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Characterization of Reclaim rubber and Reclaim rubber/Natural rubber blend

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Abstract : The applicability of reclaim rubber (RR) and a blend of reclaim rubber and natural rubber composite (RR/NR) has been tested using various characterization techniques. Using FTIR, complete vibrational band analysis of RR and blend of RR/NR composite are made available which confirms their chemical structure and the functional moieties present in them. The present work analyses the dielectric constant of rubber materials by using the method proposed by Robert and Von-Hippel. Dielectric constant values have also been evaluated to substantiate the insulating nature of RR and RR/NR blend over a range of frequency and temperature using impedance analyzer. The polarizability value was calculated from penn analysis and Claussius-Mossotti relation. The thermal stability of RR and RR/NR blend was compared from Thermogravimetric (TG) curves and the activation energy, frequency factor and other activation kinetic parameters were calculated using Coats-Redfern method. The major thermal transitions were detected from Differential thermal (DT) curves.

Keywords : FTIR;Reclaim rubber; RR/NR blend;dielectric constant;activation energy.

1. Introduction

Around 70% of the world's natural rubber is used as tires for aeroplanes and other automobiles. But after a long run when these tires are not serviceable, they need to be discarded when only a small proportion of rubber (<1%) would have abraded out from the tire and discarding the entire amount of rubber is obviously not environment friendly. Degradation of natural rubber[1]may take several generations due to crosslinks in rubber as a result of vulcanization and reinforcement. The reclaimed or regenerated rubber is the solution for this environmental problem.Reclaim rubber (RR) or regenerated rubber is the product resulting from the treatment of ground vulcanized scrap rubber tires and miscellaneous waste rubber articles by the application of heat and chemical agents, followed by intense mechanical working[2]. The regenerated rubber is partially de-vulcanized (cleavage of many but not all S-S bonds and some C-C bonds) and has almost the original plasticity of virgin rubber, permitting the same to be compounded, processed and re-vulcanized or reused so that it can be made available for individual rubber products. During reclamation, the molecular weight of the elastomeric component is substantially reduced; however the chemical unsaturation of finished reclaim is essentially unchanged from that of the original vulcanized scrap. Reclaim rubber has found a cosmopolitan application due to its fine quality, efficiency and durability.

In this paper, FTIR spectroscopic technique has been employed for the qualitative analysis of reclaim rubber and blend of reclaim rubber/natural rubber (RR/NR). A systematic approach suggested by Robert and Von-Hippel was successfully employed where in microwave test bench method is utilized to study the dielectric properties of RR and RR/NR blend. The dielectric behavior as a function of frequency and temperature has also been studied using impedance spectroscopy. This can be used as a tool to understand the charge transport mechanism in the insulating polymer matrix and in a morphology that consists of insulating matrix and carbon black filler[3].The thermal behavior of RR and RR/NR blend was comparatively studied using TGA and important thermal transitions were detected using DTA technique. Further, activation energy and other thermokinetic parameters were determined using Coats-Redfern plot. Completely discarding the scrap rubber tires and miscellaneous waste rubber articles is not environmental friendly in the present scenario. Thus a sincere attempt has been made to comparatively study the structure-property relationship of reclaim rubber and reclaim rubber/natural rubber composite.

2. Experimental

2.1Materials and synthesis of cured RR and RR/NR blend

Reclaim rubber was manufactured in the industrial lab of Central Institute of Plastics Engineering and Technology (CIPET), Chennai, India by reclaimator process wherein; whole tires were cracked to a convenient size, and the fibre was removed mechanically. The relatively fiber-free scrap was grounded to approximately 30 mesh before mixing with chemical agents and hence the scrap was reclaimed continuously in thereclaimator. The temperature range was 204-260^{o}C and the devulcanization time was 4 minutes. In the mastication step, the reclaimed rubber was masticated on laboratory two-roll mill equipment for 5 min. The combined cure package comprises the cure agent sulphurtogether with accelerators like Dibenzothiazyl disulfide (MBTS) and Tetra Methylthiuram Disulfide (TMTD), activators like zinc oxide (ZnO) and stearic acid and antidegradants[4,5]. Antidegradants were used to prevent degradation by heat, oxygen and ozone. Reclaimed material was mixed and blended with small proportion of chemical and processing agents as per the specifications given in Table 1.The composites were vulcanized at 160^{o}C under a pressure of about 45kg/cm^{2}. The time of vulcanization was 30 minutes. The reinforced rubber material was obtained by mixing carbon black filler to the reclaimed rubber vulcanizates in the roll mill equipment. The carbon black filler content was 50 Phr (Phr-parts hundred in rubber). After the rubber, filler, sulphur and organic accelerators were mixed, the compound was placed in molds and subjected to heat and pressure. The rubber article was intended to adopt the shape of the mold. The samples were obtained in the form of slabs with thickness about 10 ± 0.5mm.

Further, reclaim rubber was blended with natural rubber in the ratio of 65:35[6]. The rubber master batch of RR (65%)and NR (35%) was compounded with the ingredients such as homogenizing agent sulphur, activators like zinc oxide and stearic acid, carbon black reinforcing filler and accelerators like MBTS and TMTD according to the desired formulation in the internal mixer of the roll mill equipment. The curatives were added to protect scorching of the compound. The temperature of mixing was around 160^{o}C. The blended samples were obtained from the mold in the form of slabs with thickness about 10± 0.5mm.The rubber materials obtained were cut into the required shape as per the ASTM standard D-412 and used for various characterization techniques.

Table 1.Formulations used in the preparation of Rubber material in Phr

Ingredients	RR	RR/NR
RR	100	-
RR/NR	65	35
Carbon black	50	50
Paraffinic oil	12	12
ZnO	5	5
Stearic acid	2	2
MBTS	1.25	1.25
TMTD	0.5	0.5
Sulphur	2.25	2.25

2.2Measurements and characterization

FTIR spectroscopic technique has been employed for the qualitative analysis of reclaim rubber and blend of reclaim rubber/natural rubber. It is an ever reliable technique to comment on the structure of the selected rubbers. The FTIR spectra[7,8] have been recorded for RR and RR/NR blendin the range 4000-400 cm^{-1} using Bruker IFS 66V spectrophotometer at Indian Institute of Technology (IIT), SAIF, Chennai, India. The NaCldisks with the sample film were placed in the IR cell and the spectra was recorded.The frequencies of all the sharp bands are accurate to ±1 cm^{-1}. A systematic approach suggested by Robert and Von-Hippel was successfully employed where in microwave test bench method is utilized to study the dielectric properties of RR and RR/NR blend. 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 RR and RR/NR blend[9].The dielectric behaviour as a function of frequency and temperature forRR and RR/NR blend has also been studied using impedance spectroscopy[10].The study analyses the electrical response of the polymer materials and yields information about their physicochemical properties. The impedance analyzer used for the current dielectric study is Hioki LCR Hi-Tester3532 in the frequency region 50 Hz to 5 MHz. The analyzer is connected through an interface and is controlled by software such as z plot and z view. Sample materialwas shaped in rectangular form with dimension of 5.33x2.51x1.64 mm^3 and placed between silver electrodes. The cell used for the measurements was a parallel plate circular condenser made of copper.

Thermogravimetric Analysis (TGA)is a technique in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. Analysis was carried out for RR and RR/NR blend in a high-resolution NETZSCH STA 409C/CD thermobalancewith a continuous N_2 flow at Indian Institute of Technology (I.I.T), Chennai, India. Approximately 6mg of rubber sample was heated from room temperature to 1400^{o}C with heating rate of 20^{o}C/min. When a weightloss is detected by the system, the heat rate slows down andis maintained at the lowest value of 0.01^{o}C/min until the end of weight loss[11].Differential thermal Analysis (DTA) is a technique through which changes in the polymer sample leading to absorption or evolution of heat can be detected relative to the inert reference.Approximately 6mg of the rubber material and an inert reference substance (α-aluminum) were taken in small aluminium dishes that are located above sample and reference thermocouples in an electrically heated furnace at Indian Institute of Technology (I.I.T), Chennai, India. The differential temperature between rubber sample and the inert reference material was measured and plotted against temperature.

3. Results and Discussion

3.1 Vibrational assignments and chemical structure

The vibrational spectrum of a molecule is considered to be a unique physical property which is characteristic of a molecule. FTIR spectra of RR and RR/NR blendare presented in Figure1(a) and (b). The assignments of the fundamental frequencies have been made on the basis of magnitude and relative intensities of the observed bands. The vibrational bands of specific modes of rubber materials which contain both methyl and methylene groups in their chemical structure was analyzed qualitatively. It is convenient to discuss the vibrational spectra of RR and RR/NR blend in terms of characteristic spectral region as described below:

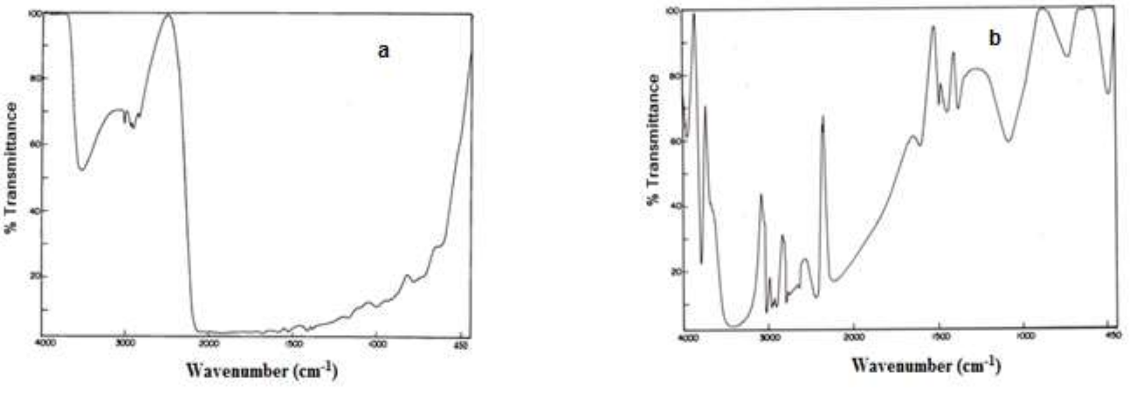

Figure1.FTIR Spectrum of (a) RR and (b) RR/NR blend

C=C vibrations:

The C=C stretching vibrations[7] are generally observed in the range of 1620-1680 cm^{-1}. A strong band which appears at 1681 cm^{-1} in the FTIR spectrum of reclaim rubber and a medium intensity band which appears at 1615 cm^{-1} inthe FTIR spectrum of reclaim rubber/natural rubber blendare ascribed to the C=C stretching mode of vibrations.

C-C vibrations:

The C-C stretching vibrations[8] show absorption in the region 1260-700cm^{-1}. Accordingly the bands observed at 1169, 1100, 1008, 904 and 772 cm^{-1} in the IR spectrum of reclaim rubberare assigned to C-C stretching vibrations. In RR/NR blend, a medium intensity band identified at 1088 cm^{-1}anda weak band identified at 720 cm^{-1}are assigned to C-C stretching vibrations.

C-H vibrations:

The C-H stretching vibrations normally occur at bands in the region 3100-3000 cm^{-1}, which is the characteristic region for the ready identification of CH stretching vibration.In this region, the bands were not affected appreciably by the nature of the substituent such as by the crosslinks introduced by sulphur in the polymer chain due to vulcanization. The presence of conjugate substituent such as C-H causes a heavy doublet formation[8] around the region 2882-2897 cm^{-1}. The experimentally observed vibrations at 3004, 2932, 2891 and 2819 cm^{-1}in the FTIR spectrum of reclaim rubber are due to C-H stretching vibrations. In the blended rubber material, vibrations occurring at 3015, 2956, 2902, 2848, 2789 and 2735 cm^{-1} in the FTIR spectrum are assigned to C-H stretching vibrations. Substitution sensitive C-H in plane bending vibrations are generally observed in the region 1417-1421 cm^{-1}and bands involving the C-H out of plane bending vibrations[12] generally appear in the range 1000-675 cm^{-1}. Accordingly, strong bands observed at 1419 and 1386 cm^{-1} in reclaim rubber and medium intensity bands observed at 1445 and 1385 cm^{-1} in reclaim rubber/natural rubber blend are attributed to C-H in plane bending vibrations. Bands that appear at 772 and 688 cm^{-1} in the IR spectrum of reclaim rubber and a band that appears at 720 cm^{-1} inthe IR spectrum of reclaim rubber/natural rubber blend are due to C-H out of plane bending vibrations.

CH_3 vibrations:

The rubber materials under consideration possess CH_3group.The CH methyl group stretching vibrations are generally observed in the range of 3000-2800 cm^{-1}.The recorded FTIR spectrum of RR has medium intensity bands at 3004, 2932, 2891 and 2819 cm^{-1}, and they are also assigned to CH_3 stretching vibrations of the rubber material. Bands at 3004 and 2932 cm^{-1} results from asymmetric stretching of CH_3 mode in which the two C-H bonds of the methyl group are expanding while the third one is contracting. Bands at 2891 and 2819 cm^{-1}emerges from the symmetric stretching of CH_3 mode in which all the three C-H bonds expand and contract in phase. The recorded FTIR spectrum of RR/NR blend has medium intensity band at 3051 cm^{-1} and very strong bands at 3015, 2956 and 2902 cm^{-1}, and they are assigned to asymmetric stretching vibrations of CH_3 mode. A band that appears at 2848 cm^{-1} in the blended polymerresults from symmetric stretching of CH_3 mode[13,14]. The torsion vibration of $CH_3$is observed at 1529 cm^{-1} in the IR spectrum ofreclaim rubber. Similarly bands occurring at 1500 and 1445 cm^{-1} in the IR spectrum of RR/NR blend is ascribed to CH_3 torsional vibration. A band occurring at 1386 cm^{-1} in the IR spectrum of RR and 1385 cm^{-1} in the IR spectrum of RR/NR blend is due to CH_3 wagging.

CH_2 vibrations:

The stretching vibrations of CH_2 methylene group usually occur in the region near 2926 cm^{-1}. The frequency of the methylene stretching is increased when the methylene group is part of a strained ring.In this case, it was observed at 2932 cm^{-1} for reclaim rubber and at 2902 cm^{-1} for RR/NR blend. The scissoring mode of the CH_2 group[7]gives rise to a characteristic band near 1465 cm^{-1}. The bands identified at 1529 and 1569 cm^{-1} in reclaim rubber have been assigned to CH_2 bending (scissoring)[15]. Absorption of hydrocarbons because of methylene twisting and wagging vibrations[8] is observed in 1350-1150 cm^{-1} region.These bands are generally appreciably weaker than those arising due to methylene scissoring. For the present case, the bands are identified at 1169, 1100 cm^{-1} in the IR spectrum of reclaim rubber.

N-H vibrations:

The N-H stretching vibrations[16,17]occur in the region 3500-3400 cm^{-1}. In the present work, a broad and medium strong band observed at 3527 cm^{-1} in RR, broad bands observed at 3408 and 3686 cm^{-1} in RR/NR blend have been assigned to N-H vibrations. Another strong band observed at 3780cm^{-1}in RR/NR blend has also been assigned to N-H vibrations. Usually the frequency of N-H vibration is decreased in the presence of hydrogen bond. The bands at 3686 and 3780 cm^{-1} are deviated trivially [18]from the expected range. This is because; the position of absorption in this region depends upon the degree of hydrogen bonding and physical state of the sample.

3.2 Microwave measurements

As rubber material is a potential candidate for materials used in various insulating devices,understanding the dielectric nature of RR and RR/NR blend becomes absolutely necessary. The effect of microwave frequency, namely 10 GHz and 26 GHz on dielectric constant values of RR and RR/NR blend was probed after bringing chemical modification in them by the processes of vulcanization and reinforcement.It is evident from Table 2 that dielectric constant decreases with increasing frequencyas the dielectric constant evaluated in K-band is lower than in X-band[19].

Table 2.Dielectric constants of RR and RR/NR blend

Sample material	Dielectric constant (ε_r)	
	X - band (10 GHz)	K- band (26 GHz)
RR	2.536	1.046
RR/NR blend	5.337	3.272

Further, Reclaim rubber blended with natural rubber has greater dielectric constant than in crude state. Physically it means greater polarisation is developed by this blended rubber material in an applied field of given strength. The scientific community has done a lot of qualitative work in this particular area. ArunGhoshet al[20]reported that higher degree of polarization at fine dispersion of fluororubber in the blend composition of 75/25silicone rubber/fluororubber makes the dielectric constant higher than that of the neat silicone rubber.Debapriyaet al[21]incorporated silica into natural rubber and reclaim rubber blend system by sol-gel technique and the microwave analysis of various sol gel vulcanizates was carried out to determine the frequency dependence of dielectric permittivity and dielectric loss.Dynamic Mechanical and dielectric properties of Modified Surface Chitosan/Natural Rubber Latex was studied by WirachTaweepreda[22] in which the dielectric constant of the polymer film increased with higher content of chitosan.Honey Johnet al[23]prepared different compositions of Pani-Natural Rubber semi-interpenetrating networks and the dielectric properties of all of the samples were determined in microwave frequencies using the cavity perturbation technique.The rubber material with low dielectric constant and high dielectric strength is an excellent insulator. Here the dielectric constant in blend state increases and the insulation characteristic decreases. Therefore, when RR/NR blend is used in electrical energy utilities care should be taken before commercialization. The polarity in reclaim rubberis found to increaseafter blending with natural rubber. Increasing the blend composition of NR in RR can eventually lead the material to dielectric breakdown which is disadvantageous. But when the same RR/NR blend is used as a dielectric material in a capacitor, the charge storage capacity is increased because with increase in polarity,the material will be able to store large amount of chargefor a given applied electrical field. Eventually, in capacitor applications, the voltage to be applied for breakdown to happen in RR/NR blend also increases.

3.3 Dielectric spectroscopic studies

Dielectric constant (ε_r) and dielectric loss (D) of RR and RR/NR blend has been studied as a function of frequency and temperature using impedance spectroscopy method. The dielectric behavior of RR and RR/NRblend was studied in the frequency region 10 Hz to 10^7Hzat various temperatures ranging from 308 K to 368 K. Figures2-3show the plot of ε_r and D as a function of frequency. Dielectric constant and dielectric loss were found to decrease with increasing frequency which can be understood by polarization mechanism.

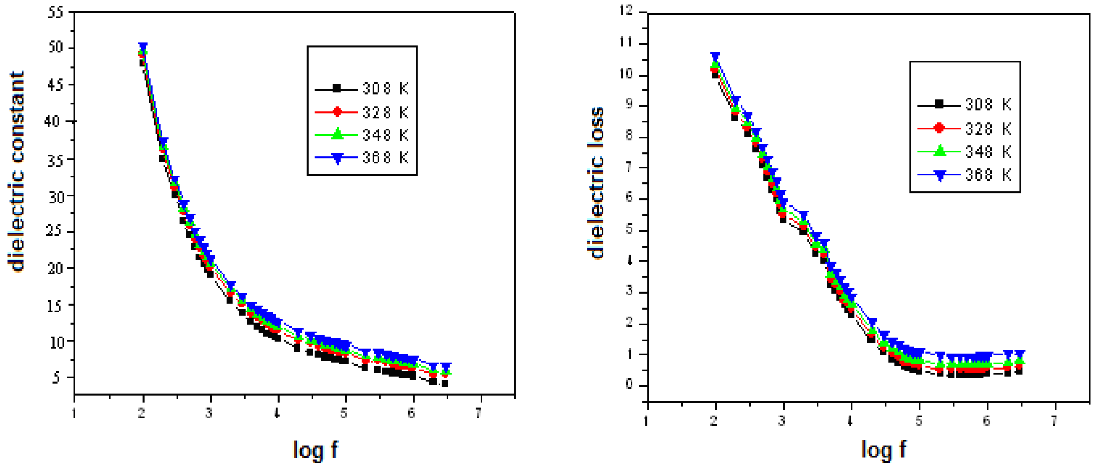

Figure 2.Frequency dependence of ε_r and D for RR

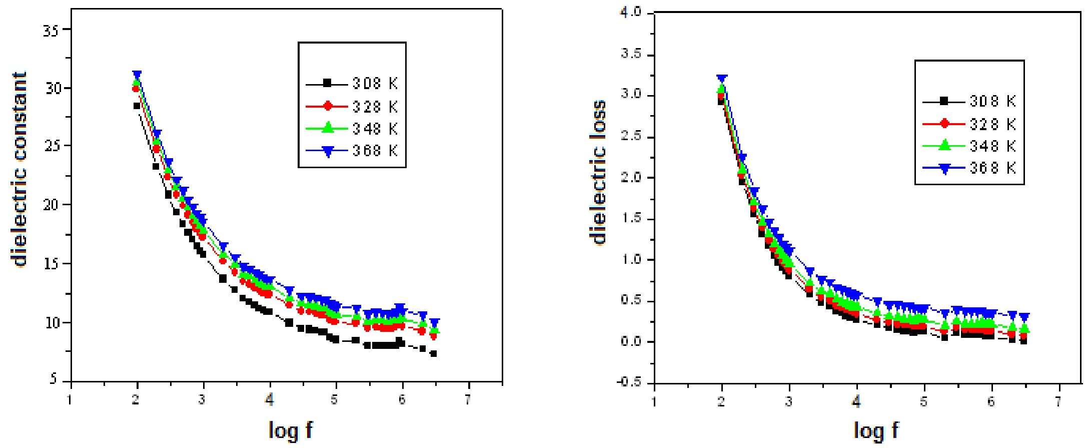

Figure 3.Frequency dependence of ε_r and D for RR/NR blend

The dielectric spectra indicate sudden increase in dielectric constant values for all temperatures in the lower frequency region (100-150 Hz). The plot also indicates that there is a domination of one type of polarization process, where the oscillation of the electric dipole moment is in phase or slightly out of phase with the applied field. The most possible mechanism in this frequency range is orientational polarization. This is supported by the fact that neither relaxation nor resonant type behavior is present in the dielectric constant versus frequency plot[24]. Further, the atomic and electronic polarizations occur at a period shorter than the period of the applied field frequency. Higher value of dielectric loss for both RR and RR/NR blend at lower frequency may be due to the presence of various resonant polarization mechanisms. Towards higher frequency, polarization mechanisms lose their significance gradually thereby yielding lower values of dielectric loss. The dielectric loss in the RR and RR/NR blend is due to the contribution from both the direct current conductivity and the alternating current conductivity. In the low frequency region, direct current conduction loss is inversely proportional to the frequency, which accounts for the increase in dielectric loss with decreasing frequency for the rubber materials[25]. Dielectric constant and dielectric loss exhibited similar variation with frequency for all the four temperatures i.e. 308 K, 328 K, 348 K and 368 K.

In applications such as wire and cable insulation, heat shrinkable materials and electronic packaging, electrical properties of a rubber material is affected by changes in temperature. So it becomes absolutely necessary to study the thermal effect on dielectric behavior of RR and RR/NR blend.The variation of dielectric constant and dielectric loss was studied with respect to temperature for four fixed frequencies such as 1 KHz, 10 KHz, 100 KHz and 1 MHz as shown in Figures4-5. ε_r and D was found to increase in the rubber materials when temperature was increased from room temperature (300K) to a high temperature such as 380 K. It has to be noted that both ε_r and D increase only slightly with temperature for a high frequency of 1 MHz.The lower value of the dielectric loss with high frequency for RR and RR/NR blend suggests that the samples possess enhanced optical quality and this parameter is a vital importance for application as non-linear optical material.

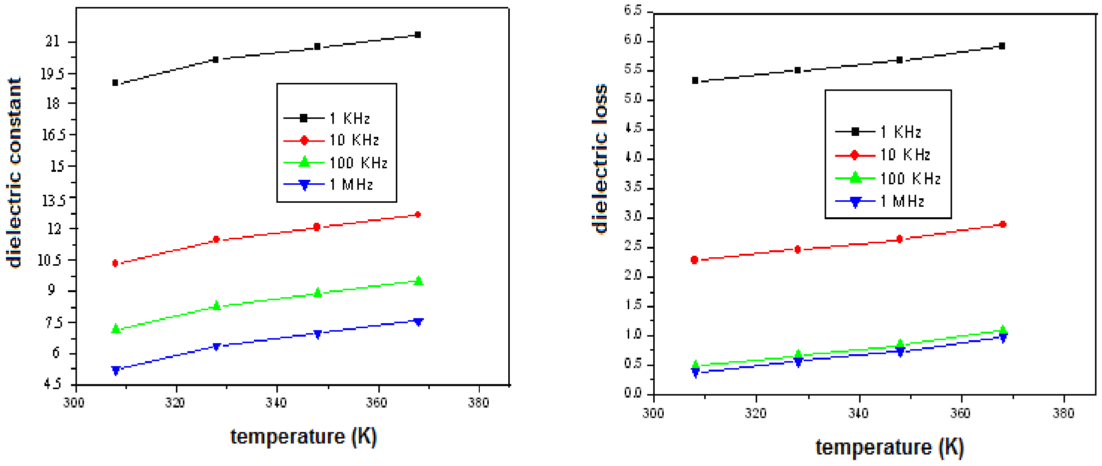

Figure 4.Temperature dependence of ε_r andD for RR

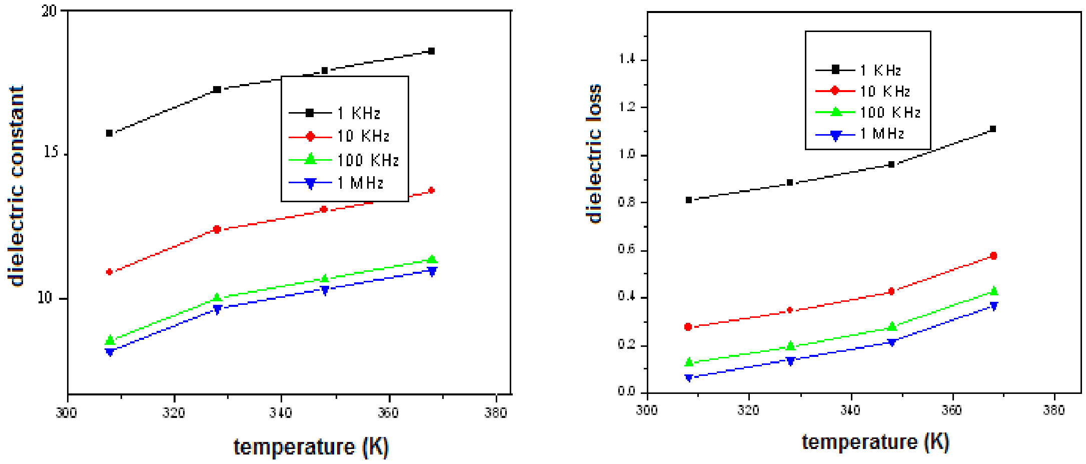

Figure 5.Temperature dependence of ε_r andD for RR/NRblend

3.3.1 Polarizability calculation

The valence electron plasma energy $\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{1/2}$ ……… (1)

where Z is the total number of valence electrons, ρ is the density and Mis the molecular mass of the rubber material. The Penn gap and the Fermi energy are explicitly dependent on the parameter $\hbar\omega_p$[26].

The Penn gap energy is given by $E_p = \frac{\hbar\omega_p}{(\varepsilon_\alpha - 1)^{1/2}}$ ……… (2)

Fermi energy is given by $E_F = 0.2948(\hbar\omega_p)^{4/3}$ ……… (3)

The polarizability α is calculated from Penn analysis using the relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_o}{(\hbar\omega_p)^2 S_o + 3E_p{}^2}\right] x \frac{M}{\rho} x0.396x10^{-24} \text{ ……… (4)}$$

The polarizability α is calculated from Claussius-Mossotti equation using the relation

$$\alpha = \frac{3M}{4\pi N_a \rho}\left(\frac{\varepsilon_\alpha - 1}{\varepsilon_\alpha + 2}\right) \text{ ………. (5)}$$

The polarizability value obtained from Penn analysis agrees very well with the polarizability value obtained using Clausius-Mossotti equation. N_a is the Avagadro number, ε_α is the dielectric constant obtained from impedance analysis at 1 MHz for RR and RR/NR blend. S_0 is a constant for the material given by the equation

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_p}{4E_F}\right]^2 \text{ ……… (6)}$$

Thevarious theoretical parameters obtained from impedance analysis for Reclaim rubber and Reclaim rubber/Natural rubber blend are presented in Table 3.

Table 3.Parameters obtained from impedance analysis

Sample	$\hbar\omega_p$(eV)	ε_α	E_p(eV)	E_F (eV)	α Penn analysis (cm^3)	α ClausiusMossotti equation (cm^3)
RR	17.8722	4.844	6.8887	13.7751	1.5338 x10^{-23}	1.5661 x10^{-23}
RR/NR	31.0442	7.549	9.5813	28.7630	3.549 x10^{-23}	3.7038 x10^{-23}

3.4 Thermogravimetric Analysis (TGA)

The continuous weight loss curves for the thermal degradation of the rubber materials are given in Figure6(a) and (b); from which the thermal stability of RR and RR/NR blend is studied. The thermal properties of the polymer blend depend very much on the miscibility of the components[27]. In the present work, reclaim rubber undergoes three-step degradation process with 80% degradation at a high temperature of 959°C.The TGA curve of RR/NR blend also shows three steps of degradation with nearly 53% of the material degraded between 300°C to 470°C. On the whole, 85% of RR/NR gets degraded at a very high temperature of 1386°C and 15% remains as the residue material. The temperatures corresponding to the various weight loss percentages of RR and RR/NR blend are given in Table 4. The temperatures corresponding to weight loss from 10% to 80% are comparatively higher for RR/NR blend than RR. Thus it can be concluded that blending reclaim rubber with 35% of natural rubber makes it more thermally stable than unblended reclaim rubber.

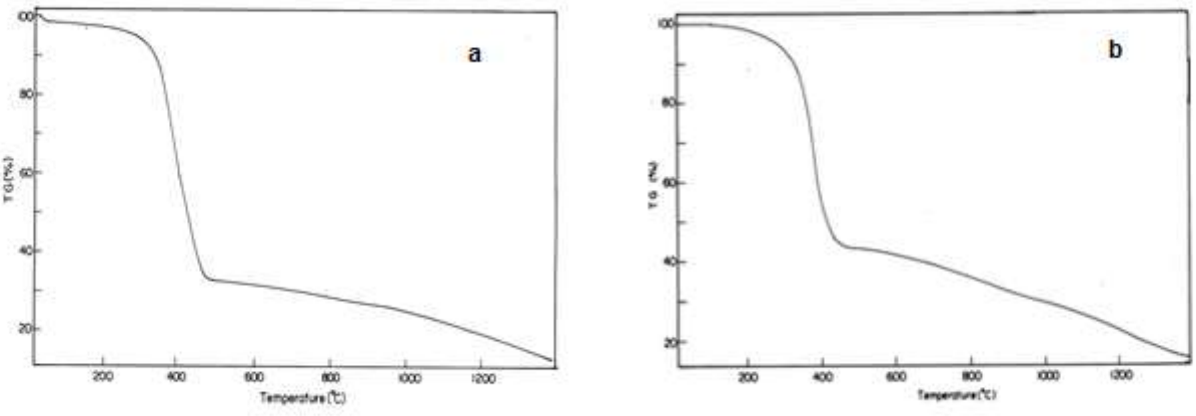

Figure6.TGA Thermogram of (a) RRand (b) RR/NR blend

Table4.Thermal Stability of Rubber Materials

Sample	Temperature (°C) corresponding to weight loss								
	10%	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**	**90%**
RR	313	326	347	359	386	427	716	959	-
RR/NR blend	340	368	381	395	439	672	982	1275	-

For both RR and RR/NR blend, the transitions which occur above 300°C have been found to be of greater significance because of a strong correlation between the thermal properties and the elastomer combustibility[28]. Therefore, the kinetic parameters have been evaluated for the major decomposition observed between 326°C and 959°C for RR and between 368°C and 1275°C for RR/NR blend. The kinetic parameters are calculated using Coats and Redfern method[29]:

$$\ln\frac{[-\ln(1-\alpha)]}{T^2} = \frac{-E_A}{RT} + \ln\frac{AR}{\beta E_a} \;\ldots\ldots\ldots\; (7)$$

where α is fraction of decomposition, E_A is the activation energy. R is the universal gas constant. β is the heating rate (20°C/min). T is the reaction temperature and A is the frequency factor that describes the number of potential elementary reactions per unit time. According to the equation, plotting $\ln\frac{[-\ln(1-\alpha)]}{T^2}$ against 1/T gives a linear correlation as given in Figure7(a) and (b); whose slope is directly proportional to the activation energy ($-E_A/R$). Activation energy was calculated from the slope of the linear correlation and was found to be 52.202 KJ/mol and 31.194 KJ/mol for RR and RR/NR blend respectively[30].

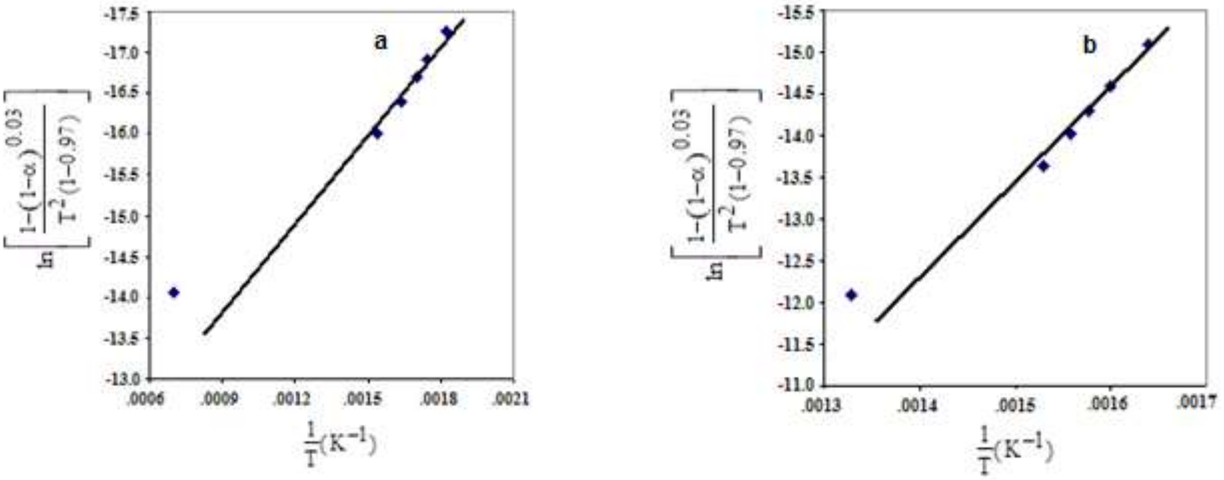

Figure7. Coats-Redfern plot for (a) RR and (b) RR/NR blend

The reaction with a higher E_A has a steeper slope as in RR for which the reaction rate is very sensitive to temperature change. In contrast, the reaction with a lower E_A is less sensitive to a temperature change which is reflected in the degradation characteristic of RR/NR blend. The frequency factor (A) and other activation kinetic parameters like activation entropy change (ΔS), activation enthalpy change (ΔH) and Gibb's free activation energy change (ΔG) were computed using the standard equations: $\Delta H = E_A - RT_i$, $\Delta S = R[\ln(Ah/KT_s)]$ and $\Delta G = \Delta H - T_i\Delta S$ and are given in Table 5. K is Boltzmann's constant, h is the Planck's constant, T_i is the influx temperature of decomposition and $T_s$is the peak melting temperature of the polymer which is obtained from DTA.

Table 5.Thermokinetic parameters of Rubber materials

Material	E_a (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (kJmol^{-1}K^{-1})	ΔG (kJmol^{-1})	A (s^{-1})
RR	52.202	-3778.436	-165.332	53431.608	1.6482×10^{-3}
RR/NR blend	31.194	-3797.618	-344.029	94767.664	1.8451×10^{-5}

From Table 5, comparison of negative values of entropy change ΔS in the polymers indicates that the thermal decomposition reaction is slower in blended material than unblended one. In other words, reclaim rubber being highly sensitive to temperature degrades quickly than RR/NR blend. The degradation of both polymers involves the volatilization of moisture from the polymer matrix with positive entropy ΔS followed by the formation of a more ordered anhydrous polymer matrix with negative ΔS value[31]. The Gibb's free activation energy change ΔG is higher in RR/NR blend than RR which means the rate of reaction for the subsequent decomposition steps is lesser in RR/NR blend than RR. The thermal data and the calculated activation kinetic parameters of decomposition show that RR/NR blend is more thermally stable than RR.This knowledge of thermal stability is absolutely essential so that the polymer material can be suitably fabricated and processed for appropriate end users.

3.5 Differential thermal analysis (DTA)

Differential thermal curves of RR and RR/NR blend consist of several peaks corresponding to the evolution or absorption of heat due to physical or chemical changes in the polymeric material. The curves as given in Figure8(a) and (b) show that the linear portions are displaced from the abscissa because the heat capacities and thermal conductivities of the polymer and reference samples are not identical. Exothermic and endothermic changes in RR and RR/NR blend are detected from DTA relative to the inert reference. Reclaim rubberexhibits glass transition temperature (T_g) at 112.6°C, crystallization temperature (T_c) at 225.2°C and RR/NR blend exhibits glass transition temperature (T_g) at 108.7°C, crystallization temperature (T_c) at 213.9°C.

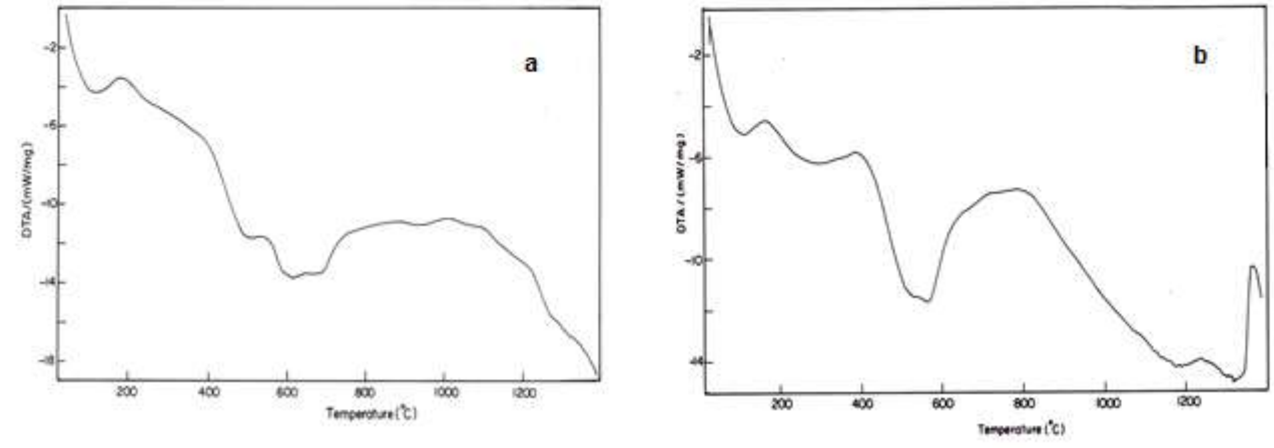

Figure 8.DTA Thermogram of (a) RR and (b) RR/NR blend The curves show that above T_g, the rubbery and flexible polymer has a higher heat capacity. RR and

RR/NR blend exhibit crystallization exotherms which means they are capable of crystallization and possess semi-crystalline structures. The ability of rubber material to crystallize also has an important influence on natural tack, a property of great importance in tyre-building operations. Endothermic peaks at 248.6°C and 253.7°C are assigned to the melting point of the RR and RR/NR blend. It is followed by the decomposition and volatilization of the rubber materials above this temperature[32]. It is also seen that glass transition temperature and crystallization temperature are higher for reclaim rubber than reclaim rubber/natural rubber blend whereas melting temperature of the crystalline domain begins little bit later for the blended rubber material. Thus DTA can be used in quantitative analysis of rubber materials, determination of their service temperature and hence in quality control of polymers in high temperature applications, reactors, explosives and resins etc.

4. Conclusions

The present study focuses on structural, dielectric and thermal investigations on reclaim rubber and reclaim rubber/natural rubber composite to check their applicability in various fields.A complete spectral analysis of unblended and blended reclaim rubber is done on the basis of all observed frequencies with probable vibrational assignments using FTIR spectroscopy. The dielectric property of RR and RR/NR blend has been studied by employing X and K band microwave test benches using the method proposed by Robert and Von-Hippel. It is seen that dielectric constant of RR/NR blend is higher than RR; hence the polarity in reclaim rubber is found to increase after blending with natural rubber. But this blended polymer can be definitely beneficial in capacitor applicationsas the charge storage capacity and breakdown voltage is increased in the material. The dielectric natureof RR and RR/NR blend as a function of frequency and temperature has also been studied using dielectric spectroscopic method. Various parameters like the valence electron plasma energy, Penn gap energy, Fermi energy and polarizability (from penn-analysis and Claussius-Mossottirelation) was calculated from impedance spectroscopy.The thermal behavior of RR and RR/NR blend was studied from TG and DT thermograms. The thermal stability was compared from TG curves and concluded that reclaim rubber blended with natural rubber has increased thermal stability than unblended reclaim rubber. The frequency factor (A), activation energy, activation entropy change (ΔS), activation enthalpy change (ΔH) and Gibb's free activation energy change(ΔG) were also calculated for the rubber materials using Coats-Redfern plot. The thermal transitions such as glass transition temperature, crystallization temperature and crystalline melting temperature were detected for RR and RR/NR blend from DTA curves.

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