

NR-BR 기반 고무소재에서 폴리부타디엔의 C-C 겔 함량과 물리기계적, 유변학적 특성 사이의 상호관계

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Correlation between Physico-Mechanical and Rheological Properties of Rubber Compounds Based on NR-BR with C-C Gel Content in Polybutadiene

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Abstract: In this study, microstructure and gel content (C-C) of polybutadiene rubber (PBR) were investigated using various techniques including ASTM D 3616, attenuated total reflectance Fourier transform infrared spectrometry (ATR FTIR), differential scanning calorimetry (DSC) and nuclear magnetic resonance spectroscopy (NMR). The ATR FTIR spectra of the samples were investigated to determine the *cis*, *trans*, 1, 2-vinyl and the C-C gel content in PBR. The absorbance ratios of specific peaks in different grades of PBR were correlated with the C-C gel content measured by the ATR FTIR techniques. Physico-mechanical and rheological properties of rubber compounds based on BR with various amounts of gel were determined. The results showed that there is an acceptable correlation between these properties and the C-C gel content of PBR.

Keywords: polybutadiene rubber, C-C gel content, ATR FTIR, physico-mechanical and rheological properties, NR/BR blend.

Introduction

Polybutadiene rubber (PBR) is regarded as a polymer consisting of three isomeric units, *cis*-1,4, *trans*-1,4, and 1-2 vinyl. It is used for the producing of rubber compounds in the manufacture of car tires; it contains *ca.* 97% of *cis* structure. It is known that polybutadiene rubber is one of the most popular synthetic rubbers due to its excellent mechanical properties when combined to form blends. Hence the control of these structural factors is significantly important for getting a good performance of rubber compounds. The polybutadiene is used primarily in the sidewall of truck tires, this helps to improve fatigue to failure life due to the continuous flexing during run. It is also used in the tread portion of giant truck tires to improve the abrasion, *i.e.* less wearing, and to run the tire comparatively cool, since the internal heat comes out quickly.¹⁻⁴

PBR may be prepared with a variety of architectural structures such as linear, ring, star, branched, ladder and dendritic chains and they may also be three dimensional network structures,⁵ that some of these structures causes the C-C gel is formed. Generally the C-C gels can be regarded as particles formed by the joining of large polymer molecules into a crosslinked three dimensional structure, increasing C-C crosslinked density causes properties entirely different from the parent polymer chains due to their restricted mobility and interaction.^{6,7} C-C gel may be introduced intentionally in some rubbers. Polymer gels are generally inhomogeneous for the network size, and properties of polymer gels naturally depend on their spatial inhomogeneity. The existence of spatial inhomogeneity has been detected by light scattering as speckles.^{8,9} As for chemically-crosslinked polymer gels, the relationship between speckles and spatial inhomogeneity has been elucidated.¹⁰⁻¹⁴ Network size and its distribution over polymer gels have also been studied through the diffusional behavior of probe molecules in the gel phase.¹⁵⁻¹⁷ Understanding the effect of various

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types of gel on raw rubber properties, especially on the rheological properties, is of great commercial importance, since it may lead to the advent of even superior processing grades of rubber than the existing ones. Several researchers have reported the effect of gel (C-S crosslink) and their particles in the vulcanization process and also changes in physical, mechanical and rheological properties were examined. They found that the relation between the amount, type and size of gel content (C-S crosslink) with these properties.¹⁸⁻³⁰ Rheological methods present the most effective and practical way to monitor the evolution of network structure during gelation.

Common techniques include measuring the steady shear viscosity or dynamic mechanical shear properties as a function of reaction time and frequency.³¹⁻³⁵

In this paper, we continue to examine the question of the correlation between gel content and thermal stability of PBR. First of all we have characterized the C-C gel content in PBR by various and reliable techniques such as derivative thermogravimetry - differential scanning calorimetry (DTG-DSC) and attenuated total reflectance Fourier transform infrared spectrometry (ATR FTIR) methods and as a main scope of our work we have described the effect of C-C gel content on the process ability of PBR and its effect on the cured rubber compounds based on PBR properties. C-C Gel content reduces the chemical bonding and adhesion during the mixing process and eventually the effect on the physico-mechanical and rheological properties of obtained rubber compounds and performance properties of tires.

Experimental

Sample Preparation. The PBR (*cis*-1220) was manufactured by the Arak Petrochemical Company, Iran, that they were prepared in different dates. The gel formed inside the PBR reactor was obtained as factory waste from Arak Petrochemical unit. The toluene used as a solvent was supplied by Merck, Germany. Zinc oxide and stearic acid were of chemically pure grade. The rubber compounds formulation is given in Table 1.

Table 1. Rubber Compound Formulation for the Conventional Vulcanizing System

	Components	Phr ^d	Company
BR ^b	Cis-1220	25	Arak Petrochemical, Iran
NR ^c	STR 20/BN	75	Thaihua, Thailand
Carbon black	N-330	45	Pars Tire, Iran
Stearic acid	PLMAC 1600	3	Acid Chemie, Malaysia
Sulfur		1.3	Tesduck, Iran
ZnO		4	Shekoieh, Iran
Rio wax	Anti Lux 654	2	Rhien Chemie, Germany
6PPD ^d	Pilfex 13	1.5	Nacil, India
TMQ ^e	Antioxidant RD	1	Nanjing, China
OBTS ^f	Vulcacit/MOZ	0.8	LG/Lanxess, Belgium

^aphr: part per hundred of rubber.

^bBR: Butadiene rubber.

^cNR: Natural rubber.

^d6PPD: *N*-Isopropyl-*N'*-phenyl-*p*-phenylene diamine.

^eTMQ: 2,2,4-Trimethyl-1,2-dihydroquinoline.

^fOBTS: *N*-Oxydiethylene-2-benzothiazole sulfonamide.

Gel Content Determination. The gel contents of PBR were determined according to ASTM D 3616. Approximately 0.4±0.05 g of each sample was exactly weighed and placed on screens (NO.50) in a borosilicate bottle and deliver 100 cm³ of toluene into the bottle. The gel content was determined by the following eq. (1):

$$\text{Gel}\% = \frac{A-B}{A} \times 100 \quad (1)$$

Where *A* is the mass of the original samples, *B* is the residual mass after evaporation of solvent. A test result is the average of five determinations. Samples with different gel content (2.1, 2.5, 3.1, and 3.7%) are shown as BR_{2.1}, BR_{2.5}, BR_{3.1} and BR_{3.7}.

Rubber Compound Formulation. All components of rubber compounds were kept constant except PBR with different percentages of C-C gel content. Mixing was done on a laboratory a roll mill mixer, by careful control of temperature, time of mixing and uniform cutting operation. After mixing, the samples were kept undisturbed for 1 hr for maturation. This removed the air bubbles introduced into the compound while compounding. The compounds are denoted as Table 2 showed, S₁, S₂, S₃ and S₄. The molding conditions were determined from torque data by a (Hiwa) rheometer for 20 min at

Table 2. Formulation of Rubber Compounds Based on NR/BR with Various Gel Contents (phr)

Compounds	BR	%Gel in PBR	NR	Carbon black	Stearic acid	ZnO	Sulfur	Rio wax	6PPD	TMQ	OBTS
S ₁	25	2.1	75	45	3	4	1.3	2	1.5	1	0.8
S ₂	25	2.5	75	45	3	4	1.3	2	1.5	1	0.8
S ₃	25	3.1	75	45	3	4	1.3	2	1.5	1	0.8
S ₄	25	3.7	75	45	3	4	1.3	2	1.5	1	0.8

160 °C.

Thermo Gravimetric Analysis. The thermal performance of the rubber is of key importance for industrial applications and thermo gravimetric evaluation is one of the most widely accepted methods for studying the thermal properties of polymeric materials. Thermo gravimetric data provides information on thermal breakdown, mass loss of the material in different stages, threshold temperature, and the nature and the extent of the degradation of the material.³⁶⁻³⁸

The thermal degradation studies were performed on a thermo gravimeter (Sinco STA 1500). The analysis is performed by a weighing the uncured specimen (15-16 mg), heated from the room temperature to the temperature of higher than 600 °C and establishing the nitrogen atmosphere. The heating rate was kept at 20 °C/min and continued from ambient temperature to 700 °C.

Differential Scanning Calorimetric Analysis. DSC provides unique information by characterizing interfacial behavior and miscibility with higher solution. From DSC traces the glass transition temperature, T_g , and state transition temperature. In this study DSC was used to monitor the melting and crystallization behaviors of the BR polymer with different gel contents. DSC was determined by a Sinco STA 1500 diamond. All operations were performed under nitrogen purge. Sample weight for each experiment was about 10 mg.

ATR FTIR Measurements. Infrared spectroscopy can be used efficiently by polymer and rubber technologists for identification of polymer, polymer-blend ratio calculation, raw material evaluation, study of reaction mechanism, microstructure determination, *etc.*³⁹ Perkin Elmer FTIR-2000 spectrometer equipped with a Mid IR (MIR) source and a triglycine sulfate detector were used to determine the changes of different specimen. ATR spectra were obtained with the horizontal attenuated total reflectance accessory. The internal reflecting element (IRE) was a ZnSe crystal set an incidence angle of 45°. Sections of thickness 1 mm were cut from the samples. The percentages of gel content, *cis-trans*, and 1,2-vinyle butadiene isomers content of samples were determined.

The peak intensity was measured from the absorbance value after base line correction (valley to valley).

NMR Measurements. Nuclear magnetic resonance (¹³C NMR) allows identification of functional groups in polymers and provides information of their global chemical structures. Also a convenient application of NMR is the estimation of the crosslink density responsible for important mechanical characteristics of polymers. The crosslink density is related to the size of pores or cavities inside solid polymers. There are several useful NMR parameters to get the information on the crosslink density, for example magnetic relaxation and the dipolar correlation effect.^{40,41} These methods directly observe the NMR parameters of the polymer itself. On the other hand, one can use small particles to look inside the polymer, thus observing it indirectly through the behaviors of those probes.

NMR measurements were performed on a Bruker AM-125 MHz spectrometer with TMS as internal Standard to determine the chemical changes of different sampling. The Sample concentration was 25% (w/v) for ¹³C NMR using a 5 mm NMR tube at 20 °C and it was placed in the spectrometer magnetic field after 20 min in order to reach a steady state.

The ¹H NMR spectra were obtained on a Bruker AM-500 MHz and after the phase correction; the spectra were referenced by setting the internal TMS frequency to 0 ppm. The chemical shifts of ring protons and methyl protons were measured.

Rheological Properties. Rheological techniques present the most effective and applied way to monitor the network structure during gelation. Rubber compounds were prepared of NR has a low thermal conductivity, consequently is generally done at low temperatures; *i.e.*, less than 170 °C. The higher the cure temperature of the samples, the poorer is the mechanical properties of the vulcanize.⁴² The start of vulcanization scorch time (t_{s2}), optimum curing time (t_{90}) and cure rate index (CRI), minimum torque (M_L), and maximum torque (M_H) are shown in Table 3. The effects of increasing the gel content percent on the rheological properties of blends are presented in Figure 8.

Mechanical Properties. Crosslink density of a rubber vulcanized determines the physical properties such as modulus,

Table 3. Rheological Properties of NR/BR Blends

Compounds	% Gel in different PBR	t_{s2} (s)	t_{90} (s)	M_L (dN·m)	M_H (dN·m)	CRI (s ⁻¹)
S ₁	2.1	251	625	0.96	9.10	860
S ₂	2.5	247	618	1.10	7.86	866
S ₃	3.1	255	609	1.24	7.58	867
S ₄	3.7	203	580	1.36	7.42	860

hardness, resilience, elongation at break. In this work to study the stress-strain behavior of rubber compounds tensile tester (Testometric-M350-5KN, ASTM D412-98a, Die C) was used. The samples were cut from molded sheets in the dumbbell shape, placed in the sample holder and its length and with the thickness were measured. The gauge length between the jaws at the start of each test was adjusted to 25 mm and the measurements were carried out at a cross head speed of 500 mm/min. Every value of changes in load is placement was recorded by the computer. In tensile testing machine, the stress is increased slowly and then the elongation of the sample undergoes at each stress level is measured. The process keeps doing this until the sample breaks down.

Results and Discussion

Thermogravimetric Analysis of PBR. The thermal stabilities of four samples with different C-C gel content have been investigated by TG under Nitrogen flows, respectively (Figure 1). As DTG plots shows, the thermal degradation behavior of all samples at a heating rate of 20 °C/min starts at

an earlier temperature of 350 °C, approximately reaches a maximum at 465 °C and ends at 490 °C. Therefore the DTG curves of the butadiene polymers are exposed that the qualitative analysis of PBR forms is impossible because of their very close thermal decomposition behaviors, and despite the presence of different C-C gel content, it does not show any significant changes. Thermo gravimetry data of all specimen showed that we could not observe the phenomena of weight loss with increasing temperature, indicating that melting, crystallization, and glass transition reaction occurs on the polymer chains with different gel content under nitrogen atmosphere at higher temperature. At the same time, it can be observed that the slope of the falling region of TG curves of all samples indicate the fastness of degradation process.

Differential Scanning Calorimetry Analysis. The heating curves for PBR samples with different C-C gel contents (2.1, 2.5, 3.1, 3.7%) were indicated in Figure 1. Although, there is not weight loss before 350 °C in the TGA curve, but it is seen that there are mainly two exothermic peaks between 200-220 °C and 300-400 °C in DSC curves (Figure 2), which is indicated that cis-trans isomerization and cyclization process

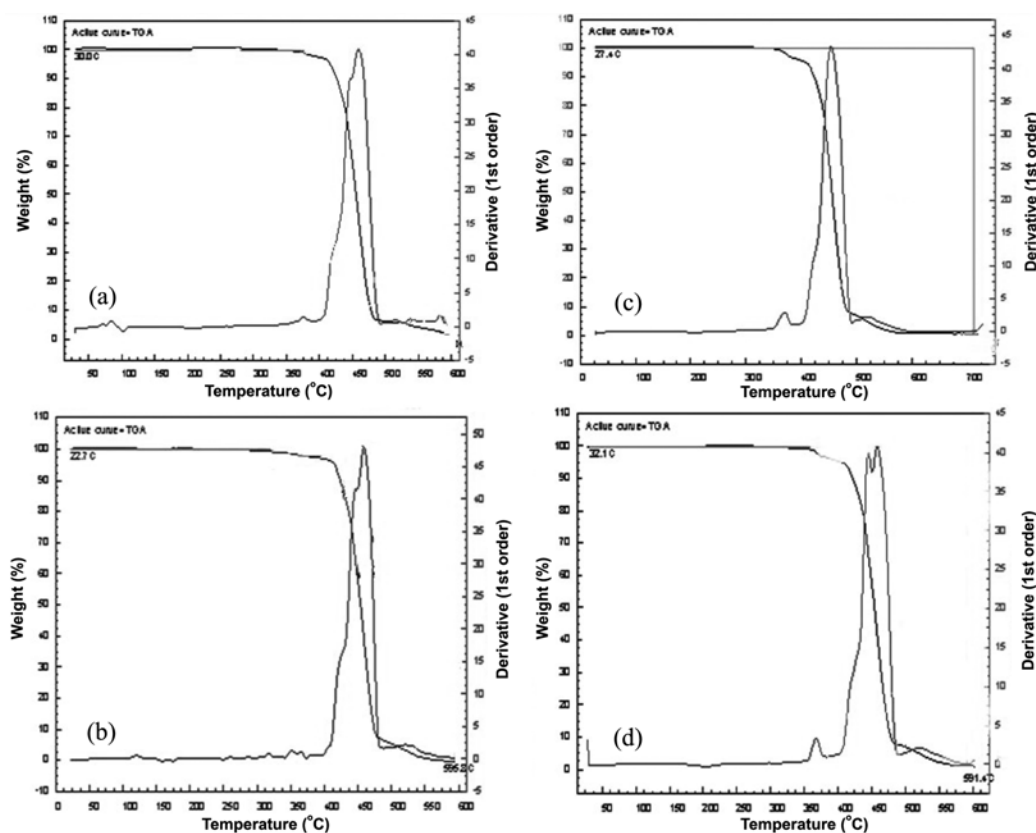


Figure 1. TGA and DTG curves for PBR: (a) BR with 2.1% of gel content; (b) BR with 2.5% of gel content; (c) BR with 3.1% of gel content; (d) BR with 3.7% of gel content.

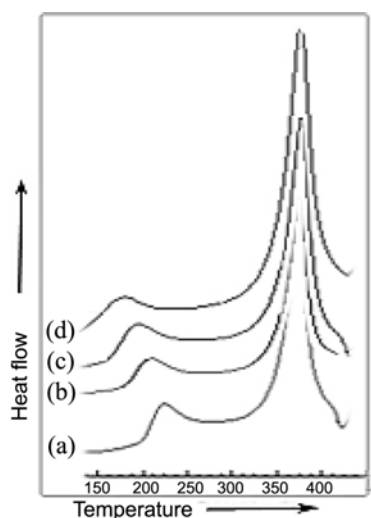


Figure 2. DSC curves of PBR: (a) BR with 2.1% gel content; (b) BR with 2.5% gel content; (c) BR with 3.1% gel content; (d) BR with 3.7% gel content.

occurred.

As Figure 2 shows the general trend in each graph is a decrease in the peak area and a shift to the lower temperatures as gel concentration increases; this reflects that, physical crosslinking increases the ability of the poly butadiene mol-

Table 4. Obtained Parameters from DSC Graphs of the PBR with Different Gel Contents

Sample	$T=210\text{ }^{\circ}\text{C}$		$T=375\text{ }^{\circ}\text{C}$	
	ΔH (J/g)	Heat flow (mw)	ΔH (J/g)	Heat flow (mw)
BR _{2.1}	52.1	6.3	339.4	56
BR _{2.5}	48.5	5.3	324.5	52
BR _{3.1}	45.9	4.4	314.5	47
BR _{3.7}	41.2	3.2	302.3	42

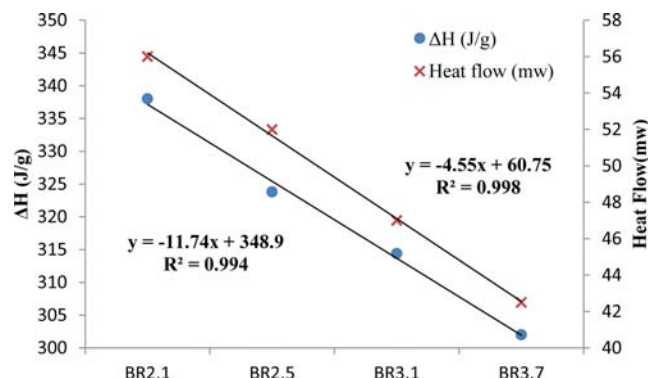


Figure 3. Correlation between enthalpy and heat flow with gel content of PBR at 370 °C.

ecules to be arranged in cyclization structures.

Isomerization occurs at 200-220 °C and cyclization happens of PBR at about 375 °C as major reaction is proceeding with larger heating on the DSC curve appears.⁴³ Heat flow and energy released were determined from DSC curves for all samples of PBR (Table 4).

Figure 3 shows that there is a linear correlation between heating rate and enthalpy with gel content in PBR.

ATR FTIR Analysis. The ATR-FTIR results are presented in Figure 4. The C-H deformation for hydrogen atoms attached to alkenic carbons in 1,4 *cis*, *trans*, and 1,2 vinyl PBR are seen at 738, 965, and 910 cm^{-1} , respectively.⁴⁴

As Table 5 showed the amounts of these isomers are calculated for each specimen using the integration of peak area according following equations:

$$\% \text{ 1,4 } cis \text{ isomer} = S_{738} / (S_{738} + S_{910} + S_{965}) \times 100 \quad (2)$$

$$\% \text{ 1,4 } trans \text{ isomer} = S_{965} / (S_{738} + S_{910} + S_{965}) \times 100 \quad (3)$$

$$\% \text{ 1,2 vinyl isomer} = S_{910} / (S_{738} + S_{910} + S_{965}) \times 100 \quad (4)$$

Where S_{738} , S_{965} , and S_{910} are peak area at 738, 965, and 910 cm^{-1} absorption.

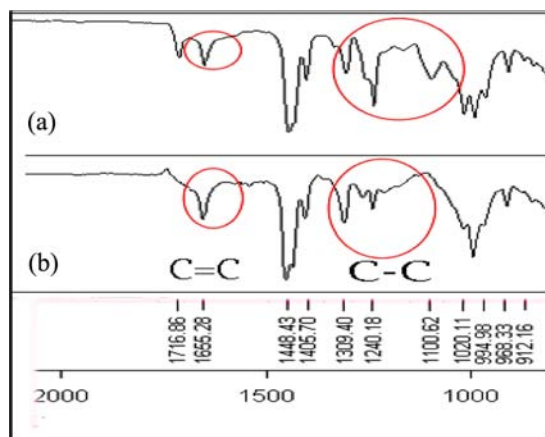


Figure 4. Typical example of obtained ATR FTIR spectrum (1000-2000 cm^{-1}): (a) the sample obtained as factory waste; (b) the sample of PBR with 3.1% gel content.

Table 5. Characterized Properties of Different PBRs Investigated with ATR FTIR

Sample	1,4- <i>cis</i> (%)	1,4- <i>trans</i> (%)	1,2-vinyl (%)
BR _{2.1}	96.11	2.39	1.50
BR _{2.5}	96.13	2.28	1.59
BR _{3.1}	95.42	2.64	1.94
BR _{3.7}	95.10	2.55	2.36

C-C Gel Content Determinations. The C=C peak appears at 1650 cm^{-1} and the range of $1100\text{--}1300\text{ cm}^{-1}$ is assigned to the C-C bond.³⁹ The spectra for the four samples of PBR with different gel content and the sample obtained as factory waste are shown that with increasing the C-C gel content of butadiene samples the intensity of peak absorbance at 1650 cm^{-1} (corresponding to the C=C double bonds absorption) will slightly decreased. The bonds at $1100\text{--}1300\text{ cm}^{-1}$ is markedly altered by the increasing the density of C-C bond.

Therefor the ratio of regions of absorption at “ $1100\text{--}1300\text{ cm}^{-1}/1650\text{ cm}^{-1}$ ” called as band ratio factor is increased by rising gel concentration (Figure 4).

Figure 5 demonstrated the plot of band ratio “ $1100\text{--}1300\text{ cm}^{-1}/1650\text{ cm}^{-1}$ ” vs, the C-C gel content of different samples estimated using ASTM D-3616. The relevant data is given in Table 5. From the graph, the correlation coefficient was found to be 0.99.

To verify the correlation coefficient, three samples of unknown gel content PBR were prepared and their gel contents were calculated from the above calibration curve (Figure 5). The calculated values are reported in Table 6. The gel content calculated showed good agreement with the experimental value and the variation was found to be within $\pm 5.0\%$.

The results shown in Table 7 suggest that no significance differences are absorbed between experimentally and calcu-

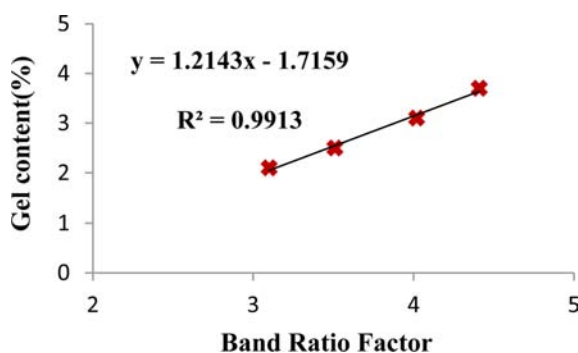


Figure 5. Calibration curve for determination of band ratio factor.

Table 6. Calculation of Gel Content from ASTM Method and Corresponding ATR FTIR Band Ratio Factor

Sample	Calculated gel content (%) by ASTM	ATR FTIR band ratio factor
1	2.1	3.1
2	2.5	3.51
3	3.1	4.02
4	3.7	4.41

Table 7. Gel Content from ASTM Method and Corresponding Calculated Gel Content from ATR FTIR

ATR FTIR band ratio factor	Calculated gel content from calibration curve (%)	Gel content from ASTM method (%)	Variation ($\pm\%$)
2.95	1.86	1.95	+4.5
3.20	2.15	2.07	-4
4.20	3.37	3.45	+2.2

lated results by ATR FTIR.

Linear range of the curve is less than 10% and it can use for commercial samples of BR containing C-C gel is usually between 1-10 percent.

NMR Analysis. Crosslinking occurs either between 1,2-vinyl groups and methylene carbon of *cis* or *trans* isomer, or between two 1,2-vinyl groups. In both the cases, methyl groups are produced which appear in the NMR spectrum regarding their chemical shifts. In all possible mechanisms, chain scission produces chain ends containing methyl groups. It has been shown that the presence of 1,2-vinyl isomer in PBR induces crosslinking and chain scission reactions.⁴⁵ Because of the unsaturated structure of PBR in its repeating units, it can be main factor for different reactions. For studying and characterization of polymer structure the nuclear magnetic resonance spectroscopy (NMR) can be used.

¹³C NMR spectra appeared two clear peaks of methyl carbon (*cis* position) and small peaks correspond to the *trans* and 1,2 vinyl isomers, as shown in Figure 6. Because of these small peaks, the NMR spectra cannot be used for determination of isomeration ratio.

¹H NMR can be quantitatively measured sequences of isomers in PBR. Figure 7 shows a significant the intensities of 5.4 ppm (CH=) and 2.1 ppm (CH₂-) signals from olefinic and aliphatic groups of *cis* and *trans*.⁴⁶ Displacement of the chemical shift of the peaks can be a little different because depends on the temperature, analytical and solvent used. The amounts of these isomers are calculated for each specimen using the integration of peak area according following equations:

$$\% \text{ 1,4 } cis \text{ isomer} = S_{5.37}/(S_{5.40}+S_{5.37}+S_{4.7}) \times 100 \quad (5)$$

$$\% \text{ 1,4 } trans \text{ isomer} = S_{5.40}/(S_{5.40}+S_{5.37}+S_{4.7}) \times 100 \quad (6)$$

$$\% \text{ 1,2 vinyl isomer} = S_{4.7}/(S_{5.40}+S_{5.37}+S_{4.7}) \times 100 \quad (7)$$

Where $S_{5.40}$, $S_{5.37}$, and $S_{4.7}$ are peaks area at 5.40, 5.37, and 4.7 ppm region. The calculated values are reported in Table 8.

The results shown in Table 5 and 8 suggest that there are not

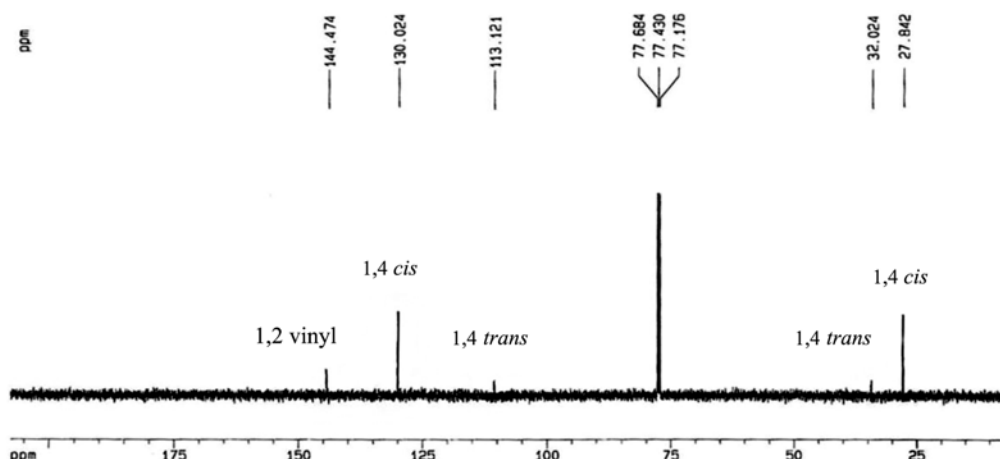


Figure 6. Typical example of ^{13}C NMR spectrum (PBR_{3.1}).

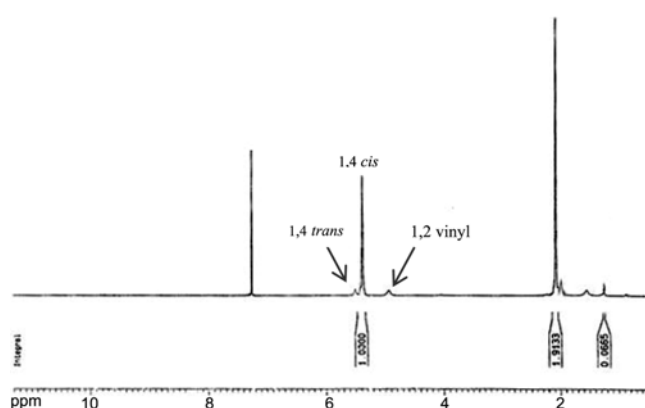


Figure 7. Typical example of ^1H NMR spectrum (PBR_{2.5}).

Table 8. Characterized Properties of Different PBR Investigated with ^1H NMR

Sample	1,4- <i>cis</i> (%)	1,4- <i>trans</i> (%)	1,2-vinyl (%)
BR _{2.1}	96.65	2.10	1.25
BR _{2.5}	96.35	2.15	1.50
BR _{3.1}	95.10	2.80	2.10
BR _{3.7}	94.82	2.76	2.42

significance differences between determinations of micro-structure by two different methods and there is not a disparity between the data.

Rheological Properties. The rheological parameters of blends showed (Figure 8) that increasing the gel content of PBR in the blends to an insignificant decrease in the scorch time, optimum curing time and increasing minimum torque. But the cure rate index of the samples did not change significantly when the content of gel changed. The higher the minimum torque obtained, the higher the number of uncured

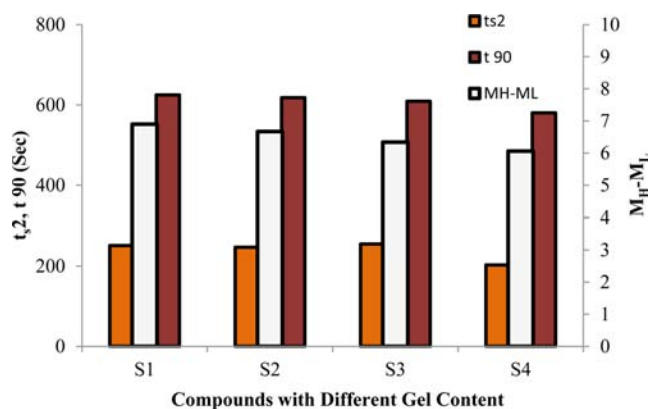


Figure 8. Correlation between rheological properties with gel content of PBR.

physical crosslinks or chain entanglements and the maximum torque presented the degree of vulcanization or chemical crosslink density.

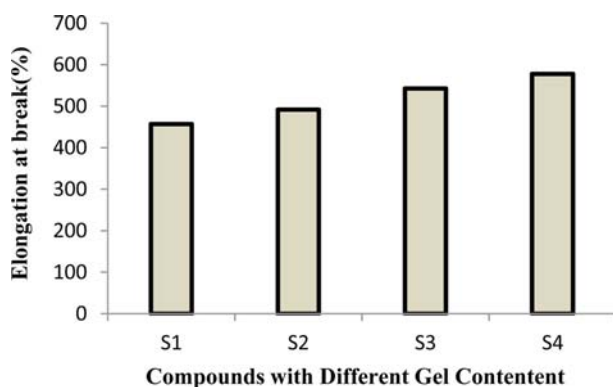
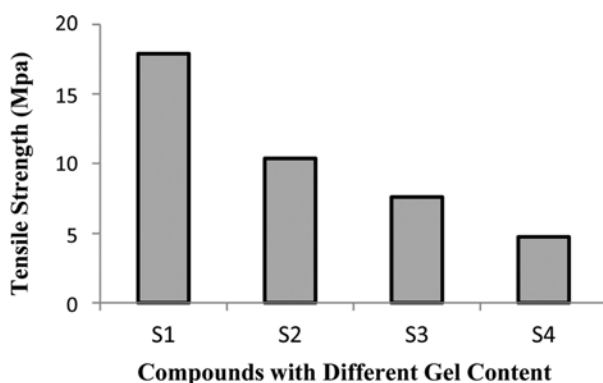
Mechanical Properties. The physicochemical properties of rubber compounds listed in the previous Table 9.

According to the data show in Table 9, there is a significant variation in of rubber compounds with the increasing of gel content. The slightly higher hardness result values are attributed to the short and rigid C-C crosslinks between macromolecules chains.⁴⁷⁻⁵⁰

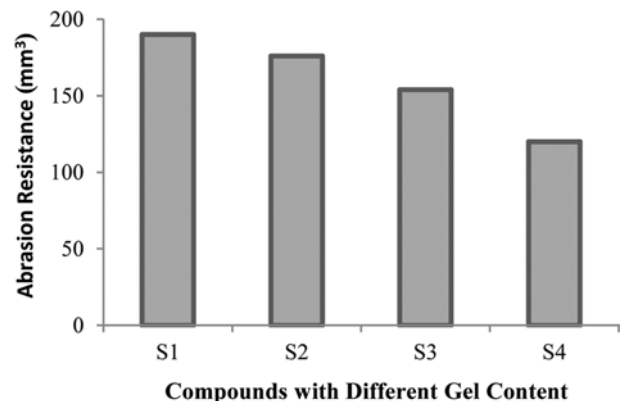
Figure 9 presents the results of elongation at the breaking point of the samples, increases in the elongation at the break was observed. This can be attributed to improving of network flexibility which facilitates the mobility of the polymer chains. As a general trend, the modulus at 300% increased and Tensile Strength decreased (Figure 10), this is probably due to the increase the uncured physical crosslinks density.

Table 9. Mechanical Properties of NR/BR Vulcanization

	Formulation			
	S ₁	S ₂	S ₃	S ₄
Physico - Mechanical properties				
Density (g/cm ³)	1.03	1.05	1.08	1.10
Hardness, Shore A	43	44	45	49
Strain (%)	457	492	543	578
Tensile strength (MPa)	17.89	10.36	7.57	4.74
Modulus, 100% (MPa)	1.62	1.15	1.07	0.93
Modulus, 300% (MPa)	6.24	4.02	3.88	3.22
Elongation at break point (%)	396	443	543	627
Abrasion resistance (mm ³)	190	176	154	120
Resilience (%)	45	42	37	37
Fatigue (cycle/s)	300000	300000	277000	182000

**Figure 9.** Correlation between elongation at the break point and gel content.**Figure 10.** Correlation between tensile strength and gel content.

Abrasion resistance is shown in Figure 11. It can be noticed that these behavior can be attributed to the increasing of networking in PBR.

**Figure 11.** Correlation between abrasion resistance and compounds with different gel contents.

Conclusions

In the present investigation, the microstructure and C-C gel content as well of PBR were determined by ASTM, ATR FTIR and NMR techniques. Also they were characterized by differential scanning calorimetry method. The described ATR FTIR method can be used to determine the C-C gel content in PBR. Although, the results were found to be reproducible, slight difference might arise from the manual valley to valley base line setting during the measurement. Also, the work can be used for commercial PBRs having C-C gel content less than 10%.

The rheological and physico-mechanical properties of the rubber compounds based on NR/BR with various of amounts of C-C gel were investigated. The results show that elongation at break and strain of obtained rubber compounds improve but tensile strength, abrasion resistance and fatigue decreased with increasing of C-C gel content. Therefore, gel formation (C-C crosslink) reduces the curing quality of rubber compounds (C-S crosslink) and adhesion during the mixing process and affect on the phisico-mechanical, the rheological properties of rubber compounds and performance properties such as groove cracking of produces tires also.

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