. Single run or Conventional Scanning (CS) is the same as isothermal + nonisothermal test procedure that was applied before. Single Annealing (SA) procedure contains a 2 hr isothermal relaxation and preheating to peak temperature (130°C), which was decided from previous experiments, 10 min annealing at this temperature, cooling up to isothermal test temperature (25°C), and conventional scanning again. As you see, Double Annealing (DA) procedure is quite different; the first three steps were completely as same as SA procedure. The fourth step was repetition of the first two steps. In the fifth step, classical TSSR test procedure was performed.

In Figures 8–11, normalized relaxation spectrums of NR, EPDM-0, EPDM-A, and EPDM-A30 vulcanizates were depicted for the cases CS, SA, and DA, respectively. The most conspicuous observation is increasing second peak area (pronounced after 60°C) with longer annealing periods. The second issue is that annealing leads relaxation curves to shift higher temperatures. For correlating strain-induced crystallization phenomenon and annealing application, $A_{Ent+Cry}$ values were calculated and given in Table 3. Here, $A_{Ent+Cry}$ values represent the total change in normalized strength due to crystallization and entropic chain relaxation during heating. The values are related to the peak area under the reference line between F/F_0 at the beginning of the relaxation test (equals to 1) and relaxation curve. Reference line is also indicated in Figures 8–11. In annealing, it could be assumed stationary entropic contribution due to unchanged cross-link density. Therefore, calculated peak area was directly correlated with crystallization of the polymer, and hereafter, it was called crystallization peak area. As it can be seen from Table 3 that crystallization peak area was increased by increasing total annealing time for all the vulcanizates. Besides, difference between the peak areas for unannealed (CS) and 10 min annealed (SA) vulcanizates was more pronounced than that of between the cases CS and DA (20 min annealing). This finding indicates that SA could be assumed to be sufficient for improving service temperatures for the related materials.

In Table 3, characteristic temperatures T_{10}, T_{20}, and T_{50} were also given. Indeed, annealing has a considerable effect on shifting the vulcanizate characteristic temperatures. For EPDM-A, T_{50} could be shifted to a temperature higher than 300°C by an increase in more than 40°C, whereas it was 167.2°C for conventional EPDM vulcanizate (EPDM-0).

As it was clearly seen from both Figures 6 and 8, NR did not exhibit crystallization phenomena during classical TSSR test. However, in its annealing applications, a significant level of crystallization has been revealed. This behavior was attributed to dominant entropic contribution after annealing,

Sample-scanning procedure	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	$A_{Ent+Cry}$
NR-CS	129.0	142.8	163.7	14.8[a]
NR-SA	141.5	148.6	166.2	97.5
NR-DA	142.8	149.6	166.4	105.7
EPDM-0-CS	162.5	167.2	167.2	130.2
EPDM-0-SA	170.9	205.7	205.7	149.8
EPDM-0-DA	174.3	181.3	208.4	157.6
EPDM-A-CS	188.4	204.7	260.6	177.9
EPDM-A-SA	202.5	216.0	295.3	192.2
EPDM-A-DA	206.0	221.0	>300	194.4
EPDM-A30-CS	188.7	199.4	249.0	170.4
EPDM-A30-SA	198.0	209.2	257.4	194.6
EPDM-A30-DA	200.3	212.4	267.5	197.6

[a]Value represents only entropic contribution (A_{Ent}).

TABLE 3 T_{10}, T_{20}, T_{50} service temperatures of natural rubber and ethylene propylene diene rubber samples and peak area of entropic and crystallization contribution ($A_{Ent+Cry}$)

whereas relaxation (or thermal expansion) suppresses the increase in nominal stress due to insufficient time to crystallization for unannealed NR. On the other hand, NR could not reach the same crystallization peak area with none of the EPDM vulcanizates after annealing.

3.4.1 | Wide angle X-ray scattering study

For the identification of annealing on the morphological changes of new grade EPDM-A, WAXS experiments were performed with unannealed (EPDM-A) and single-annealed (EPDM-A-SA) and double-annealed (EPDM-A-DA) samples. WAXS measurements were recorded immediately after annealing (in 5 min) to observe strain-induced crystallization and to prevent reorientation of chains by relaxation. WAXS profiles of EPDM-A, EPDM-SA and EPDM-DA are given in Figure 12. In the q range of 1.3–1.8 $Å^{-1}$, two peaks were observed all samples and $q_1 = 1.369$ $Å^{-1}$ ($d_1 = 4.58$ Å) and $q_2 = 1.764$ $Å^{-1}$ ($d_2 = 3.56$ Å) were more significant in the profile of EPDM-A-SA. q_1 and q_2 peak positions of EPDM-A and EPDM-A-DA is very close to peak position of EPDM-A-SA.

Comparing the WAXS profiles, it has been observed that peak intensities of EPDM-A-SA and EPDM-A-DA were higher than unannealed samples, and this result clearly indicated that annealing increase the crystallinity or chain orientation of EPDM-A. On the other hand, the WAXS peak intensities of EPDM-A-SA and EPDM-A-DA were quite close to each other; spectrums had good correlation with Figure 8.

The WAXS experiments indicate that annealing process affects chain structure of new-generation EPDMs with high ethylene content, high molecular weight, and narrow molecular weight distribution. However, to detect real-time crystallinity changes and nano formations during annealing, WAXS and SAXS experiments must be performed by temperature controlled and strain-controlled instruments simultaneously. These experiments were planned as our further studies with new-generation EPDMs having interesting structural properties.

4 | CONCLUSION

In this study, natural rubber, traditional EPDM, and a new grade EPDM with modified structural properties have been evaluated by means of tensile properties, characteristic temperatures, cross-link density, isothermal and nonisothermal relaxation behaviors through TSSR method. Alternative EPDM exhibited improved tensile strength relative to traditional EPDM, thanks to its linear chain structure. Variation in isothermal relaxation properties due to molecular weight distribution could be successfully revealed by TSSR measurements. The most important output of nonisothermal relaxation tests was highlighting the high temperature crystallization tendency of alternative EPDM. Besides, during nonisothermal relaxation tests, shifts in characteristic temperatures were correlated with faster property loss due to oil incorporation. Annealing study results showed that strain-induced crystallization of the related vulcanizates strongly depends on total annealing time. Furthermore, annealing could improve the service temperature of EPDMs with regard to successive crystallization. In conclusion, TSSR technique was concluded to be a fast and practical technique for correlating crystallization tendency and service temperature as well as measuring cross-link density of NR and EPDM elastomers.

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