Comparative Study of Butyl Rubber (IIR) and Bromobutyl Rubber (BIIR) based on FTIR, Dielectric and Thermal Studies

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Abstract: The study aims for a comparative study of butyl rubber (IIR) and bromobutyl rubber (BIIR) based on spectroscopic, dielectric and thermal characterization. Using FTIR, complete vibrational analysis of butyl rubber and bromobutyl rubber are made available which confirms their chemical structure and the functional groups present in them. The effect of microwave frequency, namely 10 GHz and 26 GHz on dielectric constant values of IIR and BIIR was studied by using the method proposed by Robert and Von-Hippel. The thermal behavior of the rubber materials was studied from Thermogravimetric (TG) and Differential Thermal (DT) thermograms. The thermal stability of IIR and BIIR was compared from TG curves and the thermal transitions such as glass transition temperature (T_g), crystallization temperature (T_c) and crystalline melting temperature (T_m) were detected from DTA curves.

Keywords: IIR · BIIR · FTIR · dielectric constant · thermal stability

1. Introduction

Butyl rubber (IIR) is a copolymer or isobutylene and a small percentage of isoprene which has excellent impermeability and good flex properties resulting from low levels of unsaturation between long poly-isobutylene segments. With careful compounding, butyl compound can be made to acquire really good tensile strength. Halogenated butyl rubber improved the properties of butyl rubber by providing much higher curing rates and enabling co-vulcanization with general purpose rubbers. Bromobutyl rubber (BIIR) consists predominantly of saturated polyisobutylene and the bromine functionality makes it more reactive.

2. Experimental methods

Samples of butyl rubber and bromobutyl rubber were procured in the form of slabs of crossection 6 x 4 cm and 6.5 x 5 cm respectively with thickness about 14 mm from SunMaarc Rubber Products, Chennai, India. Sulphur was used as the principle-vulcanizing agent and Carbon black was used as the reinforcing filler for curing the rubber material in the industrial lab. The combined cure package comprises the cure agent sulphur, reinforcing carbon black filler together with accelerators like Dibenzothiazyl disulfide (MBTS) and Tetra Methylthiuram Disulfide (TMTD), activators like zinc oxide (ZnO) and stearic acid, paraffinic oil to avoid cracks in the final product and antidegradants to prevent degradation by heat, oxygen and ozone. The major ingredients for the formation of vulcanized and reinforced IIR and BIIR as per the desired formulations are presented in Table 1. The curatives are added on the two-roll mill to avoid scorching of the rubber material. Initially, IIR and BIIR were masticated in a two-roll mill equipment of the industrial lab. The composites were vulcanized at 170°C under a pressure of about 46 kg/cm^2. The vulcanization time for each rubber material was 30 minutes. Even vulcanized rubber materials do not exhibit satisfactory tensile strength and abrasion resistance in many applications[1]. So IIR and BIIR were compounded with reinforcing filler in order to obtain vulcanizates with adequate mechanical properties for the present work. The carbon black filler content of 50 Phr (parts hundred in rubber) was mixed with the vulcanizates in the roll mill equipment. After the rubber, filler, sulphur, organic accelerators, activators and antidegradants were mixed, the compound was placed in molds and subjected to heat and pressure. IIR and BIIR were intended to adopt the shape of the mold within three minutes. The rubber materials obtained were cut into the required shape as per the ASTM standard D-412 and used for various characterization techniques. The FTIR spectra have been recorded for IIR and BIIR in the range 4000-400cm^{-1} using Bruker IFS 66V spectrophotometer at IIT, SAIF, Chennai, India. The NaCl disks with the sample film were

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placed in the IR cell and the spectra was recorded. A microwave test bench system with an X-band in the frequency range 8.2-12.4 GHz and a K-band in frequency range 18.0-26.5 GHz were employed for determining dielectric constants of IIR and BIIR using Von-Hippel method. The rubber samples of thickness (t) were intercepted in the path of the microwave and readings corresponding to the standing wave pattern were noted. The samples were exactly shaped to the dimensions of the waveguide before taking measurements.

Table 1 Formulations used in preparation of IIR and BIIR (parts per hundred in rubber)

Component	IIR	BIIR
IIR	100	-
BIIR	-	100
Carbon black	64	64
Paraffinic oil	12	12
ZnO	5	5
Stearic acid	2	2
MBTS	1.25	1.25
TMTD	0.5	0.5
Sulphur	2	2

TGA was carried out for IIR and BIIR in a high-resolution thermobalance (NETZSCH STA 409C/CD instrument) at IIT, Chennai, India. Approximately 5mg of rubber sample was heated from room temperature to $1400^{o}C$ with a continuous N_2 flow. The heating rate was $20^{o}C$/min. The sample weight and its rate of weight loss were continuously measured as a function of temperature and the thermal stability was studied. For recording DTA curves, the temperature difference that develops between rubber sample and α-aluminum was measured, when both were subjected to identical heat-treatments. This differential temperature was then plotted against temperature.

3. Results and Discussion

3.1 Vibrational assignments

The chemical structure of butyl rubber which is a combination of isobutylene and isoprene is given in Fig. 1. The specific modes of vibration in IIR and BIIR which contain both methyl and methylene group in their chemical structure was analyzed qualitatively from FTIR spectra and are presented in Figs. 2-3. The assignments of the fundamental frequencies have been made on the basis of magnitude and relative intensities of the observed bands. It is convenient to discuss the vibrational spectra of IIR and BIIR in terms of characteristic spectral region as described below:
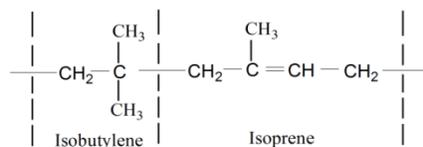
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Fig.1 Chemical structure of butyl rubber

C=C vibrations:

The isoprene units of butyl rubber present double bonds between carbons. The C=C stretching vibrations are generally observed in the range of 1620-1680cm^{-1}. According to Klöpffer, C=C stretching in IR generates low intensity bands in polymers[2]. Hence, medium strong bands which appear at 1646cm^{-1} in the FTIR spectrum of butyl rubber and 1626cm^{-1} in the FTIR spectrum of bromobutyl rubber are assigned to the C=C stretching mode of vibrations.
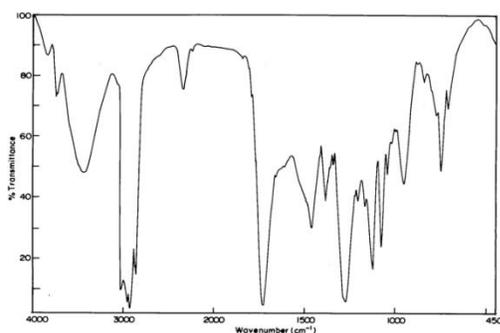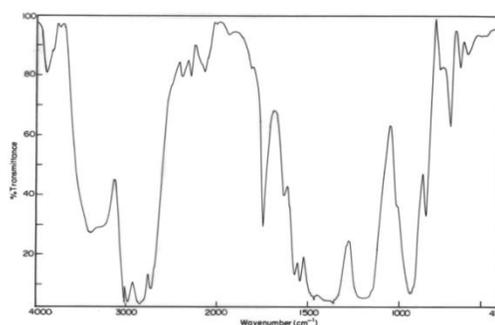

Fig.2 FTIR spectrum of IIR

Fig.3 FTIR spectrum of BIIR

C-C vibrations:

The C-C stretching vibrations[3] show absorption in the region 1260-700cm^{-1}. Accordingly the medium strong bands observed at 725, 752, 821, 943, 972, 996 and 1009cm^{-1}, strong bands observed at 1042, 1137 and 1179cm^{-1}, very strong bands observed at 1092, 1247 and 1265cm^{-1} in the FTIR spectrum of butyl rubber are assigned to C-C stretching vibrations. Also, a weak band identified at 859cm^{-1} is also assigned to C-C stretching vibrations. In BIIR, a medium strong band observed at 749cm^{-1}, strong bands observed at 837, 1016 and 1275cm^{-1}, very strong bands observed at 908, 933, 1141, 1158 and 1227cm^{-1} are assigned to C-C stretching vibrations.

C-H vibrations:

From the FTIR spectrum of butyl rubber, very strong vibrational bands observed at 2923, 2953 and 3029cm^{-1} are ascribed to C-H stretching vibrations. Similarly, very strong vibrational bands occurring at 2985 and 3021cm^{-1} in the FTIR spectrum of BIIR are assigned to C-H stretching vibrations. Also a strong band occurring at 3195cm^{-1} in the spectrum of BIIR is also assigned to C-H stretching vibrations. Substitution sensitive C-H in plane bending vibrations[3] are generally observed in the region 1417-1421cm^{-1} and bands involving the C-H out of plane bending vibrations[3] generally appear in the range 1000-675cm^{-1}. Accordingly, strong band observed at 1439cm^{-1} in IIR and very strong bands observed at 1424 and 1456cm^{-1} in BIIR are attributed to C-H in plane bending vibrations. Medium strong bands appearing at 725, 943, 996, and 1009cm^{-1} and medium intensity bands appearing at 680, 752, 784, 821 and 859cm^{-1} in IIR are due to C-H out of plane bending vibrations. Similarly, very strong bands occurring at 908 and 933cm^{-1}, strong bands occurring at 837 and 1016cm^{-1}, a medium strong band occurring at 685cm^{-1} and a medium intensity band occurring at 749cm^{-1} in the IR spectrum of BIIR are due to C-H out of plane bending vibrations.

CH₃ vibrations:

Both isobutylene and isoprene units of IIR and BIIR possess CH_3 group. The CH methyl group stretching vibrations[3] are generally observed in the range of 3000-2800cm^{-1}. The recorded FTIR spectrum of IIR shows very strong intensity bands at 3029, 3000, 2923

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and 2852cm^{-1} respectively, and they are assigned to CH_3 stretching vibrations of the rubber material. The first two frequencies results from the asymmetric stretching of CH_3 mode. Bands at 2923 and 2852cm^{-1} emerges from the symmetric stretching of the methyl group. The recorded FTIR spectrum of BIIR shows very strong intensity bands at 3021, 2985, 2854 and 2806cm^{-1} respectively, first two are assigned to asymmetric stretching vibrations of CH_3 mode and the last two are assigned to symmetric stretching vibrations of CH_3 mode in the polymer. A strong band observed at 1444cm^{-1} in IIR and a very strong band observed at 1465cm^{-1} in BIIR are assigned to torsion vibration of CH_3. Bands occurring at 1319, 1336 and 1363cm^{-1} in the IR spectrum of IIR and 1358cm^{-1} in the IR spectrum of BIIR are due to CH_3 wagging.

CH$_2$ vibrations:

The stretching vibrations of CH_2 methylene group usually occur in the region near 2926cm^{-1}. Very strong intensity bands observed at 2953 and 2923cm^{-1} in the recorded spectrum of IIR may be due to CH_2 asymmetric and symmetric stretching vibrations. Similarly, very strong intensity bands observed at 2985 and 2854cm^{-1} in BIIR may also be due to CH_2 asymmetric and symmetric stretching vibrations. The scissoring band of the CH_2 group in the spectra of hydrocarbons occurs in the region near 1465cm^{-1}. Absorption of hydrocarbons because of methylene twisting and wagging vibrations is observed in 1350-1150cm^{-1} region. These bands are generally appreciably weaker than those arising due to methylene scissoring[4]. The bands identified at 1444 and 1465cm^{-1} in IIR and BIIR have been assigned to CH_2 bending (scissoring). In IIR, bands identified at 1336 and 1319cm^{-1} are assigned to methylene twisting vibrations and bands identified at 1179, 1137cm^{-1} are assigned to methylene wagging vibrations. In BIIR, band identified at 1358cm^{-1} is assigned to methylene twisting vibrations and bands identified at 1158 and 1141cm^{-1} are assigned to methylene wagging vibrations.

O-H vibrations:

The OH stretching vibrations exhibited by the chosen rubber materials is purely due to trapped moisture or water molecules; which then forms a hydroxyl functional group in the polymer matrix. The OH group vibrations[4] show pronounced shifts in the spectra of the hydrogen-bonded species and are generally observed in the region around 3500cm^{-1}. Medium strong band observed at 3431cm^{-1} in the FTIR spectrum of IIR and 3223, 3390cm^{-1} in the FTIR spectrum of BIIR are assigned to OH stretching vibrations. Bands observed at 1179 and 680cm^{-1} may be due to OH in plane and out of plane bending vibrations in IIR. Bands observed at 1158 and 685 cm^{-1} may be due to OH in plane and out of plane bending vibrations in BIIR. In general, for all the observed IR frequencies, the intensity of an absorption in the IR spectrum depends on the change in dipole moment that occurs during the vibration. Therefore, the vibrations that produce a large change in dipole moment result in a more intense absorption.

3.2 Dielectric measurements at microwave region

It is evident from Table 2 that dielectric constant evaluated in K-band is lower than in X-band. Hence, dielectric constant decreases with increasing frequency and the result is in coincidence with literature[5]. Bromobutyl rubber has greater dielectric constant than butyl rubber. Physically it means greater polarization is developed by brominated butyl rubber in an applied field of given strength. Dielectric constant is an important parameter in deciding the insulation characteristic of the material as the rubber material with low dielectric constant is an excellent insulator.

Table 2 Dielectric constants of IIR and BIIR

Sample	Dielectric constant (ε_r)	
	X- band	K- band
IIR	3.478	2.3621
BIIR	4.054	2.6874

The polarity in butyl rubber is found to increase after bromination. Increasing the bromine content in IIR can eventually lead the material to dielectric breakdown which is disadvantageous. Hence testing should be done before commercializing bromobutyl rubber in applications such as line and cable insulation.

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3.3 Thermogravimetric Analysis (TGA)

The thermoanalytical curves of IIR and BIIR as given in Figs. 4-5 were interpreted; from which the thermal stability[6,7] of rubber materials was studied. It is seen from TG curve that butyl rubber undergoes 65% degradation at a very high temperature of $1307^{o}C$ and degradation process is multistage. 5% of the material degrades at $229^{o}C$ which means 95% of the material is thermally stable till $229^{o}C$. The degradation process of BIIR is single stage with 10% degradation at a temperature of $318^{o}C$ and 90% degradation at a temperature of $454^{o}C$.
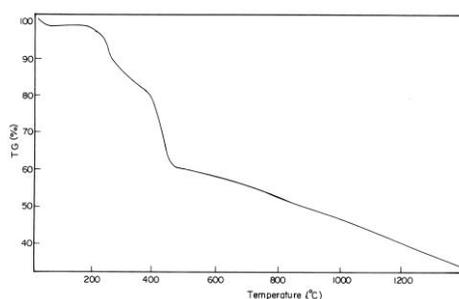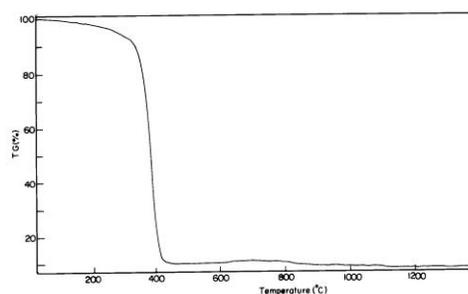

Fig.4 TGA of IIR   **Fig.5 TGA of BIIR**

The temperatures corresponding to the various weight loss percentages of IIR and BIIR are given in Table 3. The temperatures corresponding to weight loss from 20% to 70% are comparatively higher for IIR than BIIR. Also BIIR degrades quickly within the temperature interval of $318-454^{o}C$ whereas IIR undergoes 70% degradation at a very high temperature of $1386^{o}C$. Thus it is concluded that butyl rubber is more thermally stable than bromobutyl rubber.

Table 3 Thermal Stability of Rubber Materials

Weight loss	Temperature(^{o}C)	
	IIR	BIIR
10%	257	318
20%	380	339
30%	420	351
40%	494	358
50%	865	362
60%	1192	369
70%	1386	376
80%	-	387
90%	-	454

3.4 Differential Thermal Analysis (DTA)

The glass transition temperature (T_g), crystallization temperature (T_c) and crystalline melting temperature (T_m) obtained from DTA are important transition temperatures that characterize a polymer[8]. T_g is the temperature at which the amorphous domains of a polymer are transformed to a glassy state. The temperature of formation of crystalline domains in the polymer is T_c. T_m is the melting temperature of the crystalline domains of the polymer. DTA thermograms of IIR and BIIR are shown in Figs. 6-7. T_g, T_c and T_m for IIR and BIIR are given in Table 4.
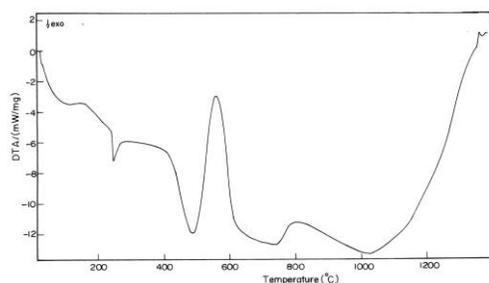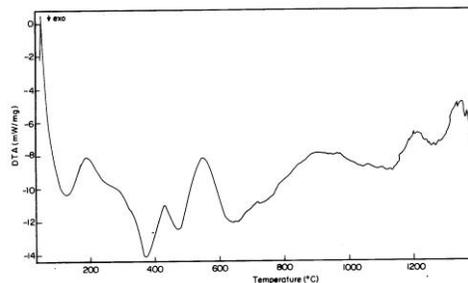
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Fig.6 DTA of IIR

Fig.7 DTA of BIIR

Table 4 Thermal Transition of Rubber Materials

Sample	Peak Temperature (^{o}C)		
	T_g	T_c	T_m
IIR	117.6	237.8	393.5
BIIR	123	224.3	263.7

Conclusion: Structural, dielectric and thermal investigations on butyl rubber and bromobutyl rubber have been performed and comparatively studied. Using FTIR, spectral analysis of polymers is done on the basis of all observed frequencies with probable vibrational assignments. From microwave analysis, it is seen that dielectric constant of BIIR is higher than IIR. Thus the polarity in IIR is found to increase after bromination. The thermal stability was compared from TG curves and concluded that IIR is more thermally stable than BIIR. The major thermal transitions were detected for IIR and BIIR from DTA curves.

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