Fire Resistance and Temperature dependent Electrical properties of Chemically modified Styrene Butadiene Rubber

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ABSTRACT

In this paper, the crystalline, fire resistance, thermal stability and temperature dependent electrical properties such as AC conductivity and dielectric properties of metal- chloro and nitro functional group introduced styrene butadiene rubber were carried out at various frequencies (10^2-10^6 Hz) and temperatures (303K-343K).The XRD analysis revealed that the amorphous nature of SBR was decreased by the attachment various functional group in SBR. The fire resistance of chemically modified SBR were found to be increased with increase in level of chemical modification, whereas the thermal decomposition temperature decreased by the attachment of functional group in SBR. The effective dielectric constant (ϵ_r) of modified SBR decreased with the frequency of applied field while the AC conductivity increased as the frequency of applied field increases. The temperature dependence of AC conductivity and dielectric constant increases not only with temperature but also with the increase in concentration of chlorine and metal nitro attached in the SBR segments. From the AC conductivity measurement of rubber, the activation energy was calculated. The activation energy decreases with increase in temperature in all compositions.

KEY WORDS: Chloro-nitro SBR, XRD, fire resistance, TGA, electrical properties, activation energy.

1. INTRODUCTION

Styrene butadiene rubber (SBR) is an important commercial elastomers having excellent abrasion resistance (Ramesan and Alex, 2000, Wang, 2011). But SBR have poor tensile strength, weather resistance, oil and fire resistance (Lyon, 2003, Varghese, 1989). Many attempts have been made to increase the properties of SBR (Ramesan, 2001). Chemical modification on elastomers leads to the attachment of polar functional groups in the main chain of SBR with an enhancement in physical and chemical properties (McManus and Rempel, 1995). For many material applications, the major information is needed on their properties such as thermal conductivity, heat capacity, flame retardency electrical conductivity (Nihmath and Ramesan, 2014). The main objective of the work is to study the effect of temperature on electrical properties of (AC conductivity and dielectric properties) chloro and nitro functional group containing SBR. Also to investigate the effect of functional group on thermal stability and fire retardancy behavior of chemically modified SBR.

2. EXPERIMENTAL

2.1. Materials: Styrene butadiene rubber (Synaprene1502) was obtained from Synthetics and Chemicals Ltd, Bareilly, U.P. India. Toluene, mercuric chloride, sodium nitrite, cetyl trimethyl ammonium bromide (CTAB) and isopropyl alcohol were procured from Merck India Ltd, Mumbai.

2.2. Preparation of Chloro-nitro functional group containing SBR: Addition of different functional group (NO_2 and $HgCl_2$) group to SBR was carried out by the simple nitro mercuration reaction with the help of phase transfer catalyst as describe previously (Anil and Ramesan, 2009). Briefly, SBR was dissolved in toluene, the phase transfer catalyst (CTAB) was added to this and the mixture was allowed to stirr. To this appropriate amount of mercuric chloride was added followed by sodium nitrite. The reaction product was then washed with hot water and cold water, until it free from chlorine. Finally, the product was coagulated with isopropyl alcohol and re precipitated from toluene solution.

2.3. Characterization: Fire resistance test of SBR and chemically modified SBR were carried out by the limiting oxygen index (LOI) test as per ASTM D 2863-77 procedure using a Stanton Redcroft FTA flammability tester unit, under nitrogen–oxygen environment. Thermal stability of the modified polymer was investigated by a Perkin Elmer thermo gravimetric analyzer with pure nitrogen gas at a heating rate of 10 °C/ min. AC resistivity of the samples was measured by Hewlett–Packard LCR Meter, fully automatic system in a frequency range 100–10^6 Hz at different temperature. Dielectric constant or relative permittivity were calculated using the formula

$$\varepsilon_r = Cd/ \varepsilon_o A$$

where d be the thickness of the sample, C the capacitance, A the area of cross section of the sample and ε_o be the permittivity of free space. ε_r be the relative permittivity of the material which is a dimensionless quantity. The activation energy of conduction was estimated using the relation

$$\sigma_{ac} = \sigma_o \exp(-E_\alpha/kT)$$

Where σ_o is a constant, E_α is the activation energy, k is Boltzmann's constant and T is the absolute temperature.

3. RESULTS AND DISCUSSION

3.1. XRD analysis: X-ray diffraction studies are employed to study the chemical composition and the crystalline nature of chemically modified and unmodified SBR, is given in Figure 1. The XRD of pure SBR shows a broad amorphous diffraction peak at $2\theta = 19.7^0$. It is observed from the figure that the functional group introduced SBR shows the diffraction pattern at $2\,\theta$ = 17.1, 21.74, 26.21, 30.6, 35.4, 40.2 and 54.84 ^{o} indicating the semi crystalline nature of the polymer. This means that the functional groups are uniformly attached into the *trans*- butadiene unit of SBR. Also the amorphous peak of chemically modified SBR is found to be shifted to a lower XRD region *ie.*, from $2\,\theta = 19.7^0$ to 18.4^0 with a decrease in intensity of the amorphous region. The shift in diffraction peak with decrease in intensity of chemically modified SBR indicated that the functional groups are regularly attached in the main chain of SBR (Ramesan and Lee, 2008).

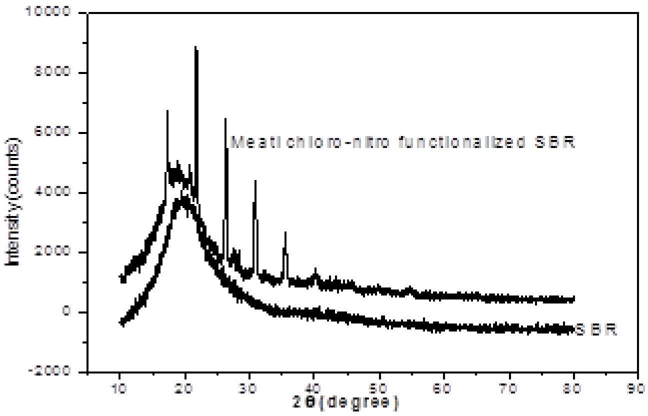

Figure.1.XRD patterns of SBR and chemically modified SBR

3.2. Fire resistance: Fire resistance of SBR and functional group containing SBR were measured in terms of Limiting Oxygen index (LOI) value. The LOI values of SBR and chemically modified SBR is shown in Figure 2. LOI is the minimum amount of oxygen that supports the combustion of elastomer. The results from LOI showed that chemical modification on SBR imparts better flame resistance value (LOI) compared to pure SBR. The better flame retardancy indicated that the metal chloro and NO_2 ash in modified SBR could enhances the fire resistance of polymer. Improved fire resistance of the polymer can be described by the thermal insulation of flame retardant elements present in the polymer. When the polymer is burned the chlorine present inside the macromolecular chain is decomposed to chlorine ash and this ash covered the remaining elastomer after the decomposition of chlorine. So the covered ash prevented the combustion between the polymer and oxygen that cause a higher LOI value for modified polymer. The lower LOI value of SBR is due to absence of flame retardant elemnets in the polymer.

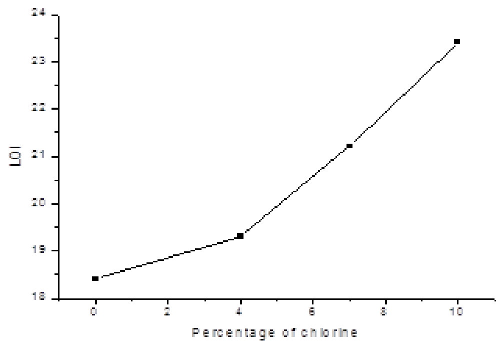

Figure 2. Fire resistance behavior of SBR and chemically modified SBR

3.3. Thermal stability: The thermal degradation behavior (TGA) of SBR and 10% chlorine containing chemically modified SBR are given in Figure 3.

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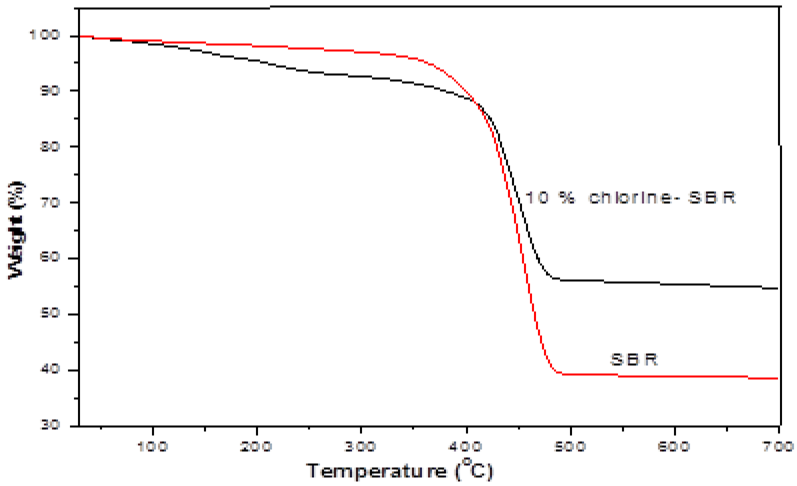

Figure.3.Thermal degradation curve of SBR and functional group introduced SBR

It can be seen that SBR shows a single stage decomposition at 414 °C where as the different functional group containing SBR exhibited two stages of thermal degradation. The initial stage of weight loss of modified SBR is at 210 °C, attributed to the removal of chloro and nitro functional group from the main chain of SBR. The second weight loss at 210 °C, assigned to the decomposition of the remaining polymer chain. It is interesting to see that the percentage of final char residue of the chemically modified sample is 55 % while SBR is only 37%. Higher amount of char residue remained at 500 °C indicated that modified elastomer have better flame retardancy than pure SBR. Hence it can be concluded that the chemical modification can impart better flame retardency to SBR.

3.4. AC conductivity: The AC conductivity of metal chloro-nitro functional group containing SBR was evaluated with varying function of temperature and frequency and it is illustrated in Figure 4.

From the graph, an increase in AC conductivity value of polymeric system is observed with increase in temperature. It can be seen from the figure that the increase in conductivity is more sensitive at higher temperature and frequency region for modified SBR. The higher conductivity with increase in temperature would be attributed to the polaron hopping by the thermal excitation of macromolecular molecules (Ramesan and Pradyumnan, 2011).

3.5. Activation Energy: The plots of AC conductivity versus temperature of chemically modified SBR with different content of chlorine (3, 5 and 10 %) are given in Figure 5-7. The activation energy of the conductivity is influenced by temperature, which is the minimum energy required to overcome potential barrier in the composite system. The linear regression of the Arrhenius plot log σ_{ac}(S/cm) versus1000/T (K^{-1}) gives the slope of E_α values. The increment in temperature provides an increase in free volume and segmental mobility. These two entities permits free charges to hop from one site to another thus increase conductivity. The conductivity increases with temperature indicates more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites, which is temperature dependence. The sharp increase of AC conductivity between the temperatures from 303 K to 343 K can be attributed to large heat energy absorbed by the samples and thus induce mobility of electrons (Ramesan, 2015). It is suggested that in this region, the band gap between valence band and conduction band is reduce significantly and provide easiness for electrons to hopping from valence band to conduction band and hence gives higher AC conductivity values as compared to other temperature. From Table 1, the activation energy of elastomer decreases with increase in level of chemical modification on SBR.

3.6. Dielectric constant: Figure 8 shows the dielectric constant of metal chloro-nitro SBR with different level of chemical modification at different temperature were measured within the frequency range of 10^2-10^6 Hz. Dielectric constant is used to characterize the molecular relaxation and it is the measure of energy stored in a sample during the cyclic relaxation (Subbaraj, 2014).

It is obvious that the dielectric value of polymer is increases with increase in temperature whereas the magnitude of dielectric property decreases with increase in frequencies. From the figure it is also evident that the dielectric constant increases with increase in the level of chemical modification. This would be explained by the increase in polarity of elastomer in the interfacial region. As the level of chemical modification increases, more and more functional groups are attached to the main chain of SBR, that leads to strong polar-polar interaction in the macromolecular chain of SBR that eventually boost the dielectric properties (Ramesan, 2014, Ramesan, 2014). The chemical modification on SBR imparts good fire resistance, AC conductivity and dielectric properties, which indicated that the developed metal nitro-chloro SBR can be used in various applications indicating antiseptic coating, anticorrosion application and antistatic coating.

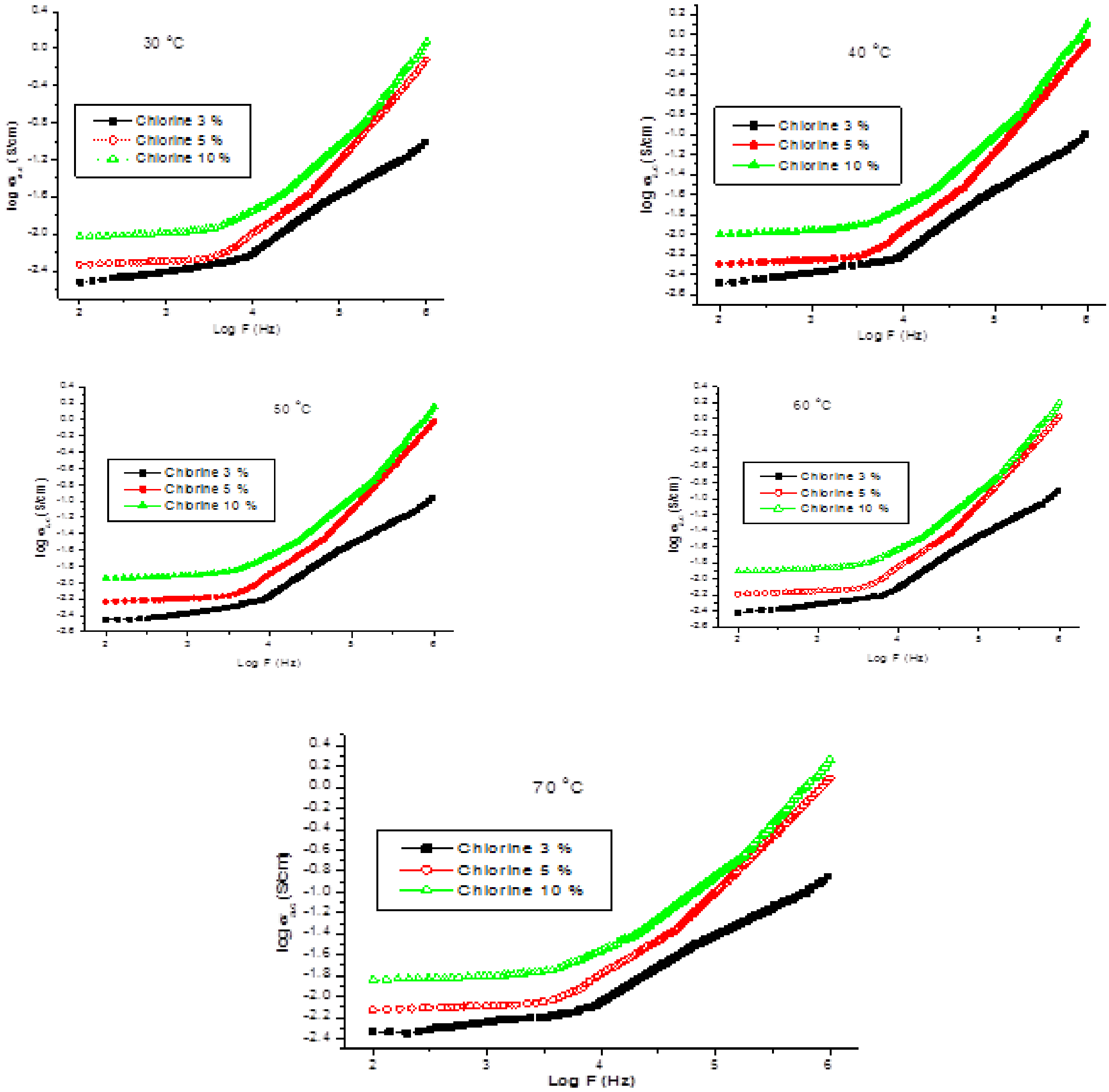

Figure.4.AC conductivity of MSBR with different content of Cl @ various temperatures

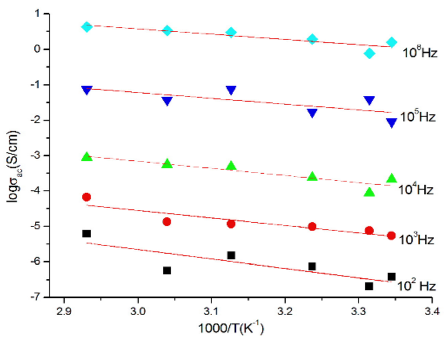

Figure.5.Variation of log σ_{AC} with 1000/T (K^{-1}) of 3% Cl sample

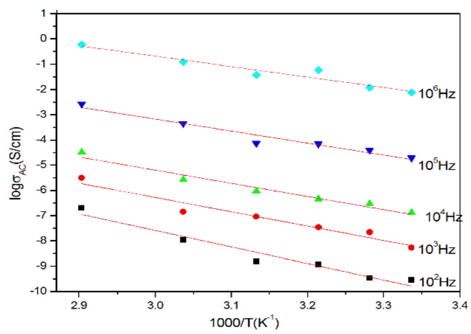

Figure.6.Variation of log σ_{AC} (σ_{AC} in S/cm) with 1000/T (K^{-1}) of 5 % Cl sample

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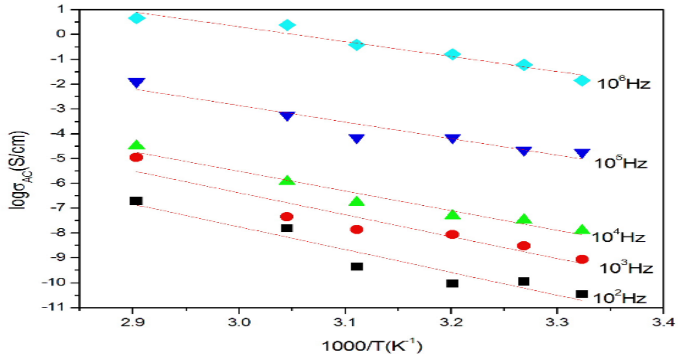

Figure.7.Variation of log σ_{AC} (σ_{AC} in S/cm) with 1000/T (K^{-1}) of 10% Cl sample

Table.1.Activation energy of chemically modified SBR with different level of modification (with different % of chlorine)

Samples	Frequencies (Hz)				
	10^2	10^3	10^4	10^5	10^6
Chlorine 3 %	-2.63	-2.12	-2.01	-1.63	-1.48
Chlorine 5 %	-6.530	-5.672	-5.216	-4.757	-4.103
Chlorine 10 %	-9.147	-8.84739	-7.95698	-6.677	-5.99156

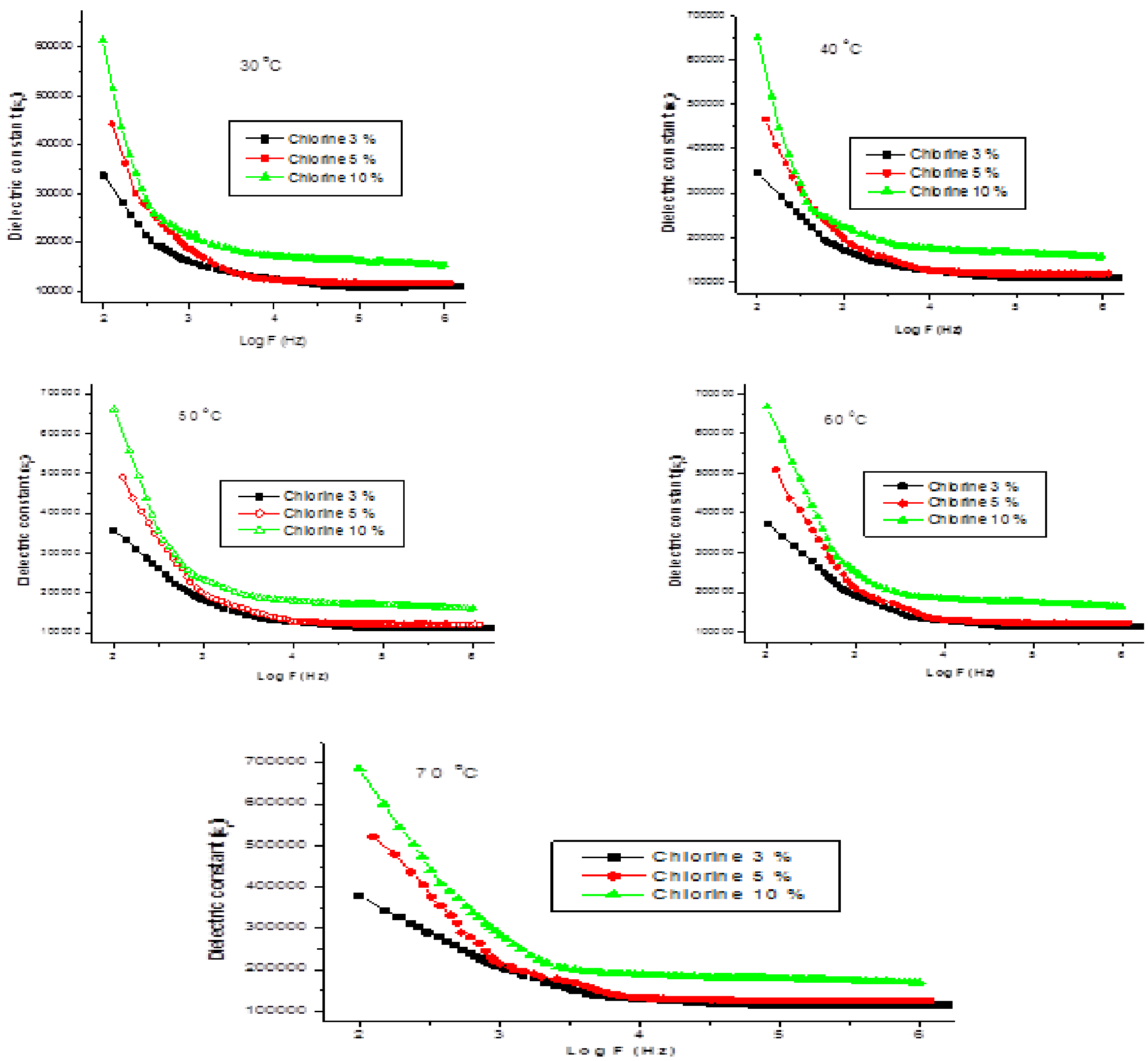

Figure.8.Dielectric constant of modified SBR at different temperatures

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4. CONCLUSIONS

In this work, we report the structural arrangement, fire resistance, thermal, temperature dependence AC conductivity and dielectric properties of chemically modified SBR with different functional group. The crystalline nature of samples were carried out by XRD, indicated that the chemical modification could impart some slight semi-crystalline nature to SBR. Fire resistance properties of the polymer were found to be increases with the increase in level of chemical modification is mainly because of the presence halogen in the SBR chain. The results from TGA demonstrated that the thermal stability of the modified polymer was lower than that of SBR. The enhancement in AC conductivity with the increase in temperatures and also with the level of chemical modifications were attributed to the increase in number of conduction path created by the increase in polarity of elastomers through the attachment of functional group in SBR. Dielectric constant of the modified elastomers was increases with the raise in temperatures because of the segmental mobility of macromolecular segments. The activation energy decreases with increase in temperature. The high dielectric constant values of different functional group containing SBR at low frequencies (around 10^2 Hz) suggest that, these elastomeric materials could be used for capacitor applications.

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