Thermally Induced Microstructural Changes and Its Influence on Electrical Conductivity of a Polymer-Based Bakelite RPC Detector Material: A Positron Lifetime Study

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ABSTRACT: Annealing studies have been carried out to understand the temperature induced microstructural changes in Bakelite (P-120 NEMA LI-1989 Grade XXX) Resistive Plate Chamber (RPC) detector material using Positron annihilation lifetime spectroscopy (PALS), Fourier transform infrared spectroscopy (FTIR), and XRD. The variation of positron lifetime parameters viz., ortho-Positronium lifetime (τ_3) and free volume size (V_f) increases marginally above glass transition temperature T_g as a result of structural changes due to segmental mobility. The drastic increase of free volume parameters above 240°C attributed to the reduction in strength of C—H bond of the aliphatic bridges and cleavage of methylene bridges of the polymer network, which is supported by the FTIR results. The XRD results show the reduction in crystallinity and average crystallite size of Bakelite on annealing correlates well with the free volume and electrical conductivity. The temperature induced electrical conductivity and activation energy is also correlated with the positron lifetime parameters. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 793–800, 2013

INTRODUCTION

There has been a great deal of development in the field of high energy Physics in the recent past, especially in neutrino physics and neutrino Astronomy. Neutrino oscillations and the inferred evidence on neutrino mass are likely to have far-reaching consequences in particle physics. The phenomenon of neutrino oscillations can provide a fruitful evidence for Physics beyond the so called standard model of particle physics. The Resistive Plate Chambers (RPCs)[1,2] as detectors are widely used in many High Energy Physics experiments like cosmic ray studies and new accelerators, which are made up of high resistive materials like glass or Bakelite sheets[3] because of their excellent performance and low cost. RPCs are designed to be used as the active detectors in ICAL (Iron Calorimeter) for muon detection, aimed at studying atmospheric neutrinos in the proposed India based Neutrino Observatory (INO) Project.[4] When used in such experiments; the electrode material (RPC) can undergo straining either from direct mechanical stress or from a change in temperature or both at the same time. The first material of importance in making RPCs is a polymer viz., Bakelite and it has shown tremendous possibilities for the fabrication of RPCs[5] compared with glass.

High energy particle physics experimentalists, especially in the detection of neutrinos with RPCs as detector materials are facing a serious problem with regard to their aging, when they are continuously operated at higher operating voltages.[6] It was realized in such experiments that Bakelite RPCs exhibit high leakage current at higher operating voltages compared to glass RPCs which is not desirable.[3,7] However, Bakelite has several advantages over glass RPCs and as such it is essential to understand the origin of this leakage current. Unfortunately, this problem has not been tackled in the past and it is interesting to find whether the large leakage current owes it origin to the microscopic level structural properties of the Bakelite material, since it acts as the electrode in detector design. The studies on these aspects will help us to find ways to reduce the leakage current at higher operating voltages and thereby enhance RPC efficiency in its application.

Generally, RPCs are operated at high voltages (about 8–10 kV) and due to the variation of temperature under experimental conditions, might lead to changes in microstructural properties of the Bakelite over a period of time. It was noticed that the Bakelite resistivity changes as a function of temperature and humidity.[8,9] This is the indication that Bakelite RPCs are expected

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to suffer severe structural damages when operated at high voltages continuously for longer periods. Recent research clearly suggests that the nature of molecular motions in the amorphous phase of the polymer and the manner in which these motions determine the viscoelastic response of the polymer to various perturbations is of great importance. When a polymer is subjected to heat treatment up to the melting point, the temperature promoted relaxation will occur, which may erase the previous thermo mechanical history but a partial structural recovery of the material may happen through change in enthalpy and crystallinity values. Below glass transition temperature (T_g), the molecular mobility is likely to be frozen in to the glassy matrix. When the temperature is increased above T_g, the segmental relaxation rate is faster than the volume relaxation rate and hence excess free volume will be trapped within the polymer. As a result, there will be an increase in size of the free volume of a polymer.[10–12] Upon cooling, the molecular segments begin to relax towards an equilibrium state.

From the literature survey, the authors found that studies on thermally induced structural properties of Bakelite reveals that the activation energy (E_a) may tends to increase with increasing atomic size and in the resole resin, with the changes in Formaldehyde/Phenol (F/P) molar ratio.[13] The activation energy sharply decreased at first and then remained almost constant as the thermal decomposition of the resole resins proceeded.[13] The decrease in E_a value indicates that the reaction proceeded at a faster rate at a given temperature, which may induce the high electrical conductivity of the material.

Amorphous dielectrics with electrolyte impurities may show increasing conductivity with temperature because ions are continuously liberated from salts contained within them or ions already present are removed from the inner surfaces to which they are adsorbed to the more mobile condition. Therefore, it appears feasible to explain the conduction process in terms of the assumption that the movement of ions regulated mainly by the distribution of free volume. Motivated by the above said facts, in order to correlate the temperature induced electrical conductivity with free volume parameters, we have carried out the electrical conductivity of the Bakelite sample. In order to study the microstructural changes with annealing temperature, we have carried out free volume measurements on Bakelite samples using one of the well established sophisticated tools viz., Positron Annihilation lifetime Spectroscopy (PALS). This is a unique experimental technique capable of determining the nanometer sized free volume cavities and concentration of free volume sites in the amorphous region of the polymer in terms of positron lifetime of the injected positrons.[14] Because of the technological and scientific applications of Bakelite, particularly in the field of high energy physics specially for neutrino experiments , it was felt desirable to study the positron lifetime parameters and other thermally activated microstructural changes in it. Such studies have not been reported on Bakelite RPC detector material so far in the literature. The RPC efficiency depends on the leakage current and time resolution which in turn depends on the environmental factors like temperature and humidity etc. Sudden fluctuations in temperature or voltage will affect the material characteristics of RPC, and hence its per-
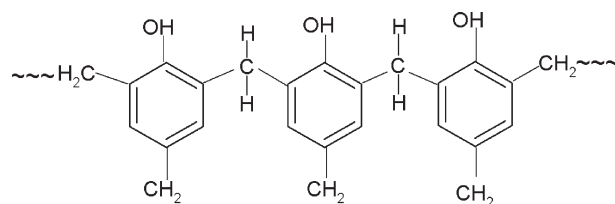

Figure 1. Chemical structure of bakelite.

formance. To understand the microstructural changes of Bakelite which could happen over a long period of time at lower temperature (practical condition), we simulate this situation in an approximate way by conducting the annealing experiment on Bakelite RPC material starting from room temperature to high temperature of 270°C. The changes in microstructure have been monitored by positron annihilation lifetime technique with FTIR as the complementary method.

EXPERIMENTAL

Sample Preparation
The Bakelite samples used in making of RPCs to be used in India Based Neutrino Observatory (INO) underground laboratory are used in this experiment. Bakelite samples (P-120, Matt finished NEMA LI-1989, Grade XXX) of density 1.22 g cm^{-3}, manufactured by Bakelite Hylam, India were collected from VECC-Kolkata in the form of sheets. Rectangular samples of dimension 1 cm x 1 cm x 0.175 cm were cut and cleaned in ethyl alcohol. These samples were employed to measure positron lifetime spectra using the positron lifetime spectrometer. The chemical structure of Bakelite is shown in Figure 1.

Differential Scanning Calorimetry (DSC) Analysis
The glass transition temperature (T_g) of the as received Bakelite sample was measured by DSC scans taken from Sophisticated Analytical Instrument Facility, Cochin (SAIF-Cochin) using Mettler Toledo DSC 822e. DSC Thermogram of the Bakelite sample (weighing 3.55 mg) was recorded with the heating rate of 10°C min^{-1} from 25 to 260°C. The glass transition temperature (T_g) of the sample obtained from the DSC thermogram is 46°C and is as shown in Figure 2.

Annealing
Annealing studies have been carried out for the pure Bakelite sample of thickness 0.175 cm at different temperatures starting from room temperature to 270°C. The Samples to be annealed were equilibrated for the required temperature in the Thermotek tubular oven. The samples were annealed at set temperature for 1 h. The annealed samples were allowed to cool in the oven for an hour, and then they were used in Positron Annihilation Lifetime measurement. The annealed samples in the powder form were used in FTIR and XRD experiments.

X-Ray Diffraction Studies
XRD spectra for annealed Bakelite samples at various temperatures have been recorded by powder X-ray diffractometer. The X-ray diffractometer, RIGAKU-DENKI II miniflex with Ni filtered CuKα X-rays of wavelength 1.5406 Å and a graphite monochromator in the diffracted beam was used. Fine powder of Bakelite sample was taken in a glass sample holder and X-ray
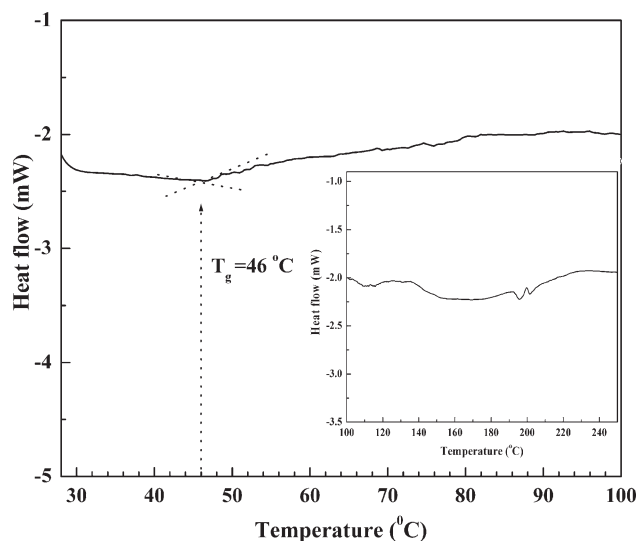
Figure 2. DSC scan of bakelite sample. Arrow mark indicates the glass transition temperature (T_g) Inset-DSC thermogram of Bakelite from $100°C$ to $250°C$.

Scanning was performed in the 2θ range $6–60°$ with scanning step of $0.02°$. The crystallinity of the original and annealed samples at different temperatures was calculated and also, physical quantities like the average crystallite size and average strain have been studied using Williamson-Hall (WH) Plot method.[15–17]

Positron Annihilation Lifetime Measurements
Positron annihilation lifetime spectra were recorded for the Bakelite sample using positron lifetime spectrometer. The positron lifetime spectrometer consists of a fast–fast coincidence system with BaF_2 scintillators coupled to photomultiplier tubes type XP2020/Q with quartz window as detectors. The BaF_2 scintillators were shaped to conical to achieve better time resolution. The two identical pieces of the samples were placed on either side of a 15 μCi - [22]Na positron source, deposited on a pure Kapton foil of 0.0127 mm thickness. This sample-source sandwich was placed between the two detectors to acquire lifetime spectrum. The ^{60}Co prompt spectrum gave 180 ps as the resolution function. However, to have increased count rate, the spectrometer was operated at 220 ps. All lifetime measurements were performed at room temperature and two to three positron lifetime spectra with more than a million counts under each spectrum were recorded in a time of 1–2 h. Consistently reproducible spectra were analyzed into three lifetime components with the help of the computer program PATFIT-88[18] with proper source and background corrections. Source correction term and resolution function were estimated from the lifetime of well annealed aluminum using the program RESOLUTION.[18] Since, the single Gaussian resolution function did not converge the lifetime spectrum; the resolution function was resolved further into three Gaussian components, which gave quick and good convergence. The net resolution function for this turned out to be 220 ps. The three Gaussian resolution functions so determined were used to estimate the lifetime parameters of some of the well-characterized polymers like polycarbonate,

PTFE, etc. Therefore, the three Gaussian resolution functions were used in the present analysis of positron lifetime spectra of the Bakelite (Phenol formaldehyde resole resin) samples. The lifetime parameters were found to be in good agreement with the values reported in the literature in case of general resins.[19]

The o-Ps lifetime τ_3 is related to the free volume hole size by a simple relation given by Nakanishi et al.,[20] which was developed on the basis of theoretical models originally proposed by Tao[21] for molecular liquids and later by Eldrup et al.[22] In this model, Positronium is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_o with an electron layer in the region $R < r < R_o$. The relation between τ_3 and the radius R of the free volume hole or cavity is,

$$\lambda = \frac{1}{\tau_3} = 2P = 2\left[1 - \left(\frac{R}{R_0}\right) + \left(\frac{1}{2\pi}\right)\text{Sin}\left(\frac{2\pi R}{R_0}\right)\right] \quad (1)$$

where $R_o = R + \delta R$ and δR is an adjustable parameter.

By fitting eq. (1) with τ_3 values for known hole sizes in porous materials like zeolites, a value of $\delta R = 0.1657$ nm was obtained. With this value of δR, the free volume radius R has been calculated from eq. (1) and the average size of the free volume holes (V_f) is evaluated as

$$V_f = \frac{4}{3}\pi R^3 \quad (2)$$

The fractional free volume or the free volume content (F_v), can then be estimated as

$$F_v = CV_f I_3 \quad (3)$$

where C is structural constant whose value is taken as 0.0018 $Å^3$,[23] V_f is the free volume hole size, and I_3 is the o-Ps intensity.

FTIR Studies
The Fourier Transform Infrared Spectra (FTIR) of the Bakelite sample was recorded in the range of 4000–400 cm^{-1} using JASCO-460 Plus, Japan at a resolution of 4 cm^{-1}. FTIR spectrum was used to identify the variations in the functional groups of the polymer Bakelite, based on the position of peak values in the region of infrared radiation upon annealing.

Electrical Conductivity Measurements
The electrical conductivity of the Bakelite RPC sample as a function of annealing temperature was measured with the aid of Thermotek tubular oven and Keithley 2636A dual channel Source Meter. For this, the Bakelite sample of dimension (1.2 cm × 1 cm × 0.175 cm) was used. The sample was sandwiched between two electrodes pasted with silver paste. The computer program Lab Tracer 2.0 was used to record the voltage and current data. From the recorded voltage and current data, the value of the bulk resistance (R_b) is calculated. The electrical conductivity (σ) was obtained by the relation $\sigma = t/R_bA$, where t and A are the thickness and the area of the contact respectively. The electrical conductivity values with annealing temperature so obtained are tabulated in Table I.

Table I. Temperature Dependence of Electrical Conductivity in Bakelite

Temperature T (°C)	Conductivity (σ) (Ω m)$^{-1}$
25	1.23×10^{-8}
40	2.23×10^{-8}
60	7.08×10^{-8}
80	1.24×10^{-7}
100	1.49×10^{-7}
120	2.23×10^{-7}
140	5.74×10^{-7}
160	1.30×10^{-6}
180	2.42×10^{-6}
200	3.80×10^{-6}
220	5.12×10^{-6}
240	6.08×10^{-6}
260	6.85×10^{-6}
270	2.33×10^{-5}

RESULTS AND DISCUSSION

Positron Lifetime Results

From the positron lifetime parameters derived from the PATFIT program, only the third and long lifetime component viz., o-Ps lifetime (τ_3) and o-Ps intensity (I_3) are reported here. Since, we are interested in free volume cavity size and their concentration in the Bakelite samples. The values of these two parameters for as received Bakelite sample are 1.63 ns and 13.27% respectively. Figure 3(a,b) shows the plots of o-Ps lifetime (τ_3), free volume (V_f) and o-Ps intensity (I_3) as a function of annealing temperature. We observe that as the annealing temperature of the Bakelite sample is increased, there is a continuous increase in o-Ps lifetime (τ_3) from 1.63 ns to 1.78 ns, that means according to eq. (1) free volume cavity size (V_f) also increases from 64.90 Å^3 to 78.22 Å^3. We can explain the observed variation of lifetime for the present sample as follows: In the lower annealing temperature region, below 40°C, the change in lifetime or free volume cavity size is marginal and beyond this (above glass transition temperature, $T_g = 46$°C) these two parameters show slight increase up to 100°C. With increase in annealing temperature up to 100°C, the polymer molecules could acquire side chain mobility with the thermal energy provided, results in a small increase in free volume in the polymer matrix. We know that positronium (Ps) formation takes place preferentially in the regions of low electron density which are the free volume cavities, o-Ps lifetime get affected. Thus, an increase in lifetime reflects the decrease in electron density. Further increase of annealing temperature results in increase of free volume size up to 240°C and this can be attributed to the thermal expansion of the free volume holes on annealing where Ps was trapped.[24]

On the other hand the o-Ps intensity I_3 decreases initially at lower annealing temperature and reaches the minimum value around 90°C. The decrease in I_3 can be attributed to the reduction in number of free volume cavities, possibly due to the formation of few larger free volume cavities with the coalesce of smaller ones upon annealing. Alternatively, there may be inhibi-

tion of Positronium formation due to the free radicals formed by the chain scission of the Bakelite during the process of annealing at higher temperatures.[21] Beyond 100°C, I_3 exhibit a small increase up to 180°C but this increase is only within 1%
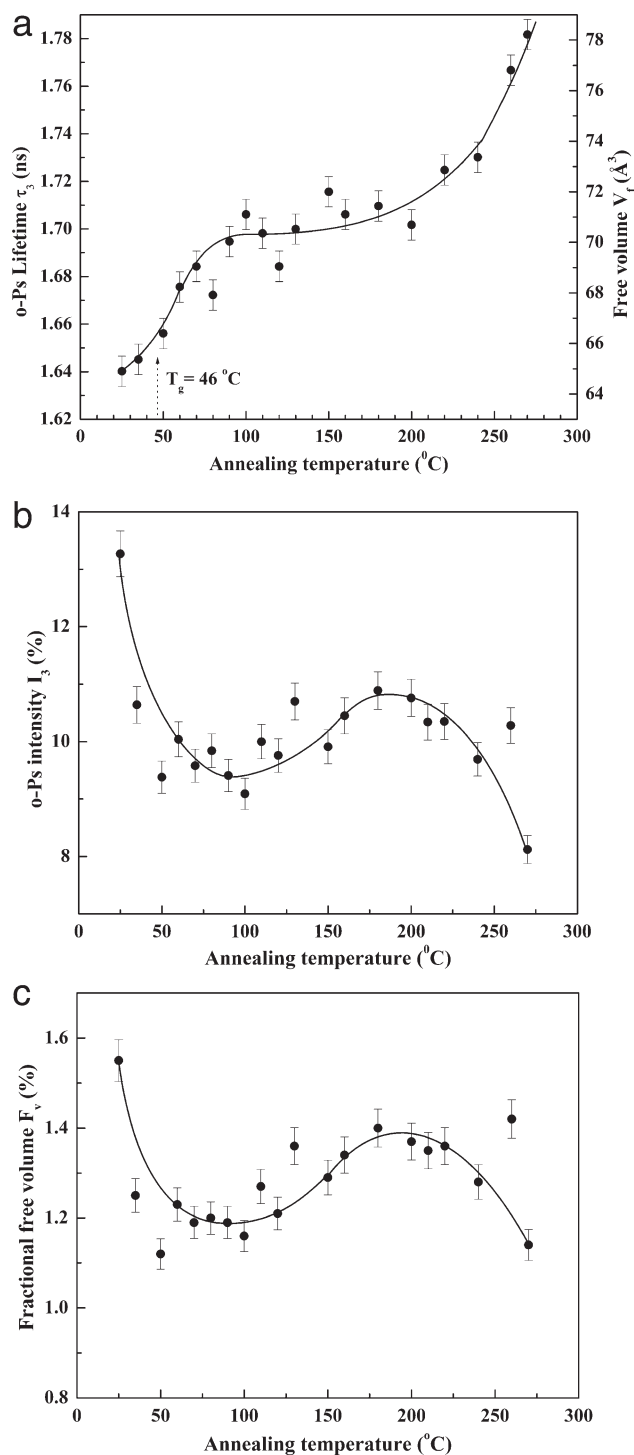

Figure 3. (a) o-Ps lifetime (τ_3) and free volume (V_f) as a function of annealing temperature. (The solid line drawn is to guide the eye). (b) o-Ps intensity (I_3) as a function of annealing temperature. (The solid line drawn is to guide the eye). (c) Fractional free volume (F_v) as a function of annealing temperature. (The solid line drawn is to guide the eye).
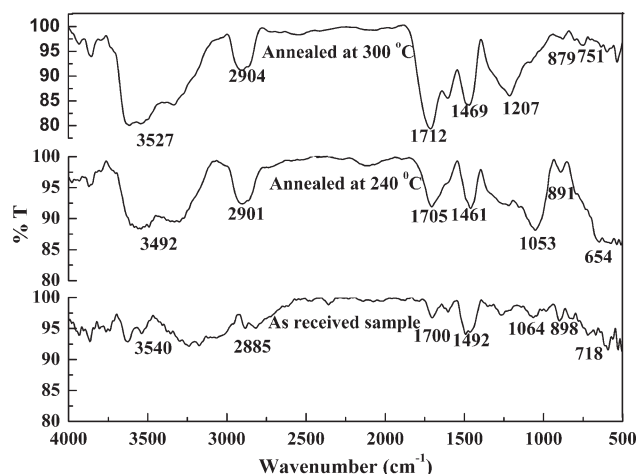
Figure 4. FTIR spectra of as received Bakelite sample and annealed Bakelite samples at 240 and 300°C.

variation. Figure 3(c) shows the variation of fractional free volume F_v calculated according to eq. (3) as a function of annealing temperature. The fractional free volume F_v exhibits exactly the same trend as that of I_3 temperature. The small variation is very difficult to prescribe to some process. After $100°C$, the o-Ps lifetime (τ_3) and free volume cavity size (V_f) are almost constant till $200°C$. This indicates the saturation of the free volume hole size. This may be due to the insufficient thermal energy for the dissociation of the C—H and O—H bonds in the Bakelite. The bond dissociation energy of CH_2, CH, OH, OH^-, and OH (phenyl) groups was found to be 24.12 kJ mol^{-1}, 19.26 kJ mol^{-1}, 24.23 kJ mol^{-1}, 26.24 kJ mol^{-1}, and 26.76 kJ mol^{-1}, respectively.[25] However, there is a rapid increase in o-Ps lifetime (τ_3 = 86.50 ps) and free volume (V_f = 7.52 Å^3) from 200 to $270°C$, which is attributed to the cleavage of bonds, and this may leads to the depolymerization of Bakelite.[26–28] This is also evident from both DSC and FTIR Spectra; particularly a prominent transition at $200°C$ is seen in DSC thermogram of Bakelite (Figure 2).

We suppose that the depolymerization of Bakelite can be understood as follows. Bakelite (Phenol-Formaldehyde) is an example of a polymer constructed by joining aromatic units with labile (methylene) bridges. Usually, single atom bridges between aromatic rings are not very labile. However, the ortho situated hydroxyl group activates the decomposition of the methylene linkage due to a keto-enol tautomerism.[29] The depolymerization process, done by breaking labile bridges, can be performed with hydrogen abstraction from either other labile bridges, if those can give hydrogen or other possible hydrogen donor species in the polymer, such as the aromatic rings. In the latter case, all the bridges can be broken, while in the former case, only part of them are actually broken. The choice of depolymerization process is based on hydrogen availability in the polymer. The weight loss of Bakelite on annealing as reported in the literature suggests the depolymerization of phenol-formaldehyde, hydrogen donation occurs from other methylene bridges.[30,31] This is also evident from the FTIR studies described in the next section.

FTIR Results

Figure 4 shows the FTIR spectra of the as received, annealed at 240 and 300°C Bakelite samples. From the figure it is clear that the transmission peaks are observed at the wave numbers (cm^{-1}), 3540, 2885, 1700, 1492, 1064, 898, and 718. These are attributed to the functional groups OH, out of phase stretching vibration of —CH$_2$— alkane, C=O stretch (overlapped with OH scissors of water), C—H aliphatic, C—O stretching vibrations of —CH$_2$OH— group, CH out-of plane, isolated H and CH out-of-plane , ortho substituted respectively.[32,33]

The FTIR spectra show shifting of peaks with the annealing temperature. There is a marginal shift in the characteristic peak of O—H of the annealed sample. The increase in intensity of the peak is also observed for the out of phase stretching vibration of -CH$_2$- alkane (2904 cm^{-1}), CH out-of-plane ortho- substituted (751 cm^{-1}). However a decrease in peak intensity is observed for C—H aliphatic and CH out-of-plane isolated H.

There are certain reported evidences in the literature about the reduction of the strength of the C—H bond of the aliphatic bridge with the annealing temperature.[31,34] Lin et al.[34] reported that the strength of the C—H bond of the aliphatic bridge decreases with increasing annealing temperature, this may be the reason for the cleavage of the methylene bridges, which is the main cause for depolymerization. The decrease in —OH— bands after heat treatment also indicates that the phenolic OH degradation occurred subsequently upon methylene bridge decomposition.[35] Trick et al.[36] reported that thermal degradation of phenol formaldehyde resin leads to the formation of phenol and cresols as a result of the scission of a terminal Benzene ring depending on the position of scission.

In this study, the reduction in peak intensity value at 1492 cm^{-1} in the FTIR spectrum indicates the reduction in strength of C—H bond of the aliphatic bridges. This peak has shifted from 1492 cm^{-1} to 1469 cm^{-1} as compared with the as received Bakelite with annealed Bakelite at $300°C$. The marginal shift in wave number corresponds to different energy levels, attributable to the cleavage of functional groups, especially O—H and C—H groups. This may be the reason for the drastic increase of positron lifetime parameters, viz., o-Ps life time (τ_3) from 1.73 ns to 1.79 ns and hence the free volume (V_f) from 73.37 Å^3 to 78.22 Å^3 after 240$°$C as shown in the Figure 3(a).

X-Ray Diffraction Results

W-H plot is the best known method for evaluating the average crystallite size and average strain in the system of study. The deviation in crystalline nature from the as received to the annealed sample is due to the systematic shift of atoms from their mean position due to temperature and the strain is because of the presence of point defects (such as vacancies, site disorder) and poor crystallinity. This exhibits the broadening of the peak in the XRD spectra.

In Figure 5, the XRD spectra of annealed Bakelite sample and in Figure 6, the average crystallite size and crystallinity of the annealed Bakelite samples are respectively plotted as a function of annealing temperature. Bakelite is highly amorphous in nature and exhibits about 19% crystallinity. The average crystallite
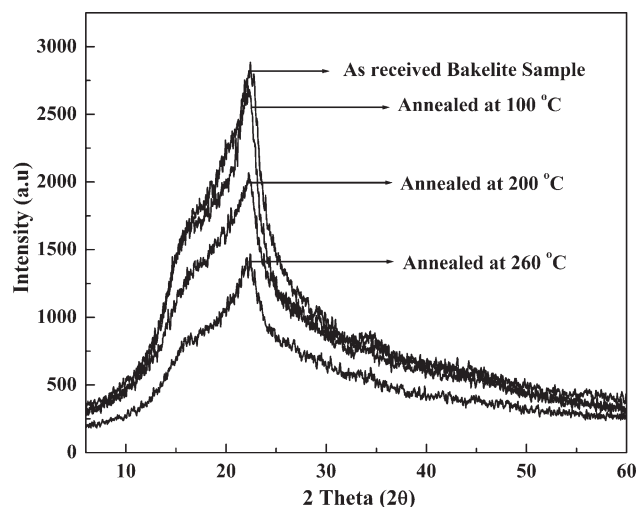
Figure 5. XRD spectra of as received and annealed Bakelite samples at different annealing temperatures.

size and crystallinity obtained from the XRD spectra indicate a sharp decrease in both crystallite size and crystallinity and an increase in free volume of the Bakelite sample on annealing. The reduction in crystallinity may be due to the increasing amorphosity of the Bakelite due to the thermal expansion of free volume holes on annealing. The observed increase in FWHM on annealing leads to the reduction in average crystallite size and hence increases amorphosity.[37]

Electrical Conductivity and Activation Energy

Polymers usually exhibit low electrical conductivity. However, if ions are liberated from the surface of the micelle to the free condition in an endothermic process, may increase the electrical conductivity.[38] This indicates that the electrical conductivity of the polymer is influenced by the mobility of the ions, and it is dominant at higher temperatures.[39]

Bakelite is a highly amorphous polymer and when it is used in RPC neutrino detector, its performances are affected by several
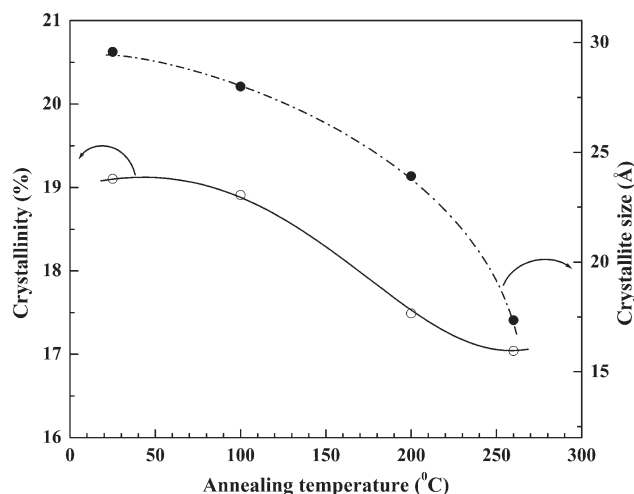
factors, viz., temperature and humidity. Therefore, it is important to study the electrical conductivity of the material and to estimate the activation energy (E_a). The apparent activation energy of the polymer network is lowest below T_g (nonpolar polymers) which infers that the electrical conductivity behavior is brought out by the interaction between the ionic charge carriers and the polymer matrix. At temperatures below T_g, the motion of chain segments is hindered by potential energy barriers and with increasing temperature the energy becomes great enough to overcome these barriers, and segmental motion occurs which results in an increase in free volume size (V_f) of the polymer. The increase in free volume facilitates the motion of an ionic charge carriers at temperatures above the glass transition temperature T_g.[40] This may increase the leakage current in Bakelite RPCs during the continuous operation at high temperature.

The linear relationship obtained from the temperature dependence of conductivity plot, the variation of ionic conductivity with temperature obeys the Arrhenius type of thermally activated process and the relation is expressed as,

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right) \qquad (4)$$

where, σ_o is the pre-exponential factor, k is Boltzmann's constant, T is the absolute temperature, and E_a is the apparent activation energy associated with the motion of charge carriers. The values of the apparent activation energy can be calculated from the slope of the Arrhenius plot given in Figure 7 and the value turns out to be 37.05 kJ mol^{-1}, which is in the same order of magnitude reported for the amorphous polymers in the literature.[41] At this energy state, bond dissociation takes place, the resistance of the material decreases and ionic mobility increases and hence the electrical conductivity. Figure 8 shows the plot of electrical conductivity (σ) and free volume (V_f) as a function of annealing temperature. The electrical conductivity of the Bakelite sample is almost constant till 100°C, and then increases
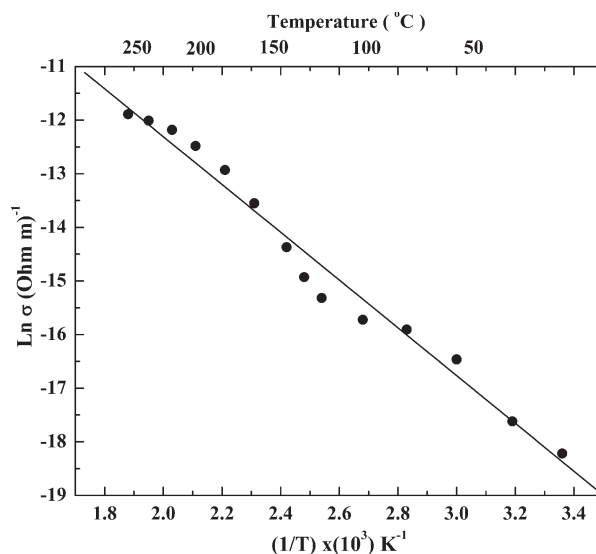

Figure 6. Plot of crystallinity and crystallite size of annealed Bakelite samples as a function of annealing temperature.

Figure 7. Arrhenius plot of electrical conductivity.
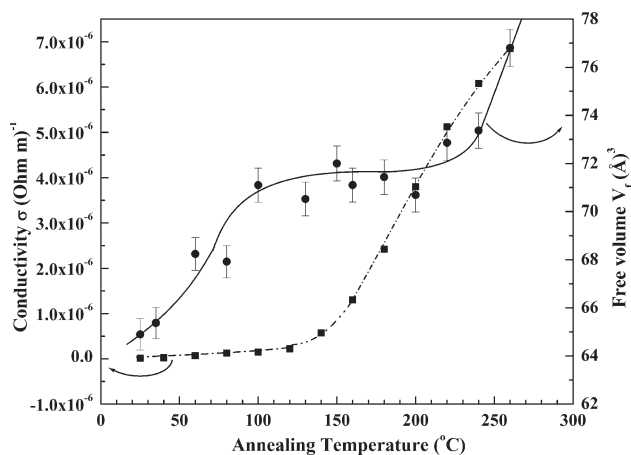
Figure 8. Electrical conductivity (σ) and free volume (V_f) as a function of annealing temperature.

rapidly above $100°C$ up to $270°C$. However, the free volume shows continuous increase with increase in annealing temperature due to the mobility of the polymer chains (as already explained) and beyond the T_g ($46°C$), this increase is more pronounced. On the other hand, at lower annealing temperature, the creation of ions (H^+ and OH^-) is not significant and hence conductivity appears to be constant in the Figure 8 but the data in Table I clearly shows that there is a small increase. Higher electrical conductivity is observed beyond $200°C$ which is identical to free volume hole size (V_f) and this is explained as follows:

Bakelite is a Phenol-Formaldehyde polymer, which is of ionic origin. The current in the Bakelite may be carried by ions of Phenol impurities, CH, OH^-, and H^+ ions.[42] The scission of OH groups and CH groups may lead to the formation of H^+ and OH^- ions, which may increase the ionic concentration in the Bakelite RPC material and hence the electrical conductivity at higher annealing temperature. Furthermore, it has also been proven that the ionic conductivity of Bakelite (polymer) sample is greatly influenced by the consequential changes in the crystallite size of the material.[43] Figure 6, clearly shows the reduction in crystallite size with the increasing annealing temperature. This may be one of the reasons for the increasing free volume hole size, and hence increase in the electrical conductivity.

CONCLUSIONS

Annealing study of Bakelite RPC neutrino detector material revealed that the thermal expansion of free volume holes along with coalesce of smaller free volume cavities occur below $240°C$. At higher annealing temperature, drastic increase of free volume size indicates the cleavage of methylene bridges, which is well supported by FTIR results. FTIR spectra shows the shifting of aliphatic C—H peaks (from 1492 cm^{-1} to 1469 cm^{-1}), which was more at higher annealing temperature and also infers the reduction in strength of the C—H bond of the aliphatic bridges and cleavage of methylene bridges of the polymer network. This might lead to the depolymerization of the Bakelite polymer. This is also well supported by the XRD results, which showed that the reduction in crystallinity and crystallite size upon

annealing. The increasing electrical conductivity of Bakelite from 1.23×10^{-8} $(\Omega$ m$)^{-1}$ at room temperature to 2.33×10^{-5} $(\Omega$ m$)^{-1}$ at $270°C$ indicated the increase of ionic mobility of OH^-, H^+ ions, and this agrees with behavior exhibited by free volume parameters. Thus, we suppose that larger leakage current observed in Bakelite RPC detectors compared to glass RPC detectors owes it origin to thermally activated processes in the Bakelite polymer microstructure. To prove this inference reasonably well, more such studies are really needed.

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